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Second Edition

CONDUCTIVE ELECTROACTIVE POLYMERS

Intelligent Materials Systems

Gordon G. Wallace
Geoffrey M. Spinks
Leon A.P. Kane-Maguire
Peter R. Teasdale



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Preface

As we enter the era of intelligent materials and embark upon a new approach to material design, synthesis and system integration, certain groups of materials will emerge as champions.

The desire to have built-in sensing, processing, actuating, energy conversion and storage functions will require the identification of dynamic materials with chemical and physical properties that are readily manipulated. The ability to create these materials in different forms to enable integration into other structures will also be important.

Even the most cursory glance at the components used by nature in the development of intelligent material systems and structures reveals that polymers are extremely powerful in this regard. It is macromolecules, for example, antibodies and enzymes, that provide the molecular recognition capabilities used so magnificently by nature. Macromolecules are also the basis of that most useful of actuator systems: muscles. Furthermore, it is the generation and transmission of electrical signals that regulate the processes behind the formation and operation of these biosystems.

The human system interacts with the environment through a range of polymeric sensors that allow us to smell, see, taste, touch and hear by converting physical and chemical stimuli into electric impulses that transmit along the nervous system. Conversely, it is the effect of electrical stimuli on other macromolecular systems that determines our ability to activate appropriate “mechanical” and other responses. Even the sophisticated innermost workings of the human system are regulated by processes occurring at dynamic “polymer” interfaces, the biological cell membrane.

It is a sobering thought that it is the combination of appropriate simple monomers, with a variety of chemical properties spatially and temporally organized in an electrolyte (salt and water) solution, that produces the basis for the human body. This same combination of chemical components, using different monomers and electrolytes, provides the basis for intelligent systems made from conducting electroactive polymers (CEPs), the subject of this book.

Rapid advances in synthetic polymer science have now placed us in a position to utilize the unique properties of this versatile class of materials. Our ability to design and assemble polymers from the molecular level, coupled with a better understanding of structure–property relationships

enables the design of sophisticated structures. Certain classes of polymers will play different roles in the creation of intelligent materials. Some will be inert and structural, while others will be more dynamic and functional, just like their natural counterparts. We believe that inherently conducting electroactive polymers will play a central role in the development of intelligent material science over the next decade.

The parameters affecting the formation of important CEPs, such as polypyrroles, polyanilines and polythiophenes are discussed. How these parameters can be used to manipulate the chemical, physical and mechanical properties of these polymers is then revealed. We attempt to clarify the chemical and energy parameters that determine the structure and, hence, the chemical, electrical and mechanical properties of these fascinating structures. We present some examples wherein the ability to manipulate the structure and properties of conducting polymers is used to produce materials with useful sensing, processing and actuating properties.

This new edition of the book provides more details on polythiophene and polyaniline systems, as well as updating the progress on polypyrroles. Significant progress in techniques for processing of inherently conducting polymers and fabrication of devices containing them has been made over the past 5 years and these areas are also expanded and updated.

Acknowledgments

The authors are indebted to a number of people whose work has enabled this manuscript to come to fruition. First, we would like to thank all research students and research fellows, both past and present, who have been associated with the Intelligent Polymer Research Institute. Their efforts have maintained the fervor necessary to progress this area of research. Numerous members of the academic and technical staff at the University of Wollongong have also been involved in advancing our research in recent years.

We are grateful to the Australian Research Council for continued financial support.

This work, of course, would not have been possible without the ongoing support of all our families.

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chapter one

Introduction

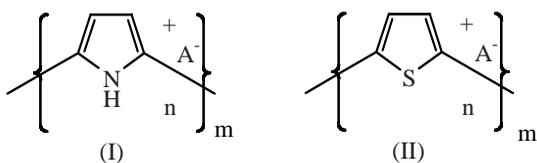
Conducting electroactive polymers (CEPs) such as polypyrrole, polythiophene and polyanilines (I-IV shown below) are complex dynamic structures that captivate the imagination of those involved in intelligent materials research.¹⁻⁵

It is possible to create conducting polymers with a diverse range of properties. For example, chemical properties can be manipulated to produce materials capable of trapping simple anions or to render them bioactive. Electrical properties can also be manipulated to produce materials with different conductivities and different redox properties. After synthesis, the properties of these fascinating structures can be manipulated further through redox processes. The application of electrical stimuli can result in drastic changes in the chemical, electrical and mechanical properties of CEPs. These complex properties can be controlled only if we understand, first, the nature of the processes that regulate them during the synthesis of the conducting polymers, and second, the extent to which these properties are changed by the application of an electrical stimulus. These dynamic properties of CEPs are the focus of this text, because it is the ability to control these in various operational environments that could lead to development of intelligent material systems.

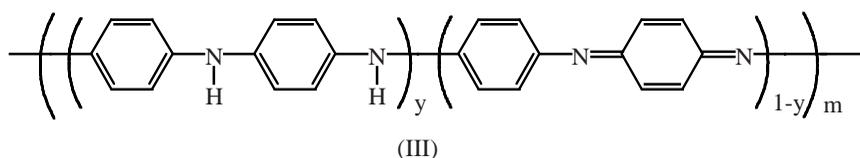
The state of the art is such that an understanding of these processes is now within our grasp, and an exciting fertile field lies before intelligent material research scientists. We can, by design, control the chemical and electrical properties of conducting polymers at the point of assembly. How these properties are likely to vary as a function of application of external stimuli can also be manipulated by the synthesis process.

Of course, the molecular organization required to achieve the desired chemical and electrical properties will also determine the mechanical properties of any practical structure we are to make. Each of these three properties (chemical, electrical and mechanical) are inextricably linked.

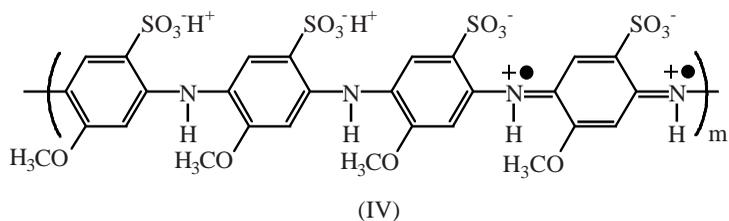
The method of assembly is also important, as it determines the physical form of the materials. A wide variety of synthesis and processing methods



[n is the number of monomer units per unit positive charge; usually 2-4 for polypyrrole and polythiophene. A^- is a counterion incorporated during synthesis, m determines molecular weight].



polyaniline: leucoemeraldine ($y=1$), emeraldine ($y=0.5$) and pernigraniline ($y=0$)



now exist that can be manipulated to produce materials in forms that can be integrated into truly intelligent structures.

Before exploring these materials in detail, some general discussion of intelligent materials science is warranted.

What are intelligent material systems and structures?

This question has already been addressed by numerous authors,⁶⁻¹⁰ and many definitions are employed. For the purpose of our work, we will use the following: An *intelligent material* is capable of recognizing appropriate environmental stimuli, processing the information arising from the stimuli and responding to it in an appropriate manner and time frame. A further desirable feature is that the material should ideally be self-powered, having energy conversion and storage functions.

What is particularly important is that the responses obtained are appropriate. That is, they must result in desirable behavior that enhances the performance of the material or structure.

No matter what definition we employ, the underlying feature that differentiates intelligent materials from more conventional materials is their dynamic character. Without such character, there can be no intelligence. However, this character must be controllable, and the time frame within which it responds must be appropriate if truly intelligent behavior is to be realized. If it is too slow, it may have no practical application. If it is too fast, it may be useless, or even dangerous.

There is little doubt that intelligence is more demonstrable when motion (mechanical activity) is apparent. However, we should remember that, in complex systems such as living entities, motion is a physical manifestation of activity at the molecular and electronic level. Similarly, motion resulting from the application of an external force causes changes within the material at both the molecular and electronic level.

If the stimuli and response required are chemical or biochemical in nature, involving only activity at the cellular, molecular or even atomic level, then use of a single intelligent material may be possible. Also, mechanical stresses of a gradual or slight nature may be recognized and responded to with a single material. However, in many applications, more than one material is required to perform the desired functions. That is, when we encounter intelligent material systems that, in turn, can be incorporated into much larger *intelligent structures* made up of a number of component systems and materials of varying kind and function. In intelligent material systems and structures, the individual functions of stimuli recognition, information processing and response generation are brought about by the combination of appropriate materials. The greater the severity and variety of the stimuli, and the more demanding the requirements of the response, the more complex the intelligent material structure must be.

But again, there is the underlying fundamental requirement that the creation of intelligent material systems must involve the identification of molecular systems whose chemical and electrical properties can be manipulated and controlled.

To continue to operate effectively, the material may be required to learn, grow and even decay in a fashion determined by the operational environment. What is clear is that the properties of such materials must change with time; that is, they must be dynamic. We must identify material systems where chronological behavior can be controlled, plotted and predicted as a function of the environmental stimuli that are likely to be encountered. Then, if the materials are to behave properly, we must develop procedures to manipulate their molecular structure, and hence their dynamic character, during the early stages of synthesis and processing.

The basis of the revolution

The diversity of approaches used to investigate intelligent material systems and structures is a healthy symptom of the early stage of development of this scientific endeavor.

At least two distinct approaches are currently obvious:

1. Integration of functions at the bulk material level
2. Integration of functions at the molecular level

The concept of intelligent material systems and structures emerged from the research activities of the United States Army Research Office. Scientists here realized that the integration of appropriate materials at the bulk *material level* could produce a system capable of monitoring and responding to environmental conditions. The concept of embedding sensors and actuators within structures coupled with localized processing is, it seems, the shortest-term approach to gaining benefits in the intelligent material area.

However, information is much easier to process and transmit in a material integrated at the *molecular level*, and preferably integrated during processing or growth. Nature and biological systems have refined this approach and provide many examples. There is, indeed, great potential for diversity at this level of organization.

Nature achieves intelligent behavior by assembling appropriate molecules in a more sophisticated and timely fashion than we humans have been, to date, able to achieve artificially. The macromolecular structures can then be integrated into systems composed of numerous other inorganic materials or, preferably, as nature has done, the active (organic) components can create the required mechanical structure. The molecular approach to the development of synthetic intelligent systems involved design and assembly of appropriate molecules to produce the properties required to sense, process and respond to information.

Progress in this approach can be accelerated by borrowing selected macromolecules, such as proteins, from nature to become active components in our synthetic structures. Nature has developed the appropriate stimuli recognition, information processing and storage and response mechanisms to allow life, as we know it, to continue to exist. This is no mean feat, and to emulate it, we must consider a macromolecular approach.

Many materials are, of course, composed of molecular building blocks. It is how we put them together, how we integrate and spatially distribute the components required for intelligence, that is important. This approach requires the identification of suitable building blocks, that is, suitable molecular components. Molecular conducting wires, molecular insulators and molecular switches are needed. It will take some time to develop, understand and integrate many of the molecular components, but much work in the field of molecular engineering and molecular electronics is already under way.

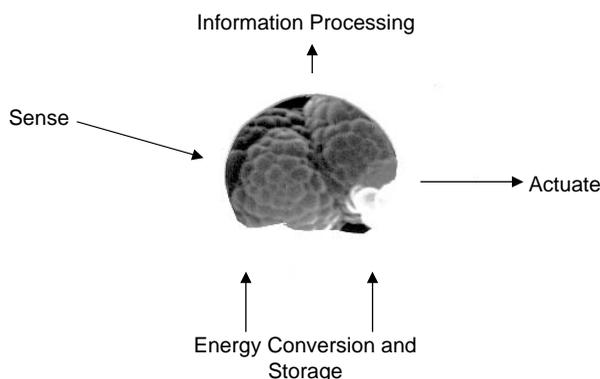


Figure 1.1 An “intelligent” polymer: The shape of the human brain with the texture of polypyrrole (as seen with an electron microscope). The necessary functions of an intelligent polymer are illustrated.

A more detailed chemical understanding of these material systems is also needed. Inevitably, they involve chemical processes occurring at a dynamic heterogeneous interface. The well-defined chemical rules that apply in homogeneous solutions no longer apply. Instead, we must deal with chemical (molecular) interactions where the spatial distribution of active sites occurs at the nanodimensional level, and the fact that the nature of these sites varies as a function of time and environmental stimuli is important.

Of course, not all molecular systems are suitable. It appears likely that only a handful of systems will be produced to solve our intelligent material systems needs. *It is not so much that sophisticated molecules are required to produce materials capable of sophisticated behavioral patterns; simple molecules, assembled creatively, may achieve our objectives.*

Identifying macromolecular building blocks

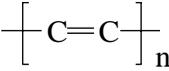
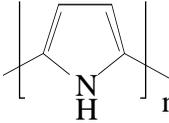
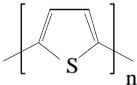
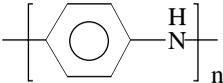
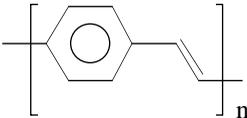
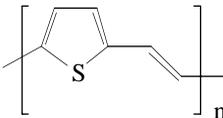
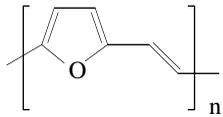
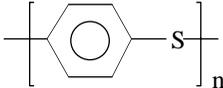
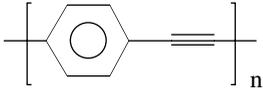
Conducting electroactive polymers have emerged as one of the champions in intelligent materials research. CEPs have all the desirable properties:

- They are readily engineered at the molecular level to recognize specific stimuli.
- Because they are conductive, they facilitate transport of electrical information.
- They are capable of localized processing as well as actuation of response mechanisms.

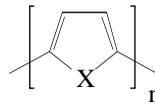
A wide range of CEPs is available (see [Table 1.1](#)).

CEPs have a further unique and practical advantage. The fact that they conduct electricity means that we can communicate with them using the electronic tools (computers and interfaces) that have become part of our

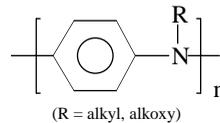
Table 1.1 Typical Conducting Polymer Structures (in Undoped Form)

Name	Structure
Polyacetylene (PAC)	
Polypyrrole (PPy)	
Polythiophene (PTh)	
Polyaniline (PAN)	
Poly(para-phenylene) (PPP)	
Poly(phenylene-vinylene) (PPV)	
Poly(thienylene-vinylene) (PTV)	
Poly(furylene-vinylene) (PFV)	
Poly(phenylenesulfide) (PPS)	
Poly(phenylene ethynylene) (PPE)	

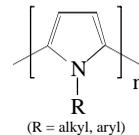
Polyseleneophene (X = Se)
Polyfuran (X = O)



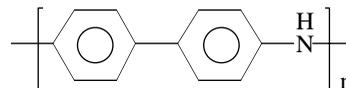
Poly(N-substituted aniline)s



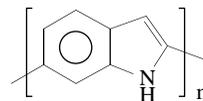
Poly(N-substituted pyrrole)s



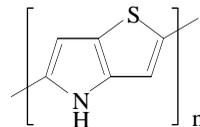
Poly(diphenylamine)



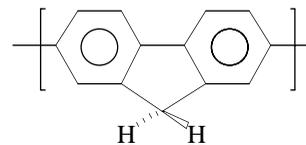
Poly(indole)



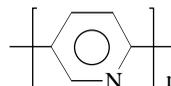
Poly(thieno[3,2-b]pyrrole)



Poly(fluorene)



Polypyridine



scientific lives. Information on the behavior of these systems can be retrieved from real *in situ* environments, using existing and emerging characterization tools (as described later). In addition, their behavior can be manipulated *in situ* using appropriate electronic stimuli (Table 1.2).

The Intelligent Polymer Research Institute (IPRI) has identified the unique features of conducting electroactive polymers, based on pyrrole, aniline and thiophene, into which stimuli recognition sites are readily incor-

porated and various response mechanisms can be integrated, and for which information processing capabilities are inherent.

Conducting polymers are a class of materials that are, no doubt, destined to play a major role in intelligent materials science. As outlined in the remainder of this text, the properties of these materials are versatile and possess the dynamism required if intelligent behavior is to be produced.

Table 1.2 Property Changes Typically Observed Upon Electrical Stimulation to Switch CEPs Between Oxidized and Reduced States

Property	Typical Change	Potential Application
Conductivity	From 10^{-7} to 10^3 S/cm	Electronic components, sensors
Volume	3%	Electromechanical actuators
Color	300-nm shift in absorbance band	Displays, smart windows
Mechanical	Ductile-brittle transition	
Ion permeability	From zero to 10^{-8} mol cm^{-2} s^{-1} in solution	Membranes

Academic research in conducting polymers

Since their discovery in the mid-1970s, conducting polymers have been a *hot* research area for many academic institutions. This research has supported the industrial development of conducting polymer products and provided the fundamental understanding of the chemistry, physics and materials science of these materials. The impact of the field on science in general was recognized in 2000 by the awarding of the Nobel Prize for Chemistry to the three discoverers of conducting polymers: Alan MacDiarmid, Alan Heeger and Hideki Shirakawa (Figure 1.2).

A search of chemical abstracts over the past 25 years shows the level of publications increasing rapidly after 1980 (Figure 1.3). The data suggest a peak in patenting in the late 1980s, while the rate of scientific publications increases unabated through the end of the 1990s. At the present time, around 40 new journal articles related to CEPs are published every week.

Figure 1.4 shows the main areas of interest for papers published on conducting (CEPs) electroactive polymers over the past 25 years, with almost half of the publications related to the synthesis of new types of CEPs or modifications to existing CEPs. The next largest area of research has been into the physics of the conduction mechanisms, while applications for CEPs accounts for fewer than 20% of publications. A further breakdown of the areas of application for CEPs sees a great deal of interest in batteries, followed by sensors, membranes and polymer light emitting diodes (PLEDs).

Research into CEPs remains extremely fruitful, with the fundamental studies underpinning the exciting commercial developments described in the following sections.



Figure 1.2 Alan Heeger, Alan MacDiarmid and Hideki Shirakawa, the three discoverers of polyacetylene, the first inherently conducting polymer.

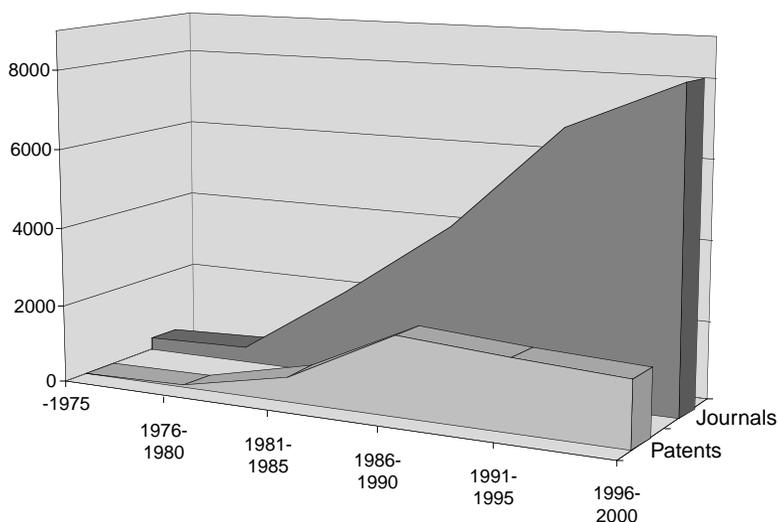


Figure 1.3 Number of scientific papers published and patents issued in the area of conducting polymers for the past 25 years (source: *Chemical Abstracts*).

Spin-offs: other applications for conducting electroactive polymer systems

In pursuing the development of intelligent materials, it is impossible to ignore the spin-off opportunities that have emerged for conducting electroactive polymers. The science is such that a better understanding of dynamic materials has been obtained. This has been used to advantage in the development of new and improved products.

The *potential* applications of conducting polymers have been discussed at length in numerous reviews.¹¹⁻¹⁸ From Figure 1.3, it is evident that the patent activity relating to conducting polymers peaked in the mid to late

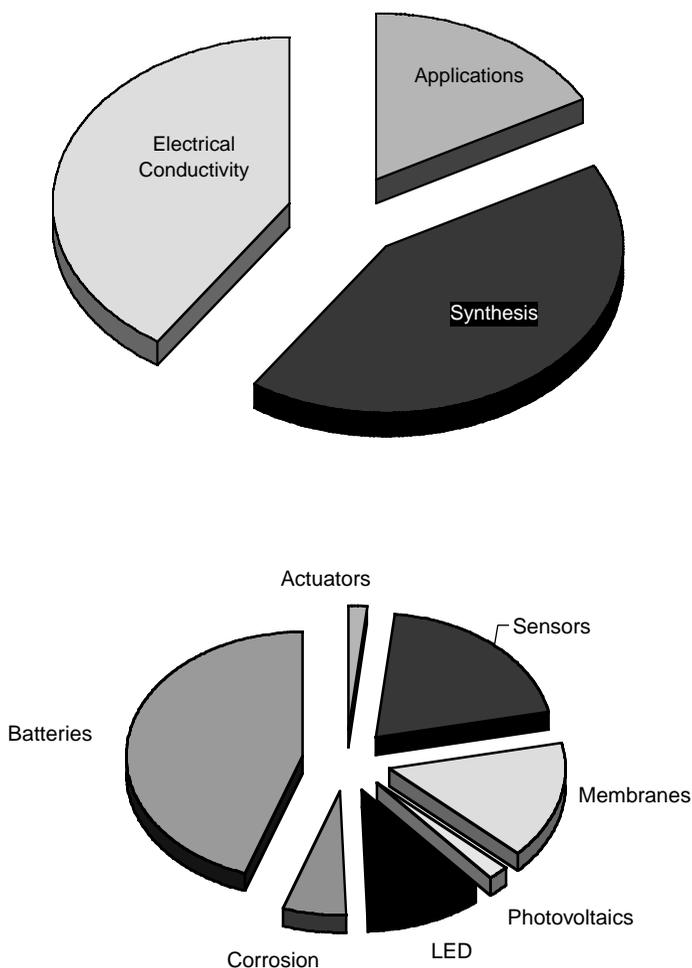


Figure 1.4 Scientific papers published on conducting polymers in the last 10 years categorized into various topics.

1980s. The rapid increase in patents in the early 1980s reflects the growing appreciation of the versatility of conducting polymers in many application areas. The commercialization of conducting polymers has been particularly boosted since the mid 1990s by breakthroughs in processing technologies that have yielded both soluble and melt-processable forms of conducting polymers. The various spin-off application areas are described in the following sections, while processing and device fabrication technologies are described in Chapter 7.

Applications utilizing the polymers' inherent conductivity

Upon realization that polymers could be made electrically conductive, the possibility that lightweight conductors capable of replacing metals in many

applications was immediately grasped. However, this promise has not been realized to date. The development of highly conducting polymers with adequate mechanical properties and stability has yet to be achieved. However, materials with lower conductivities (100–200 S/cm) that can be produced routinely are proving extremely useful in electromagnetic shielding applications.

Another area that utilizes the semiconducting nature of conducting polymers is antistatic applications. Electrostatic discharge (ESD) is particularly damaging for electronic components, where a high voltage surge can destroy components. Consequently, all electronic components are shipped inside antistatic materials. It is often desirable that the packaging material be transparent so that the contents can be viewed. The challenge for antistatic coatings (metals and polymers) is to provide both the desired level of surface conductivity and the transparency required (as well as adhesion, scratch resistance, etc.).

A number of companies seek to overcome the limitations of existing materials by using conducting polymers for ESD protection. The main methods currently in use are ionic conductors, carbon-black-filled plastics and vacuum metallized plastics.¹⁹ Ionic conductors operate by absorbing moisture from the atmosphere to form a conductive surface (10^{11} – 10^{12} Ω /square). They are highly transparent coatings, but are also highly sensitive to moisture and become ineffective when humidity is low. The ionic conductors are also easily removed by washing, so that reuse of the container is difficult. Carbon-black-loaded polymers give lower surface resistivities (10^3 – 10^5 Ω /square), which is suitable for electromagnetic interference shielding, but is too low for ESD protection. Carbon-black-filled polymers are also intensely colored and suffer from the loss of carbon particles through friction (a serious problem in clean-room applications). Metallized plastics are transparent only for very thin coatings and adhesion to the polymer is difficult to achieve. Further development of conducting polymers to give acceptable surface resistivity (especially over time and after repeated washing) and adhesion to the substrate will overcome many of the limitations of existing methods for ESD protection.

Recently, conducting polymers have been considered for micro-electronics applications. Philips Electronics is involved in the development of “plastic chip” technology using conducting polymers.²⁰ In this application, a simple processor chip is fabricated using polyaniline electrodes and a polythiénylenevinylene semiconductor layer. The layers are spin coated onto a polyimide substrate. Patterning of the polyaniline electrodes is achieved by exposing the polymer to UV light through a suitable mask. A photosensitizer molecule incorporated into the polyaniline absorbs the UV light and induces a photochemical reaction that leads to an increase in conductivity of 10 orders of magnitude. The end result is patterned tracks of conducting polyaniline in a nonconducting matrix. The performance of the all-plastic circuits is poor compared with silicon-based electronics. However, the devices are designed for applications where low cost and mechanical flexibility are desired where

this technology has several advantages. One example being pursued is the “smart label” to replace the ubiquitous barcode placed on virtually all packaged products.

Conducting polymers also have other applications in micro-electronics, as recently reviewed by Angelopolous.²¹ Polyaniline layers have been shown to improve the resolution of electron-beam patterning where the conducting polymer prevents the buildup of charge in the resist layer and so eliminates distortion. Polyaniline conductivities of 10^{-4} S/cm were shown to be effective at eliminating resist layer charging. In recent times, Mitsubishi Rayon in Japan has been producing a water-soluble sulfonated methoxyaniline polymer for use in e-beam lithography. Similarly, IBM has introduced a family of water-soluble polyanilines (PanAquas) that are effective at eliminating resist layer charging when used as 200 nm-thick layers. The same polymers were also shown to be effective in reducing charging of nonconducting specimens during scanning electron microscopy. The advantage of using conducting polymers (compared with more traditional sputtered metal coatings) is that the polymer can be easily dissolved so that specimens can be nondestructively analyzed.²² Other applications for conducting polymers in micro-electronics fabrication include the use of polyaniline coatings for electroless deposition of copper connectors, while future applications may include interconnects and even devices such as diodes and transistors.

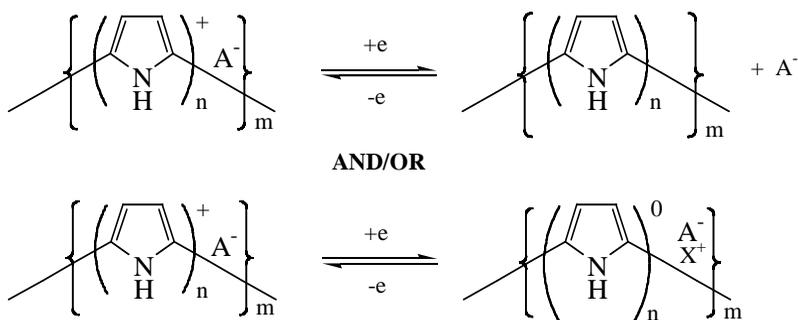
Electrochemical switching, energy storage and conversion

The next most obvious applications of conducting polymers utilize their conductivity and electroactivity. Conducting polymers such as polypyrrole are readily oxidized and reduced according to the reaction in [Figure 1.5](#) for cases where the counterion is able to freely leave the CEP matrix and where it is immobilized within the CEP matrix. The general changes in the properties of the polymer that accompany this reaction are indicated in [Table 1.2](#).

Anion movement predominates in cases where small mobile dopant, e.g., Cl^- , is used. If large anion dopants such as polyelectrolytes are employed, cation movement will predominate.

The fact that conducting polymers can be charged and discharged has aroused much interest among those involved in developing new rechargeable battery technologies. The conducting polymers are usually combined in a cell, with lithium as the other electrode and a usable voltage of approximately 3 v is obtained. The achievable energy densities are several times that of the nickel-cadmium and lead-acid batteries.

These solid-state batteries were introduced commercially in the early 1990s by Bridgestone (Japan), Allied Signal (USA) and Volta (Germany), but the products were discontinued due to low sales. The slow sales have been attributed to the release of other competing battery technologies, such as lithium-ion batteries. A breakthrough in battery design was announced by Johns Hopkins University researchers in 1996.²³ Whereas previous battery



[n, A⁻, m defined on page 1]

Figure 1.5 The electrodynamic character of polypyrroles.

designs used a conducting polymer as one electrode only (cathode) the new design incorporated a polymer cathode, anode and electrolyte. The design gives good battery performance and has the advantages of high flexibility and light weight. Such improvements may give new impetus to polymer battery commercialization.

Recent research has suggested that conducting polymers are set to emerge in devices used to store energy in the form of super capacitors and photovoltaic systems. The intense interest in these applications is driven by developments in electric-powered vehicles and alternative energy in general. Supercapacitors are those devices able to store a charge of 50 F/g (or 30 F/cm³) of the device, or higher. This high storage capacity and ability to deliver high power density can be utilized in electronic equipment and electric vehicles.²⁴ The fast discharge rate obtainable from capacitors means that high power can be delivered for short periods. Conducting polymers are being researched for "redox supercapacitors." In these devices, the redox chemistry of the polymer is used in the same way as described above for batteries. However, the design of the device is such that the conducting polymer is applied as a thin coating on a high-surface-area substrate. This design allows for very rapid charging and discharging of the polymer so that capacitor-like performance is obtained. All solid-state redox supercapacitors using PTh and PPy with a solid polymer electrolyte have been reported²⁵ as having storage capacities of 18 F/g.

Polymer photovoltaics (light-induced charge separation)

Polymer photovoltaics using conducting polymers are also being developed.¹ In a typical arrangement, the photosensitive polymer (such as polyphenylene vinylene (PPV) and its derivatives) is sandwiched between two electrodes (Figure 1.6). One is a transparent material, typically indium tin oxide (ITO)-coated glass, and the other electrode is a low-work-function metal such as aluminum or calcium. Light is absorbed by the polymer,

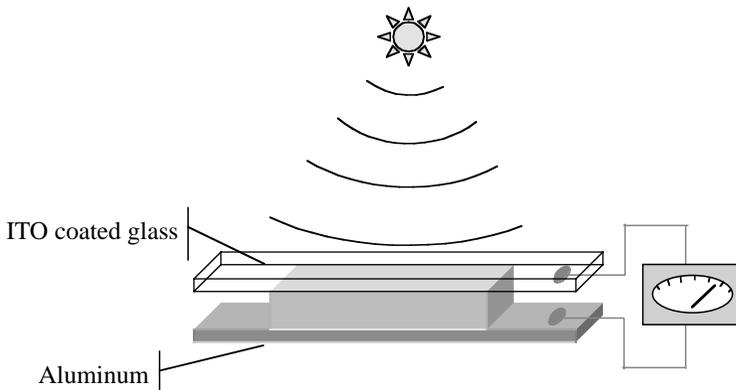


Figure 1.6 Device design for polymer photovoltaic device (the thickness of the polymer layer is greatly exaggerated).

creating excitons (electron-hole pairs) that dissociate at an appropriate interface to give charge separation and, hence, current flow.

Efficiencies of polymer-based photovoltaics are very low compared with silicon semiconductor materials. However, polymer photovoltaics have the potential to be manufactured very cheaply and can be applied to very large areas, such as rooftops and exterior walls of buildings. The large surface areas can compensate for the lower efficiencies to provide an adequate supply of electricity. Of course, efficiencies are being improved by chemical modification of the polymer and better design of the photovoltaic device. One approach to polymer modification is to attach “light harvesting” groups to the polymer chains so as to increase the amount of light absorbed. Once again, the fabrication of the device is critical in determining device performance. It has been shown that formation of interpenetrating networks of donor- and acceptor-type polymers results in marked improvements in photovoltaic efficiency, as reviewed recently.²⁶

Display technologies: electrically stimulated light emission

The process used for the photovoltaic device can be reversed to produce a light emitting diode (LED). When an electric field is applied to the two electrodes shown in [Figure 1.7](#), electrons are injected into the conduction band of the polymer layer from the cathode (usually a low-work-function metal such as aluminum or calcium). At the ITO anode, electrons are removed from the valence band of the polymer to produce vacancies, or holes. The free electrons and holes move in opposite directions under the influence of the electric field and, when they combine, a photon of light is emitted. The color of the light emitted depends on the band gap between the valence and conduction bands in the polymer. Appropriate derivation of PPV polymers has produced PLEDs that emit the three colors red, blue and green.

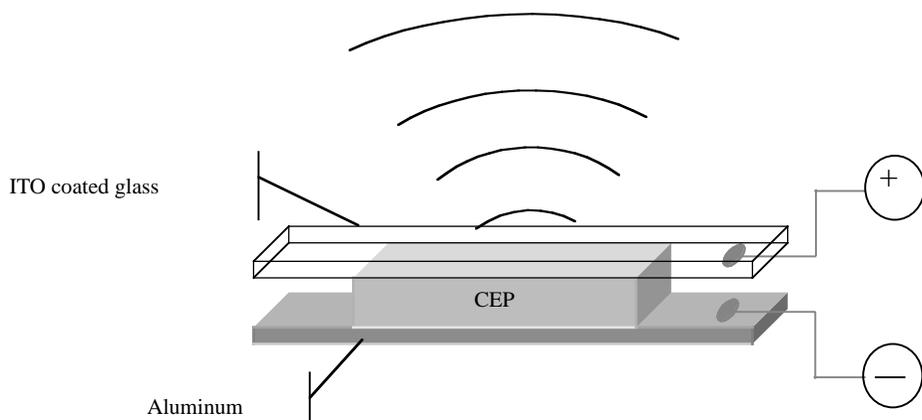


Figure 1.7 Device design for a polymer light emitting diode.

The PLED was first demonstrated by Richard Friend and co-workers at Cambridge University in 1990. The early devices had an efficiency of only 0.01%, but this has now been improved to 4% or better, which provides sufficient light to be seen in daylight. Early devices also suffered problems of stability, but improved lifetimes have been obtained by totally sealing the device from oxygen and moisture. Removal of excess heat also stabilizes the polymer against degradation.

PLEDs offer one of the most exciting prospects for conducting polymer commercialization, because they offer several advantages over existing technologies for flat panel displays. The market for PLEDs was projected to reach \$200 million in 2002.²⁷ Several breakthroughs in the synthesis and processing of electroluminescent polyphenylene vinylene (PPV) by the Cambridge University group have spearheaded the commercial development of flat screen displays. The first products were backlit displays for automobile instrument panels and mobile phones. The displays were being manufactured by Philips in partnership with Cambridge Display Technologies, a company spun off from the original research at Cambridge University. Uniax Corporation, in the USA, has also entered into a partnership with Philips to commercialize conducting polymer displays based on the research work of Nobel Laureate Professor Alan Heeger's group at the University of California, Santa Barbara. PLED development is also an interest for most major chemical companies, including DuPont, Hoechst and Dow Chemical.

Electrochromics

Another interesting application that uses the dynamic properties of conducting polymers is electrochromic devices.²⁸⁻³² For example, polythiophene and polyaniline undergo distinct color changes when an electrical potential is applied. Thin films of polythiophene can be switched from red (oxidized)

to blue (reduced), and polyaniline transcends a spectrum of colors as different potentials are applied to it. This has possible applications in advertising displays and smart windows. This bi-stable material can also be used as a memory storage device for information storage. All of the above applications use conducting polymers in the solid state in environments where the dynamic character is readily characterized, controlled and utilized.

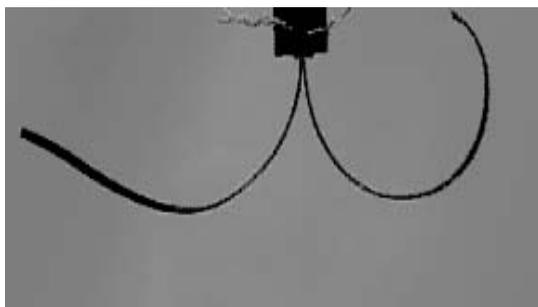


Figure 1.8 Time-lapse photographs showing the bending movement of a bimorph-type actuator (two active electrodes) made from polypyrrole and a porous membrane separator and activated by 1.5-V potential difference between the polymer electrodes.

Electromechanical actuators

More futuristic applications for conducting polymers that are receiving considerable attention include electromechanical actuators (artificial muscles).³³ Allied Signal (now Honeywell International) is interested in the development of lower power/voltage moving parts for micromachined optical devices. NASA has also been involved in the development of low-power lightweight actuators for the window wiper on the Mars Explorer.

Electromechanical actuators are materials that can change their physical dimensions when stimulated by an electrical signal. In the case of conducting polymers, the volume change occurs as a result of ion movement into and out of the polymer during redox cycling.³⁴ The change in volume can be up to 3% (although much higher-volume changes have recently been reported on very small devices).³⁵ When tested isometrically (at constant length), the stress generated by the volume changes is of the order of 10 MPa. The performance of conducting polymer actuators compares favorably with natural muscle (10% stroke and 0.3 MPa stress) and with piezoelectric polymers (0.1% stroke and 6 MPa). The piezoelectric polymers are driven by high electric fields usually requiring 100–200 V, whereas the conducting polymers require only 1–5 V to operate. Some of the disadvantages of CEP actuators include a slow response time and limited lifetime, although recent results have shown strain rates of 3%/s (natural muscle can respond at 10%/sec) giving 1% strain for more than 100,000 cycles.³⁶

An important development in conducting polymer actuators was the recent demonstration of a solid state actuating device³⁷ that will hasten the

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commercial application. [Figure 1.8](#) shows the bending operation of an actuator consisting of three layers: gold, CEP, membrane, CEP where the membrane is porous and contains the electrolyte that acts as both an ion source and ion sink.

The use of electromechanical actuators based on CEPs is currently being pursued in a number of applications. For example, IPRI is currently building on a concept introduced by De Rossi³⁸ to produce a rehabilitation glove in collaboration with North Shore Hospital Service (Sydney, Australia) ([Figure 1.9](#)). The actuators will be integrated throughout the wearable glove structure to provide assisted movement during rehabilitation.



Figure 1.9 The rehabilitation glove, showing sensor strips on each finger.

IPRI is also currently involved in the development of actuators for an electronic Braille screen ([Figure 1.10](#)) in collaboration with Quantum Technology (Sydney, Australia). A convenient user interface is the single biggest barrier to blind people's accessing information in the Internet age. The future of Braille lies in a low-cost, refreshable surface, or screen, where the individual Braille dots are raised and lowered electronically by low-voltage/low-power actuator systems, allowing changing messages or decision options to be displayed.

We envisage the screen as a device consisting of multiple rows of a new type of Braille cell. The pins making up each Braille cell of the screen are driven electronically by polymer actuators in place of the piezoelectric mechanisms of existing technology. Because of its size and simple mechanical design, the proposed cell can be used to make multiple lines of Braille. These can be manufactured in modular building blocks suitable for use in a wide variety of product configurations, from a full-page screen to electronic note-

takers, ATMs etc. The target performance characteristics for the actuating elements for the Braille cell are:

- Axial movement of 0.5 mm in 0.2 sec with a tensile load of 50 mN (1% strain/5% sec⁻¹ strain rate/0.2 MPa isotonic stress for a cell 50 mm high working against a 0.1 N/m spring)
- Operating voltage < 20 V
- Operating lifetime > 10⁶ cycles

A steerable cochlear implant with the CRC for Cochlear Implant and Hearing Aid Innovation (Melbourne, Australia) is also under development. The microactuator will assist surgeons during implantation of the “Bionic Ear” a device used to assist severely deaf patients — giving the ability to hear. The implantation process is a delicate one and the ability to steer the implant through the narrow channels will prevent any damage while leaving the device as close as possible to the inner ear after insertion.

Separation technologies

The dynamic character of conducting polymers has been used to advantage in the development of new smart-membrane technologies.³⁹⁻⁴³ A membrane consisting of or coated with a CEP can be stimulated *in situ* using small electrical pulses to trigger the transport of electroinactive ions such as K⁺ and Na⁺, metals such as Cu²⁺ and Fe³⁺, small organic molecules such as sulfonated aromatics and even large macromolecular species such as proteins (e.g., [Figure 1.11](#)). The flux and selectivity attainable are dependent on several factors:

- The composition of the membrane.
- The porosity as determined by the CEP or a more porous substrate onto which the polymer may be coated.
- The electrochemical conditions used during operation (potential pulse height and pulse width are critical).

Switching the polymer repeatedly between its oxidation states facilitates transport of molecular species through the polymer membrane. Changes in permeability between these different states occur due to their different densities and charge. Consequently, different species will diffuse through the polymer structure at different rates, depending on the oxidation state of the membrane polymer. Ionic species can also be “electrochemically pumped” through the membrane by switching between oxidation states. If the polymer is synthesized using a large immobile counterion, reduction of the polymer causes cations from the surrounding electrolyte to be incorporated into the polymer. Subsequent re-oxidation of the polymer ejects these cations. In this manner, cations can be incorporated into the polymer membrane from the feed solution and ejected into the receiving side of the membrane. Selectivity

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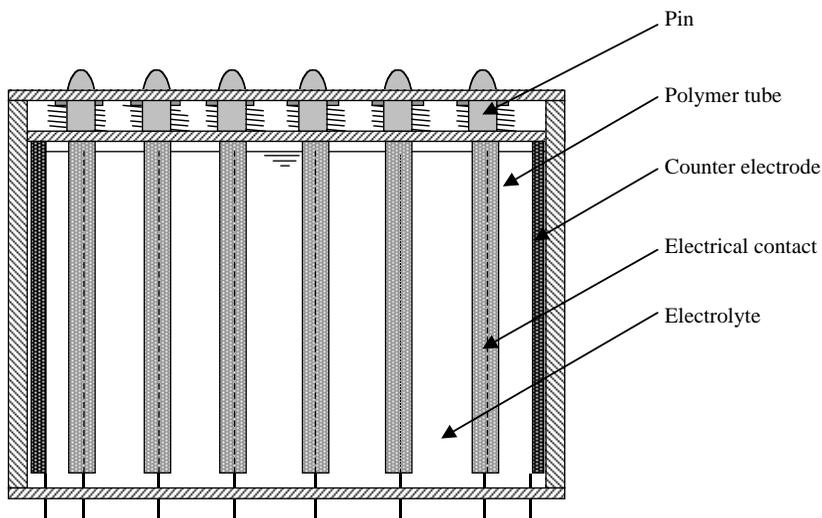
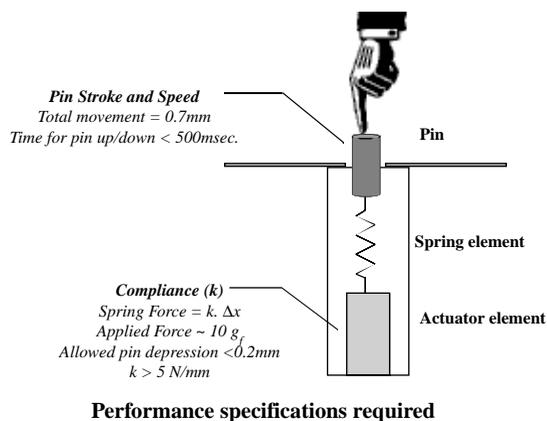


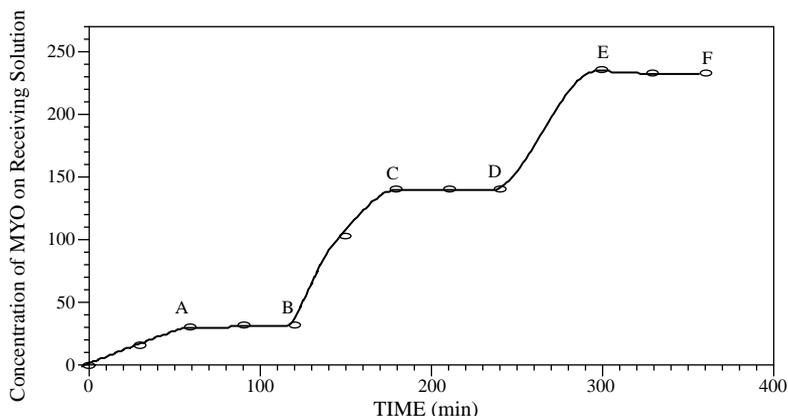
Figure 1.10 The electronic Braille screen based on inherently conducting polymers.

to certain ions is based on size and charge. An exciting prospect is in chiral separations where chiral conducting polymers can discriminate between different hands of the target molecule.

The full utilization of this fascinating new membrane technology is currently limited by our ability to process and fabricate large-surface-area membrane structures at a reasonable cost. Such separation technologies should have a widespread impact in chemical separations for processing and refining purposes and in controlled release technologies.⁴⁴ The separation of neutral volatile organic species using pervaporation has also been achieved using conducting polymer membranes,^{45,46} and recently the use of CEPs for gas separation has been explored.^{47,48}

The electrochemically controlled chemical behavior can also be used to design surfaces capable of selective molecular recognition. This has potential

a)



b)

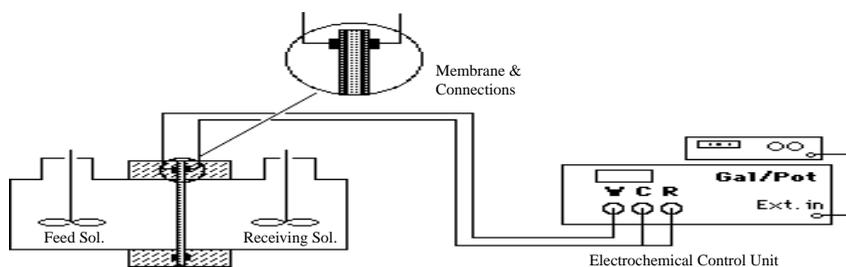


Figure 1.11 (a) Controlled transport of myoglobin (NYO) across a conducting polymer membrane. Fast transport occurs when an electrical potential is applied to the polymer (0–A, B–C and D–E). Undetectable permeation occurs when no potential is applied (A–B, C–D and E–F). (b) Schematic diagram of the membrane transport cell. The membrane separates the stirred feed and receiving solutions and is connected to a galvanostat/potentiostat for control of the electrical potential and current.

for the development of new chromatographic separation media.⁴⁹ In fact, the chemical properties of the chromatographic phase can be tuned *in situ* to effect the desired separation characteristics. Using a specially designed chromatographic column (see Figure 1.12) that allows electrical potentials to be applied during separation, the chemical affinity of the polymer can be adjusted as required.

Cellular communications

The versatility in the synthesis of some CEPs (especially polypyrrole) now enables a range of bioactive surfaces to be created. For example, the incorporation of proteins⁵⁰ such as enzymes or antibodies is readily achieved. Combined with the chemical tuning available, this should be applicable to the

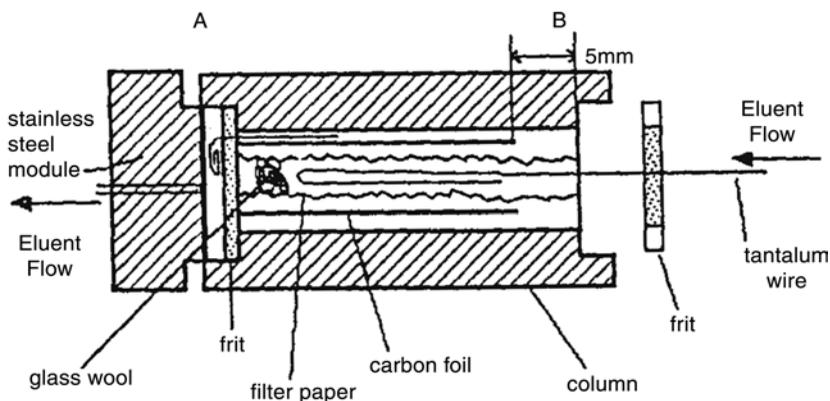


Figure 1.12 The electrochemically controlled liquid chromatography column.

development of biocompatible surfaces or new surfaces for biotechnology processing applications. Studies^{51,52} involving growth and control of biological cell cultures on conducting polymers are already in place (Figure 1.13). Using this approach, it has been shown that electrical stimuli can be used to address living cells in culture and hence stimulate and regulate growth.

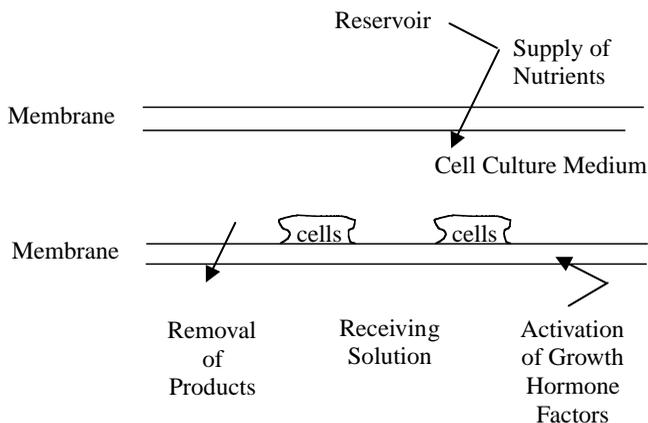


Figure 1.13 Schematic illustrating use of intelligent membranes for cell culturing.

We have shown⁵³ that the growth and differentiation of PC12 cells can be assisted by electronically controlled release of a nerve-growth-factor protein. Langer's group⁵⁴ has shown that neurite outgrowth on PPy is facilitated by passage of current through the structure. It has been shown that the ability to culture cells on CEPs is dependent on the presence of adhesion-promoting proteins.^{55,56} It has also been shown that neural glial cells can be attracted to and grown on PPy-coated electrodes containing the nonapeptide CDPGYIGSR.⁵⁷ Improved adhesion of osteoblast cells to titanium-coated PPy containing a synthetic peptide has been observed.⁵⁸

Controlled release devices

Conducting polymer films and coatings are also ideal hosts for the controlled release of chemical substances, including therapeutic drugs, pesticides, fungicides, and many others. Figure 1.5 shows that the oxidation or reduction of the polymer involves the movement of ionic species into and out of the polymer material. By incorporating the target species as the dopant in the conducting polymer, the redox chemistry of the polymer can be used to release the target species at the desired time. This has been used previously in the cell culturing experiments described above.⁴⁸

In other applications, the release can also be automatically stimulated by a change in the environment. For example, it is known that the galvanic coupling of conducting polymer coatings (such as polyaniline) to metals like steel and aluminum causes a reduction of the polymer from the emeraldine salt state to the leucoemeraldine base, and this process involves the release of the dopant ion into the surrounding electrolyte. It has been speculated⁵⁹ that the dopant could be designed such that it acts as a corrosion inhibitor for the metal and so the polymer can release the inhibitor at the point when corrosive conditions first form. Indeed, a number of studies have shown that the dopant used with PAn has a large impact on the corrosion protection provided by the polyaniline, suggesting that the inhibition process may be involved in the corrosion protection.

Both anionic and cationic species can be incorporated into the polymer and released at the desired time. Anionic species are the usual dopant ions incorporated with PPy, PAn and PTh polymers, but it is also possible to trap cations. The incorporation of cations involves synthesizing the polymer using a large immobile polyanion such as poly(vinyl-sulfonate). When this polymer is reduced, the large anion cannot leave the polymer so cations from the surrounding electrolyte are incorporated into the polymer to balance the charge of the polyanion. Subsequent oxidation of this polymer releases the cation species back into the surrounding electrolyte. The possible ion flows during redox reactions of conducting polymers PPy and PTh are illustrated in Figure 1.5.

A great many ionic species have been incorporated as dopants into conducting polymers and these have a major effect on the properties of the polymer (as discussed in later chapters).

Corrosion protection

Controlled release of corrosion inhibitors may be involved in new-generation corrosion protection coatings based on conducting polymers. Considerable evidence indicates that conducting polymers provide beneficial protection to many metals in a corrosive environment. However, the mechanism by which this protection is afforded is not well understood at the present time. Many studies since the mid 1980s have shown that a coating of PAn, PPy or PTh can inhibit the corrosion rate of mild steel,⁶⁰ stainless steel,⁶¹ aluminium⁶²

and copper.⁶³ The conducting polymer can be applied either as a neat coating or as a dispersion in another polymer binder. In most studies, a barrier topcoat is also applied over the top of the conducting polymer “primer.” [Figure 1.14](#) shows an example from our laboratories illustrating the corrosion resistance of mild steel coated with PAN primer/epoxy topcoat after 3 years’ immersion in saltwater. Although large blisters have formed (after approximately 2 years), there is little sign of rust.



Figure 1.14 Steel sample coated with a polyaniline primer and an epoxy topcoat after 3 years’ immersion in saltwater — note the absence of corrosion products in the test solution. (Courtesy A. Dominis, IPRI, University of Wollongong.)

Elucidation of the corrosion mechanism is complicated by the many testing variables involved:

- Type of polymer used
- Form in which the polymer is applied to the metal
- Use, type and thickness of a topcoat
- Preparation of the metal
- Nature of the corrosive environment

All of these factors will influence the corrosion performance. Careful studies by Tallman and co-workers⁵⁵ have given support to the concept proposed by Elsenbaumer⁶⁴ that the conducting polymer promotes the formation of a passive oxide at the polymer metal interface. It is believed that the dense nature of this oxide impedes the electrochemical corrosion reactions. Studies of the interface region have shown that oxide layers are present.⁶⁵ However, many other factors may also be involved in the overall

process: formation of metal ion–polymer complexes, release of corrosion inhibitors by the polymer, simple barrier protection and others have been suggested as being involved in the corrosion process. The use of conducting polymers as corrosion protection coatings has recently been reviewed.⁶⁶

Corrosion inhibiting paints that use polyaniline as the active ingredient are available from the German company Omecron Chemie. Other companies, such as DSM in the Netherlands, are believed to be interested in developing corrosion-resistant formulations based on PPy.

Chemical sensors

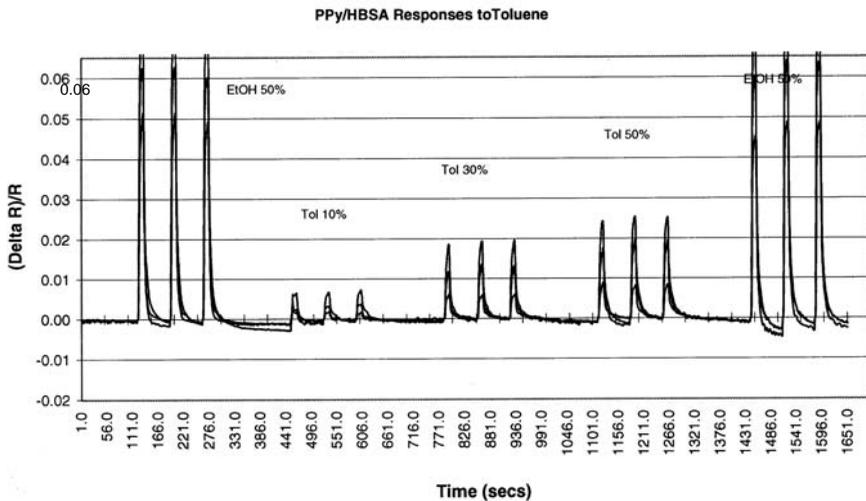
The combination of tunable chemical properties with the electronic properties of conducting polymers has also had a tremendous impact on the development of new sensors. The use of conducting polymers in sensors has been reviewed recently.^{67–72} Sensing surfaces have been designed that are capable of interacting with simple anions,⁷³ metal ions,^{74,75} small organic molecules^{76–78} or proteins.^{79,80} The electrical signals measured can be current flow, change in capacitance or change in resistance. The area of biosensors has proven particularly interesting in this regard because conducting polymer systems have been shown to be capable of *in situ* control of antibody–antigen interactions, making them reversible under selected conditions. The sensors are used in a flow-injection analysis mode enabling rapid sample throughput.

The most successful commercial sensing systems that utilize conducting polymers are the so-called electronic noses.^{81–85} These systems use arrays of robust CEPs, each with differing chemical selectivity using changes in resistance as the signal generation method. The change in resistivity (or conductivity) is brought about either through a change in doping level or through a change in polymer conformation. Vapors such as NO₂ (A), H₂S (D) and NH₃ (D) that are either electron donators (D) or electron acceptors (A) have a dramatic effect on conductivity. Changes in polymer chain conformation can also affect conductivity by increasing or decreasing the localization length over which electrons can move freely. Importantly, both mechanisms appear to be fully reversible in most cases, because the conductivity can be reset to the original values by exposing the polymer to a “neutral” vapor such as dry nitrogen (Figure 1.15).

Such an approach has been used to develop customized noses (specific arrays of polymers) for classification of beers,⁸¹ detection and identification of microorganisms,⁸³ olive oil characterization⁸⁵ and detection and classification of BTEX⁸⁴ (volatile organic carbons).

Conducting polymer sensors can be operated either to quantitatively measure the concentration of a target vapor species, or to qualitatively analyze a complex mixture of vapors. For single vapors, the detection limits can be in the low ppm region. Exposure to a mixture of vapors results in a unique pattern of responses that is usually deciphered using standard chemometric techniques. The pattern can be used like a fingerprint to identify certain products or to

a)



b)



Figure 1.15 The electronic nose. (a) Response of conducting polymer sensor to different concentrations of toluene. (b) Photograph of portable “electronic nose” with an array of conducting polymer sensors (bottom left). (Courtesy of N. Barisci and R. Stella, IPRI, University of Wollongong.)

establish the quality of foodstuffs, wines, perfumes, etc. The electronic nose has similar components to the natural nose, as illustrated in [Figure 1.16](#).

The electronic nose has found its most widespread application in the food industry. Using resistometric and other detection systems, ongoing

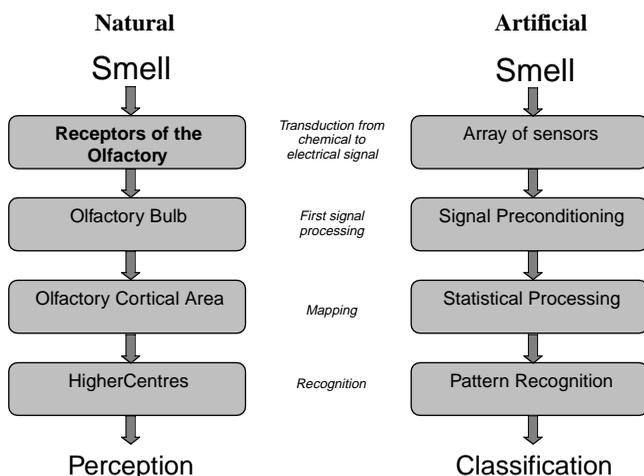


Figure 1.16 Similarities between natural and artificial noses. (Courtesy R. Stells, IPRI, University of Wollongong.)

research is aimed at improving selectivity and sensitivity both in the vapor phase and in solution. Particular emphasis has been placed on chemical functionality of the polymer to increase the selectivity of the sensor to the desired species in a complex mixture. The sensitivity at present is limited primarily by the method of sensor fabrication; the detection limit is lowered by producing ultrathin and coherent layers of the conducting polymer. Screen printing and ink-jet printing techniques provide some interesting opportunities in this regard. Improvements in device fabrication should expand applications into the environmental and biomedical areas.

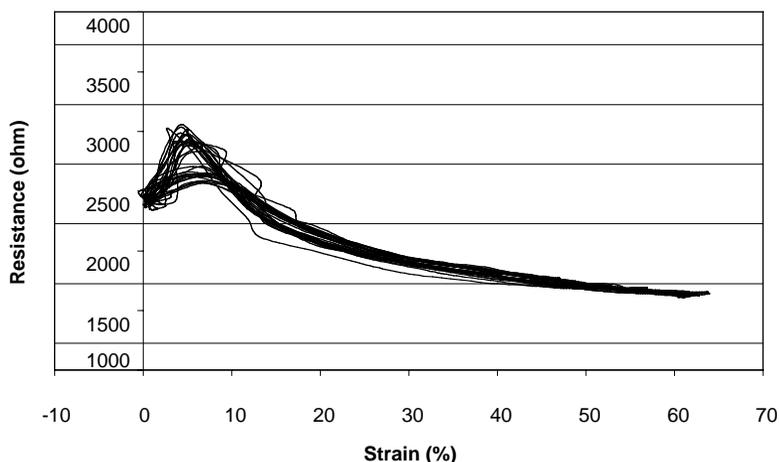


Figure 1.17 Resistance change during stretching of PPy-coated Lycra®. (Graph courtesy of T. Campbell.)

Physical sensors

Conducting polymers have also been used as sensors for the physical environment, particularly for strain or stress. Polypyrrole strain gauges have been constructed from both neat films and from coated stretch fabrics such as Lycra®. Strain gauge materials are characterized by their *gauge factor* (change in resistance per change in length), *dynamic range*, *linearity* and *hysteresis*. These parameters are illustrated in Figure 1.17. The application of PPy to stretch fabrics to yield strain gauge materials having a dynamic range up to 100% has opened up several new exciting applications. Figure 1.17 shows that an almost linear strain gauge response with low hysteresis can be obtained from PPy-coated Lycra® from 20 to 60% strain. These results compare with existing capacitive-based strain gauges that show a gauge factor of 2–4 and dynamic range to only 4%.

These materials have particular application in the field of biomechanics where the strain gauge fabrics can be incorporated into regular sports clothing. Figure 1.18 shows an example of a patented knee sleeve using PPy/Lycra® combined with a feedback device that emits an audible signal when the knee angle reaches a preset degree.



Figure 1.18 Example of fabric strain gauge for determining knee flexion; such devices can be used in sports training, biomechanics studies and rehabilitation.

Communication and characterization tools

An important criterion in choosing intelligent material building blocks is to be able to communicate with the assemblages produced from them. That is, we must be able to monitor behavior in the operational environment, apply stimuli and study property (behavioral) changes in real time. This will undoubtedly be an iterative process, with the communication tools being

refined as the science progresses. In fact, the intelligent materials produced may well serve as the future transducers and conduits of information that are required to obtain information at a molecular level. Only then can the desired behavior characteristics be understood, manipulated and imprinted into the material.

Traditionally, new material characterization is performed *ex situ* using techniques that require the use of environments that will distort the properties of the material under consideration. Consequently, they are of little use in characterizing dynamic structures. Most spectroscopic techniques, for example, are used in air or under a vacuum. For dynamic polymer systems that will be used in solution, such methods do not provide all the essential information. In addition, conventional techniques do not normally allow the imposition of stimuli capable of collecting information on the molecular changes brought about by these stimuli in real time.

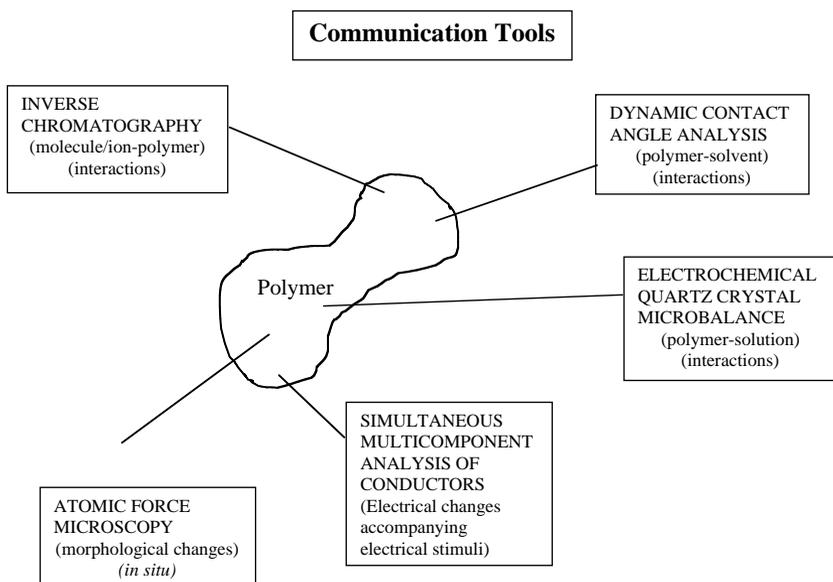


Figure 1.19 Emerging tools for “communication” with dynamic polymer structures.

Consequently, numerous techniques that allow dynamic materials such as conducting polymers to be studied *in situ* have been developed or newly applied over the last decade (Figure 1.19). These include:

- Electrochemical methods
- Dynamic contact angle measurements
- Quartz crystal microgravimetry
- *In situ* spectroscopy
- Inverse chromatography
- Scanning probe microscopy

- *In situ* mechanical testing

Electrochemical methods

Electrochemical methods are applicable in our case due to the inherent conductivity of the polymers under investigation. As will be shown throughout this work, electrochemical methods provide the major means of communicating with conducting polymer–solution interfaces. Given our current fascination with electronic communications, it is fortuitous that conducting polymers are so open to communication through this medium.

The most common electrochemical method employed for characterization is cyclic voltammetry (CV).^{86,87} This involves application of a potential gradient in forward and backward directions to the polymer as an electrode in solution. The current flow as a function of this potential variation is measured and a typical readout is shown in Figure 1.20). According to Figure 1.5, this current flow is a result of the oxidation/reduction processes and the concomitant ion flow that occurs. The readout is useful in characterizing the *electroactivity* of the material. The oxidation and reduction potentials under the solution conditions can be estimated from the peak positions, while the peak areas allow quantification of the charge passed during oxidation and reduction. Comparing the peak areas for oxidation and reduction provides an assessment of the reversibility of the electrochemical reactions.

CVs typically obtained for conducting polymers do not fit the model expected for ideal reversible electrochemical systems. Instead, CEP CVs often display a large separation between the oxidation and reduction peaks, often showing large, constant current flow over a range of voltages. These properties depend significantly on polymer composition and preparation conditions. The effect of polymer composition on the polymer electroactivity (switching properties) is considered in more detail in following chapters. A great deal of research has been conducted to elucidate the origin of specific features in the CVs of conducting polymers.⁸⁸ The current understanding is that separation of the oxidation and reduction peaks is due to the molecular reorganization that accompanies doping and dedoping of the polymer. In particular, the oxidized polymer is believed to adopt a more planar conformation to allow better conjugation. The constant current region (shown between 0 and +0.4 V in Figure 1.20) is thought to be due to the overlap of very many redox peaks. Because the polymer is a mixture of molecular weights and each has a different oxidation potential, the CV records a continuous current corresponding to the sequential oxidation (reduction) of different oligomeric/polymeric species in the sample. The practical consequence is that the oxidation and reduction potentials of conducting polymers are ill defined, and a rather wide range of potentials have been reported (Table 1.3).

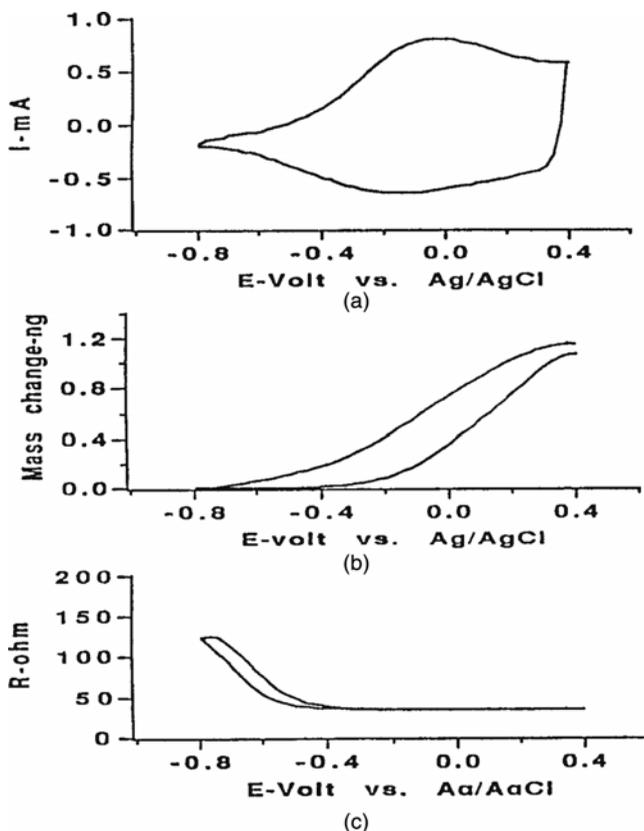


Figure 1.20 Communicating with a conducting polymer PPy/Cl in solution: (a) cyclic voltammetry — a plot of current flow vs. the electrical (potential) stimulus applied; (b) the electrochemical quartz crystal microbalance readout — mass polymer vs. electrical (potential) stimulus applied; (c) the resistometry read out — resistance of the polymer vs. the electrical (potential) stimulus applied. (Reprinted with permission from *Materials Science Forum*, Vol. 189-190, Characterization of conducting polymer–solution interfacial processes using a new electrochemical method, A. Talaie, G.G. Wallace, 1995, p. 188, Trans Tech Publications, Switzerland.)

This simple picture, accepted by many scientists for most of a decade, belies the complexity of this controllable dynamic behavior of conducting polymers. It was only the subsequent development of other *in situ* techniques that revealed the complexities that take us closer to fully understanding and controlling the behavior of CEPs.

Electrochemical quartz crystal microbalance (EQCM)

A system developed recently sheds further light on these dynamic processes. The technique is the EQCM, wherein the polymer is deposited on a gold-coated quartz crystal. Changes in polymer mass as the polymer is electro-

chemically reduced or oxidized can then be monitored *in situ*.^{89,90} For example, as the polymer is reduced, anion removal is indicated by the change in mass observed, as shown in Figure 1.20(b). This technique has proven particularly useful for the study of complex systems, e.g., those containing polyelectrolytes wherein cation movement rather than anion predominates and this is reflected in increases in mass at negative potentials.

Table 1.3 Oxidation and Reduction Potentials (vs. SCE) and Maximum Doping Levels for Selected Conducting Polymers

Polymer	E°_{ox} (V)	E°_{red} (V)	Doping Level*
Polyacetylene	0.75	-1.35	0.1
Polythiophene	0.7	+0.66	0.3
Polypyrrole	-0.2	-0.54	0.4
Polyaniline	0.6	+0.16	1

* charge per monomer unit

Resistometry

An alternative *in situ* electrochemical method provides another piece of valuable information. Resistometry, a technique invented by Fletcher and co-workers and first used for CEPs in our laboratories,⁹¹ enables changes in the resistance of conducting polymers to be monitored *in situ*. The increase in resistance of the polymer material as it is reduced is obvious (Figure 1.20(c)). The definite potential or time lag between current flow and the resistance change is also apparent. This lag is due to the finite time required for the chemical processes causing the resistance change to occur.

This method indicates that the description of Figure 1.5 is an oversimplification. While anions are expelled, it is not a simple redox process. Rather, anions are continuously expelled starting at anodic potentials, suggesting the presence of multiple redox sites, all with different standard potential (E°) values. When the polymer is grown containing a different counterion, the behavior observed can be markedly different. For example, Figure 1.21 shows the response observed with a poly-pyrrole-dodecyl sulfate when applying these same electrochemical potentials scanned in 1 M NaCl. In this case, mass loss (due to anion movement) as the potential is scanned to a more negative value is minimal.

However, excursion to even more negative potentials results in an increase in the mass of the polymer system as cation is incorporated into the polymer (see Figure 1.5). Note also that the potential-resistance profile is markedly different from that obtained when PPy/Cl is reduced.

This information is obtained using a simultaneous-analysis technique developed⁹² to allow current, mass flow and changes in electronic properties

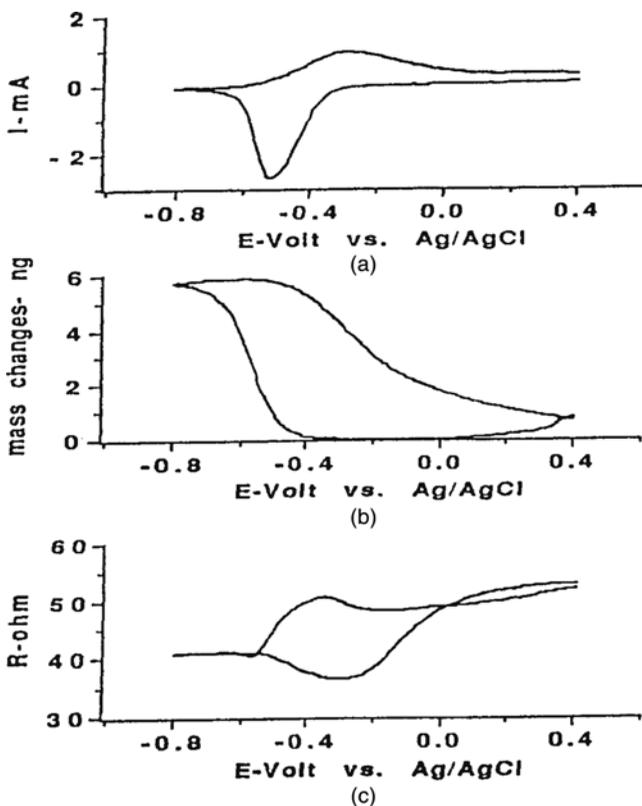


Figure 1.21 Communication with the PPy/DS electrode in solution: (a) cyclic voltammetry, (b) electrochemical quartz crystal microbalance readout, (c) resistometry readout. (Reprinted with permission from *Materials Science Forum*, Vol. 189-190, Characterization of conducting polymer-solution interfacial processes using a new electrochemical method. A. Talaie, G.G. Wallace, 1995, p. 188, Trans Tech Publications, Switzerland.)

(resistance) to be monitored simultaneously *in situ* as the polymer is stimulated by varying conditions of electrical potentials.

Electromechanical analysis (EMA)

A technique complementary to EQCM, EMA, is used to monitor volume changes during cyclic potential sweeps. This method is based on work by Pei and Ingnas^{93,94} and has been further developed at IPRI (see Chapter 3). The technique involves stretching a film of the conductive polymer in an electrochemical cell and monitoring the force or length changes within the film as the potential is cycled. Insertion of ions into the polymer causes swelling and stress relaxation, while expelling ions from the polymer causes contraction and stress generation.

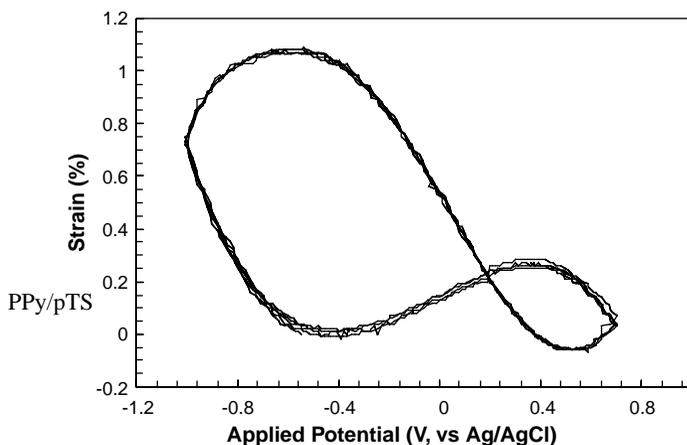


Figure 1.22 EMA data showing length changes (strain) during potential cycling of PPy-pTS.

An example of length changes from an EMA study is given in Figure 1.22, which shows the changes in length (as percentage stretch) within a PPy/pTS film as a result of swelling and contraction during a potential cycle from -1.0V to $+0.75\text{V}$ (vs. Ag/AgCl) in a NaNO_3 solution. Cation incorporation occurs at negative potentials, followed by a salt-draining process in which Na^+pTS^- ion pairs diffuse from the polymer. At positive potentials, the polymer is reoxidized and anions from the electrolyte diffuses into the polymer, which again causes an increase in length.

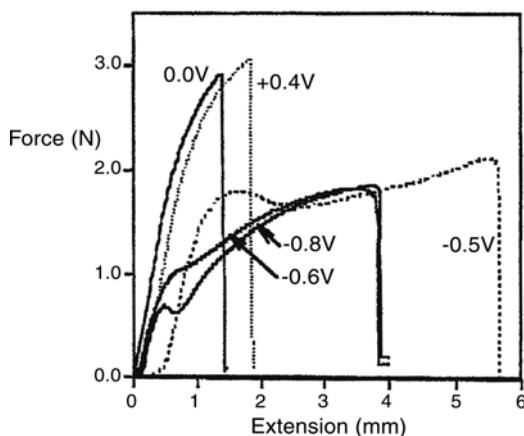


Figure 1.23 Stress-strain curves generated by tensile testing immersed PPy samples at different electrochemical potentials. (Reprinted from *Synthetic Metals*, 97 (2), 117-121, 1998, Electrochemical induced ductile-brittle transition in tosylate doped (pTS) polypyrrole, Burford, R.P. et al. With permission from Elsevier Science.

In situ mechanical tests have also been performed on conducting polymers. For PPy, a strong ductile-brittle transition was observed when the polymer was changed from the reduced to the oxidized state (Figure 1.23). The transition is similar to that observed when polymers are cooled to below their glass transition temperature. The brittleness of the oxidized state was attributed to the greater extent of intermolecular bonding occurring as a result of dipole–dipole secondary bonds within the polymer structure. These bonds restrict molecular motion and, therefore, promote brittleness.

Chemical analysis

Other *in situ* techniques have also been developed in recent years that measure changes in the chemical interactions that occur.⁹⁵ They include inverse chromatography wherein the polymer is used as the stationary phase in a column or thin layer mode, and a series of molecular probes is used to determine the molecular interaction capabilities of the polymer. These systems may be adopted to allow the application of electrical stimuli (as shown in Figure 1.24) to the polymer and to study the effect of these stimuli on the molecular interaction capabilities. The key to this technique lies in the identification of appropriate molecular probes. Such probes must be capable of interacting (reversibly) with the polymeric phase so that well-defined chromatograms can be obtained. To obtain pertinent information, the series of probes must vary in a logical and ordered fashion so that the effect of a particular molecular interaction parameter can be defined. Typically, the strength of the interaction with the polymer is related to the retention of the molecular probe (strong interactions produce long retention).

The Ge series allows interactions listed in Table 1.4 to be determined. Using column chromatography, a comparison of the retention of a test molecule with the base molecule benzene allows the presence of certain types of interactions to be assessed. Using capacity factors (k'), a quantitative measure of the interaction parameter (IP) for a hydrophobic interaction can be obtained according to:

$$\text{IP} = \frac{k' \text{ test molecule}}{k' \text{ benzene}}$$

e.g., for an ion exchange:

$$\text{IP (an ion exchange)} = \frac{k' \text{ benzoic acid}}{k' \text{ benzone}}$$

These parameters must be quoted for a particular solvent, because the solvent, as well as the intrinsic nature of the polymer, will determine what interactions occur. Selected data on conducting polymer phases obtained

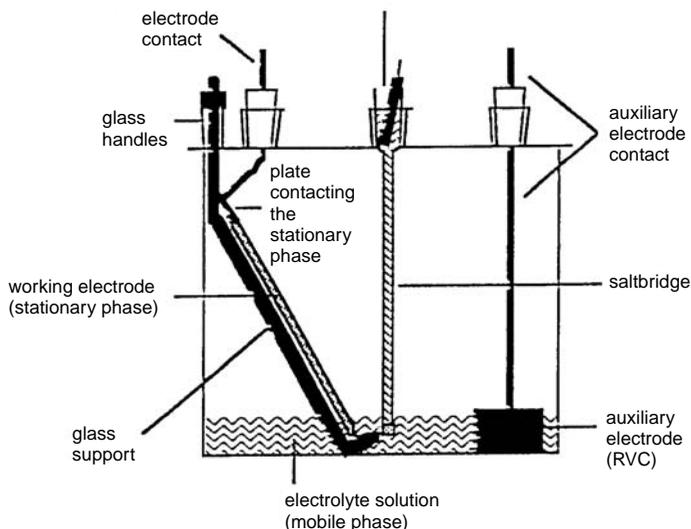
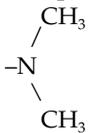


Figure 1.24 The inverse ECTLC experiment setup.

Table 1.4 A Molecular Probe Series for Inverse HPLC (Ge Series)

Molecular Probe	Functional Group	Molecular Interaction
Benzene (principal unit)		Standard
Toluene	-CH ₃	Nonpolar
Phenol	-OH	Polar, H-bonding
Benzoic acid	-COOH	Proton donor, anion exchange
Aniline	-NH ₂	Electron donor, cation exchange
N,N-dimethyl-aniline		Nonspecific adsorption

using this series are shown in Table 1.5, where they are compared with a conventional hydrophobic material, carbon (C₁₈ alkyl chains)-coated silica. The retention index obtained using toluene indicates that the conducting polymers are capable of nonpolar interactions. The high retention index obtained using benzoic acid indicates that the polymers are also strong anion exchangers.

Another interesting series of molecular probes is the polyaromatic hydrocarbons (Table 1.6). These can be used to probe the ability of new polymer phases to discriminate on the basis of molecular size and shape.

In other work, the use of inverse thin layer chromatography (ITLC), (Figure 1.24) has been investigated. This approach was found to be comple-

mentary to ITLC using HPLC, because the physical characteristics of the polymers appropriate for each method were very different. This technique is much simpler in that it does not require expensive high-pressure liquid chromatographic pumps, injectors and detectors. The chromatographic run is carried out in a basic thin layer chromatography (TLC) tank. The ability to electrically stimulate the polymer to obtain information on the molecular interaction capabilities as a function of potential is more easily achieved using the TLC approach. Detection of test molecules is usually carried out visually. We have used a series of amino acids as the molecular probes.

Table 1.5 Chromatographic Interactions on Polypyrrole-Coated C₁₈ (a Silica-Based Phase Coated with an Octadecyl Carbon Chain)

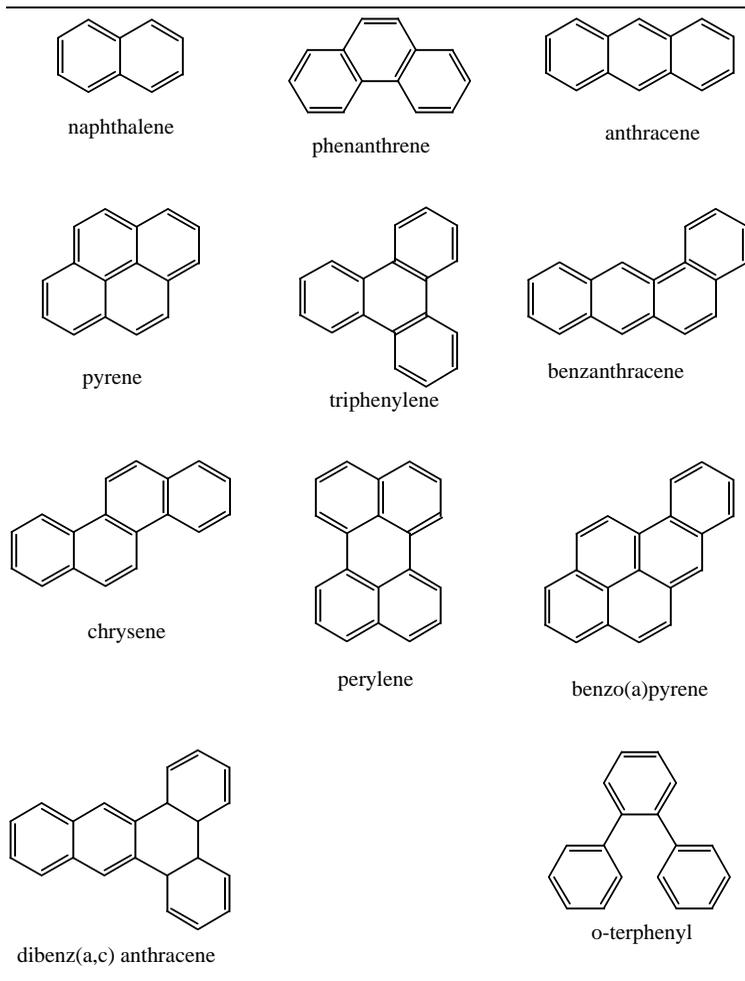
Test Compounds	C ₁₈	Polypyrrole- Chloride	Polypyrrole- Dodecyl Sulfate
	k' /k'	k' /k'	k' /k'
	Benzene	Benzene	Benzene
Benzene	1.00	1.0	1.00
Toluene	1.81	1.79	1.82
Phenol	0.30	0.38	0.33
Benzoic acid	0.06	∞	∞
Aniline	0.42	0.34	1.29
N,N-dimethyl-aniline	2.12	1.72	6.0

These exceedingly simple groups of molecules have tremendous molecular flexibility in terms of the reactions they can undergo, and they were particularly useful for ITLC. The molecules are readily visualized after transfer onto filter paper followed by a conventional chemical derivatization with ninhydrin reagent. This series has been used to study both PPy and polyaniline materials. A typical readout is shown in Figure 1.25. Using different solvents, interactions based on either hydrophobic interactions or ion exchanges were highlighted. This ion exchange selectivity was markedly different from that observed for conventional ion exchangers.⁹⁶ Other workers^{97,98} have used a series of volatile molecular probes to characterize conducting polymers using inverse gas chromatography.

Dynamic contact angle (DCA) analysis is a technique that allows polymer-solvent interactions to be quantified.⁹⁹ These are inherent for all processes occurring at polymer solution interfaces and are likely to be responsible for the dynamic behavior of conducting polymers. Information regarding these interactions is of central importance to understanding of the properties of these materials. Furthermore, it provides information on how exposure to different solvent environments affects the chemical properties of the material. It is also possible to apply electrical stimuli to the polymer during DCA analysis¹⁰⁰ to characterize the effect this has on the interactions between the polymer and its environment.

Table 1.6

The Structure of PAHs



The method is based on Wilhelmy's plate technique for measuring dynamic contact angles. The technique involves the measurement of force as a plate is (automatically) immersed in and then emerged from a liquid at a constant rate. The forces (weight) can be plotted as a function of the immersion depth and, from this, contact angles calculated (Figures 1.26a and b). The Wilhelmy's plate technique has been commercialized with computer automation and data-handling features,¹⁰¹ which has improved its utility considerably.

This technique has been used to study the wettability of different conducting polymer systems (e.g., Table 1.7) and how this is influenced by the counterion incorporated during synthesis and/or functionalization of the monomer.¹⁰²

These results indicate that the functional groups on PCMP and PCEMP act to increase the hydrogen-bonding interactions of the conducting poly-

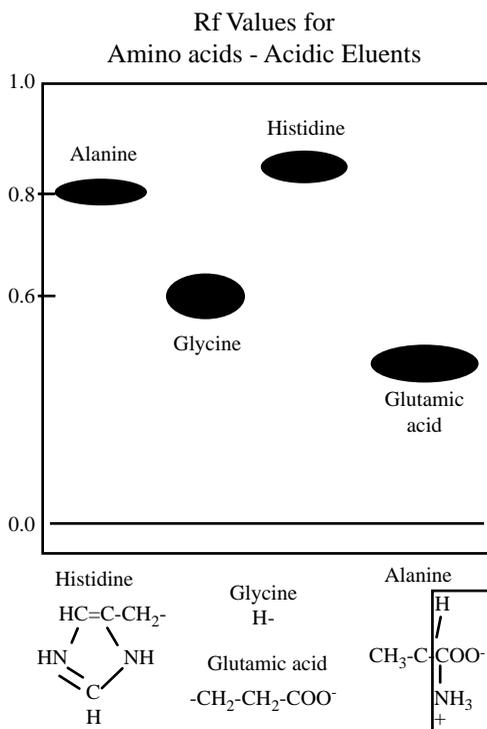


Figure 1.25 Typical readout from inverse thin layer chromatography.

mers, as the θ_a values for each of these are less than those for PPy, which is indicative of a stronger interaction between the solid and liquid phases. Also, the θ_a value for the PPy/PCMP copolymer is intermediate between the values for the constituent monomers. Furthermore, the magnitude of the trend is very close to that which could have been predicted from an analysis of the functional groups on the monomers.

Scanning probe microscopy

Since the pioneering work of Binnig¹⁰³ in the 1980s, the family of microscopic techniques collectively known as “scanned probe microscopy” (SPM) has become widely available and extensively used in conducting polymer research. SPM consists of a number of related techniques in which a fine probe is rastered across a sample surface. Interaction between the probe tip and the sample drives a feedback system that allows topographical mapping of the sample surface. Scanning tunneling microscopy (STM) uses the tunneling current between the tip and the (electrically conductive) surface, while atomic force microscopy (AFM) uses the force of attraction (or repulsion) between the tip and the sample surface. The resolution of the piezoelectric transducers used to move the tip is such that atomic scale resolution can be achieved (magnification $\times 10^9$). AFM has been further developed such that

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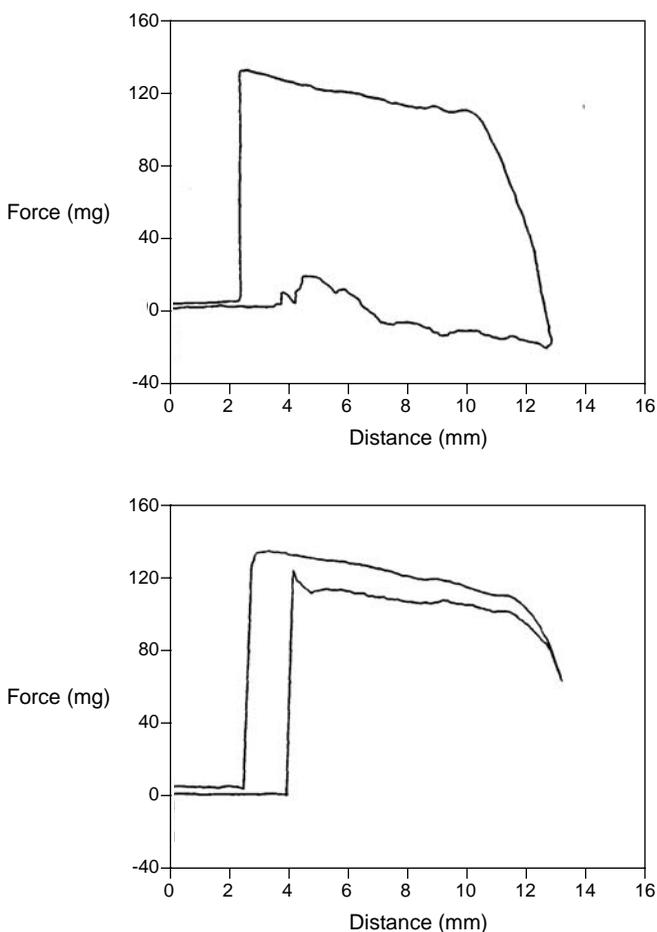


Figure 1.26 (a) Force-distance plot for polypyrrole (NO_3^-) on carbon foil. (b) Force-distance plot for polyaniline (HCl) on carbon foil.

qualitative information concerning the properties of the sample surface can also be obtained. Thus, differences in molecular friction and surface mechanical properties can be discerned. Other techniques can map the surface magnetic domains and electrical properties.

Recent applications of SPM techniques have revealed new details of the electrical properties of conducting polymers. In one example, STM images were taken of the granular structure of electrochemically prepared polyaniline films. Simultaneously, the electrical characteristics of the surface were analyzed by scanning tunneling spectroscopy (STS). In STS the tip remains at a constant vertical position above the surface and the voltage difference between the tip and sample is changed. By also measuring the current flow, the current-voltage (I-V) curve of regions of the sample surface only a few nanometers in

Table 1.7 Comparison of $\cos \theta$, θ and $\Delta\theta$ Values for Polypyrrole, Poly-3-carboxy-4-methylpyrrole (PCMP) and Poly-3-carboxy-4-methylpyrrole (PCEMP) on Glassy Carbon

Sample	$\cos \theta_a$	$\cos \theta_r$	θ_a	θ_r	Dq
Polypyrrole	0.09	1.08	85°	u	85°*
Polypyrrole/PCMP	0.048	1.01	61°	u	61°*
PCMP	0.60	1.01	53°	u	53°*
PCEMP	0.39	1.02	67°	u	67°*

θ_a = Advancing contact angle

θ_r = Receding contact angle

diameter can be obtained. Additionally, a map of the electronic properties of the surface can be obtained by taking I-V curves at discrete points in a 2-dimensional array across the sample surface. This technique is known as current-imaging tunneling spectroscopy (CITS) and CITS images of polyaniline in the doped (emeraldine salt) and de-protonated (emeraldine base) form are shown in Figure 1.27. These images show insulating regions as white and “metallic” regions as grey or black. The electronically conducting emeraldine salt displays a continuous pathway of metallic domains (20–80 nm in diameter). In comparison, the emeraldine base shows fewer metallic domains that are surrounded by insulating regions; these structures account for the very low electronic conductivity of the deprotonated polyaniline.

By applying a potential difference between an oscillating tip in the so-called “tapping mode” of AFM operation, the electronic properties of conducting materials can also be investigated. The imaging method is called electrical force microscopy (EFM) and the microscope acts like a Kelvin probe, allowing the material work function to be determined. The work function is the energy required to remove an electron from the bulk of the material to a point just outside that phase. Although measured in different ways, the work function and oxidation potential of a material are related, because both are measures of the energy needed to remove an electron. Work function (WF) measurements of conducting polymers are therefore useful in characterizing the electrochemical properties. The EFM method offers a spatial resolution of a few nanometers, so the technique provides a unique insight into the local electrical properties of a conducting surface.^{104,105}

Figure 1.28 shows the topography image and the work-function image of a sample of PPy. The topography is the granular structure typical of these polymers with grain sizes in the range 50–100 nm. The EFM image shows a distinct contrast in WF between the center of the grains and the peripheral regions, with the center showing a higher WF. The interpretation of these images is that the central regions are more highly doped and that E^0 value varies on a local scale. These results support the view that macroscopically, the conducting polymer behaves as a mixture of materials

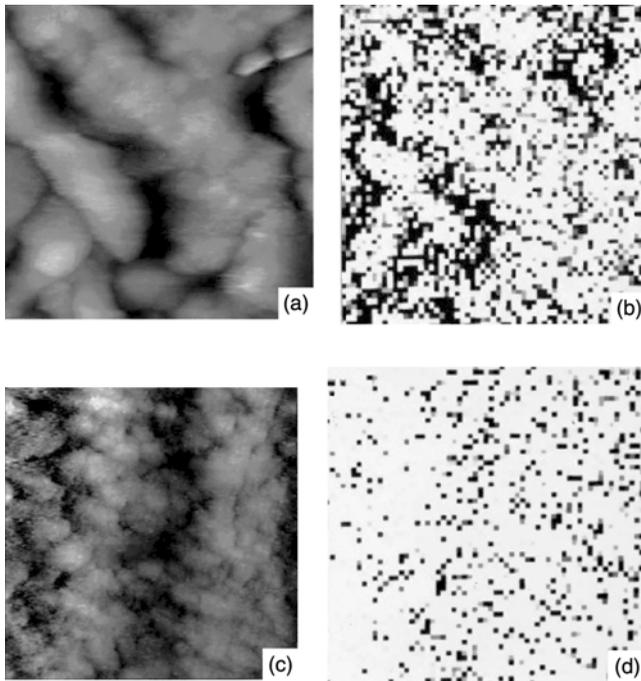


Figure 1.27 Topographical and current-imaging-tunneling spectroscopy (CITS) images of (a, b) doped and (c, d) undoped polyaniline. (Yau, S.-T., Barisci, J.N., Spinks, G.M., Tunneling spectroscopy and spectroscopic imaging of granular metallicity of polyaniline, *Appl. Phys. Lett.* 1999, American Institute of Physics. With permission.)

having slightly different E° values — as concluded from electrochemical studies (described above).

In other EFM studies,¹⁰⁴ part of the sample was electrochemically oxidized by partially immersing in electrolyte and applying a positive potential. The EFM image clearly showed a distinction between the immersed (oxidized) and nonimmersed (less oxidized) parts of the sample in terms of the relative work function. Similar shifts in work function had also been observed for polythiophenes when exposed *in situ* to UV radiation during the EFM imaging.¹⁰⁶ An increase in the work function upon UV exposure is due to the formation of electron-hole pairs that produce the photocurrent in photovoltaic devices. Thus, the EFM provides fundamental insights into the processes involved in many of the applications for CEPs.

The great advantage of SPM for conducting polymer research is its suitability for *in situ* imaging giving rise to such techniques as electrochemical AFM (EC-AFM) and electrochemical STM (EC-STM). Therefore, topography changes can be tracked as a result of electrochemical oxidation or reduction of the polymer. Chainet and Billon¹⁰⁷ have carefully imaged the same area of a PPy sample while electrochemically cycling between the oxidized and reduced states. The nodular surface features were observed to become enlarged during oxidation,

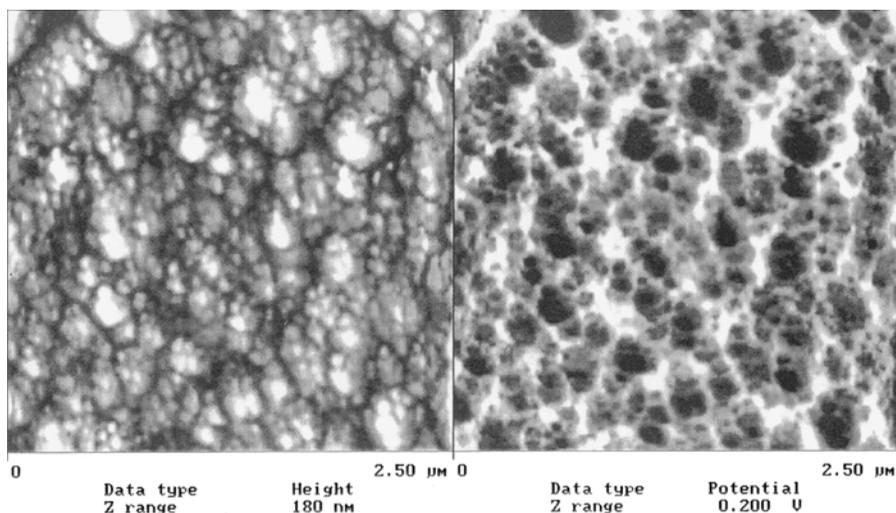


Figure 1.28 Topography image (left) and EFM image (right) of a polypyrrole film. Darker regions in the EFM image indicate higher work function. (Barisci, J.N., et al., Characterization of the topography and surface potential of electrodeposited conducting polymer films using atomic force and electric force microscopies, *Electrochimica Acta*, 2000, 46, 519–531, Pergamon. With permission.)

demonstrating the microscopic origin of the volume changes responsible for the artificial muscles described above.

Raman and UV-visible spectroscopy

In recent years, spectroscopic techniques have become invaluable tools for probing the molecular structures and interactions in CEPs; the two most useful techniques are Raman and UV-visible spectroscopy. In both cases, absorption of the incident radiation by water (and many other electrolytes) is minimal, meaning that it is possible to obtain the spectra by reflection or transmission of light from the sample while it is immersed in an electrolyte and part of an electrochemical cell.

Absorption of light in the UV-visible part of the electromagnetic radiation spectrum is very sensitive to the oxidation state of conducting polymers. Light absorption causes electronic transition between the valence and conduction bands and the specific absorption peaks in the UV-visible spectrum are indicative of the nature of the charge carriers and the number of charge carriers present.

Extension into the near-infrared (NIR) region of the light spectrum provides new insights into molecular conformations of CEPs. The classical studies have been conducted on polyaniline, where the presence or absence of a strong broad absorbance in the NIR (called the “free carrier tail”) is strongly associated with molecular conformations. The free carrier tail is produced when the polymer contains a large population of the bipolaron charge carriers. In polyaniline, the extended chain conformation is more likely to pro-

duce such charge carriers, while the tight coil conformation does not. The conformation can be altered by the use of different dopants and even by exposing the doped polymer to certain solvents (a process dubbed “secondary doping” by MacDiarmid). As the polymer conformation changes from tight coil to an extended chain, the pi-orbitals more effectively overlap to allow greater in-chain conduction. The link between the presence of the free carrier tail in the UV-visible NIR spectrum is strongly correlated with the electrical conductivity in polyaniline.

The Raman spectrum is produced by irradiating the sample with laser light of a certain frequency and analysis of the scattered radiation caused by the Stokes shift. The difference in frequency of the incident and scattered light is equal to the actual vibrational frequencies of the material. Thus, the Raman spectrum can identify and track changes in specific chemical groups. The Raman spectrum can be obtained using a light microscope so that mapping of a surface is possible to a resolution of around 1 micron.

Raman spectroscopy has been used to study the chemical stability of conducting polymers. Conductivity is known to decline upon aging in ambient environments, but the process is accelerated by elevated temperatures mainly due to the thermal loss of dopant.¹⁰⁸ In addition, high electrical potentials can also result in “overoxidation.” Overoxidation is the irreversible, electrochemical oxidative degradation of a conducting polymer under an anodic-applied potential.¹⁰⁹ During overoxidation, a polymer loses conductivity, charge storage ability, electrochromism, electroactivity, conjugation, mechanical properties and adhesion to the substrate. In fact, almost all the beneficial features of a conducting polymer are destroyed by this process.

To ensure long lifetimes for intelligent material systems using conducting polymer electrodes, it is important to understand the overoxidation phenomenon.¹⁰⁹ Raman studies have shown that PPy (doped with *p*-toluene sulfate) undergoes irreversible chemical degradation when it is immersed in aqueous electrolyte and a potential of +0.8V (vs. Ag/AgCl reference) is applied. The changes occur rather quickly (within 5 minutes) and can be ascribed to the formation of oxygen-containing groups in the polymer. The carbonyl groups (C = O) shown in Figure 1.29 are one possible source of the peak indicated as “c” in Figure 1.30, suggesting that the overoxidation rapidly reduces the conjugation of the polymer, leading to a loss of conductivity.

The polymer can be reversibly switched between the first three states at the electrochemical potentials shown (the exact potential depends on the nature of the counterion, A⁻, incorporated with the polymer). The highest oxidation state is referred to as “overoxidized” because the conductivity decreases due to the loss of conjugation; the oxidation from 3 to 4 is not reversible.

Localized electrochemical mapping

Recently, two new electrochemical mapping techniques have become available: the scanning vibrating electrode technique (SVET) and the localized

electrochemical impedance spectroscopy (LEIS) technique. These techniques provide the capability to identify and monitor electrochemical behavior down to the micron level. They represent significant advances over traditional electrochemical methods (cyclic voltammetry, EIS and even EQCM) that provide data that reflect only an average over the entire sample surface. While such data are very useful, a major drawback is that no local or spatial information is obtained.

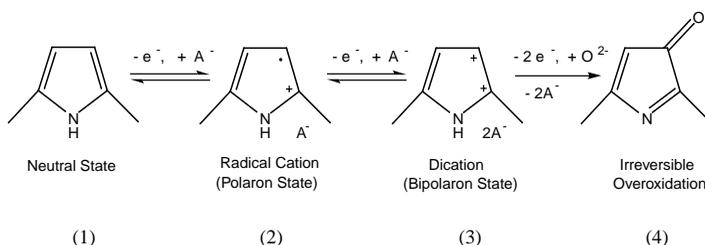


Figure 1.29 Oxidation states of polypyrrole.

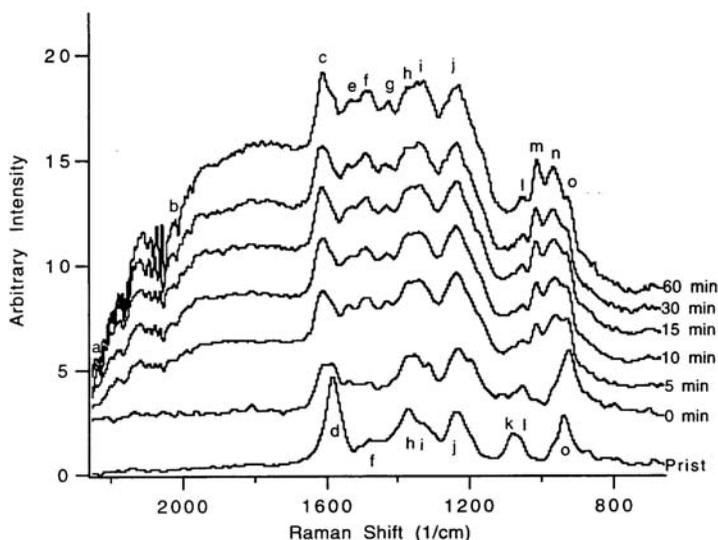


Figure 1.30 Raman spectra of PPy/pTS held at 0.8 V (vs. Ag/AgCl) in 1 M NaCl with a pH of 2.25. (Courtesy T. Lewis, Ph.D. thesis, University of Wollongong, 2000.)

The SVET detects the electrochemical potential of a sample surface (with respect to a reference electrode) with a spatial resolution of tens of microns. The technique uses a probe tip that is rastered above the sample surface and oscillated perpendicular to the sample surface with an amplitude of between 1–60 microns.

One of the first uses of SVET for conducting polymer analysis was in the area of corrosion protection.¹¹¹ In these studies, the SVET probe was rastered over a pinhole defect in a conducting polymer coating on aluminum. The SVET method clearly showed that the pinhole was anodic, while the conducting polymer coating was cathodic. After a short period of immersion, the anodic activity at the pinhole ceased, which is believed to be due to passivation induced by galvanic coupling with the conducting polymer coating.

In LEIS the full electrochemical impedance spectrum of the sample/electrolyte interface can be obtained at the sub-millimetre level. The system works by stepping a probe tip across the sample surface (smallest step size is 0.5 mm) whilst the sample (connected as the working electrode) is perturbed by an ac voltage waveform (usually about the open-circuit potential and with an amplitude typically of 20 mV). The probe tip consists of two separated platinum electrodes, separated by a known distance. Measurement of the potential difference between the two electrodes allows the calculation of the potential gradients above the sample surface, which then give the current density. Comparison of the in-phase and out-of-phase current flow produces the impedance data, as with regular EIS. The data can be plotted as Bode or Nyquist charts for specific points on the surface, or impedance maps of the sample surface can also be obtained.

Conclusions: conducting polymers as intelligent materials

The above areas of application and the ability to characterize and communicate with conducting polymers using emerging technologies highlight the versatile, dynamic, yet controllable nature of these materials. They undoubtedly possess properties that make their use in the pursuit of intelligent materials systems or structures inevitable. For example, they are sensitive to numerous stimuli and can be made to respond. They can store information and energy and are capable of performing intelligent functions. Further, we can communicate with these systems using tools now available in research laboratories.

The following chapters will describe how the design and assembly of various important polymers can be used to produce predetermined properties. (The synthesis and properties of PPys are discussed in detail.) Polyanilines and polythiophenes are also discussed, with an emphasis on the difference between these systems and PPy. A multitude of other CEP systems exist and the interested reader is referred to the extensive literature now available. Furthermore, the synthesis of CEPs to produce different forms that enable integration of all the functions required for intelligent operation or that allow incorporation into a larger structure will be described.

Undoubtedly, this pursuit will result in spin-off benefits for conducting polymer research and perhaps polymer (macromolecular) science in general. For too long, the implications of the inherent dynamic properties of polymers have been ignored, as we have devised ingenious ways to eradicate them.

A more sophisticated approach to understanding and manipulating may revolutionize polymer science in its own right.

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chapter two

Synthesis and structure of polypyrroles

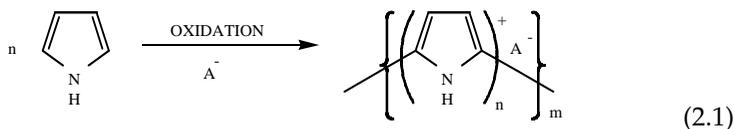
Stability and homogeneity of materials were formerly viewed as desirable properties by scientists. Any modifications made to such materials required ingenious and complex chemical processes. While such properties will always have a place in structural components, a new generation of materials that are defined by their heterogeneity and dynamic properties have been discovered by scientists. As can be concluded from studying natural materials and reactions that have evolved to a level of complexity and diversity using simple building blocks, the capability to change in response to their environment is a powerful one. We now strive to re-create such sophisticated behavior using conducting polymers as simple building blocks.

Polypyrroles (PPys) are formed by the oxidation of pyrrole or substituted pyrrole monomers. In the vast majority of cases, these oxidations have been carried out by either (1) electropolymerization at a conductive substrate (electrode) through the application of an external potential, or (2) chemical polymerization in solution by the use of a chemical oxidant. Photochemically initiated and enzyme-catalyzed polymerization routes have also been described but are less developed. These various approaches produce polypyrrole materials with different forms — chemical oxidations generally produce powders, while electrochemical synthesis leads to films deposited on the working electrode and enzymatic polymerization gives aqueous dispersions. The conducting polymer products also possess different chemical and electrical properties. These alternative routes to PPys are therefore discussed separately in this chapter.

This chapter deals with the creation of conducting polypyrroles, including the parameters that are important in affecting the polymerization process. The next chapter discusses how these synthesis parameters influence the polymer properties.

Electropolymerization: a complex process oversimplified

Polypyrrole can be formed by the oxidation of pyrrole at a suitable anode. Upon application of a positive potential, an insoluble conducting polymeric material is deposited at the anode. The polymerization reaction can be represented simply as:



[$n = 3 - 4$, m relates to the polymer chain length, which determines molecular weight].

In this representation, A^- is a counterion necessary to balance the charge on the polymer backbone. The counterion content is high (can be greater than 50% w/w) and is usually incorporated between the polypyrrole planes,¹ which are predominantly α - α bonded.² In “ideal” polypyrrole (Figure 2.1), it is assumed that the pyrrole rings alternate facing and that the geometry is such that the counterion is intercalated between the planar polymer chains.² In real materials, this idealized structure must be distorted somewhat since highly insoluble and highly crosslinked materials are formed.³ The molecular structure of PPy is further described in later in this chapter.

The simplistic polymerization process [Equation (2.1)] and the idealized structure (Figure 2.1) both belie the complexity of this polymerization process.⁴ A greater understanding of this process has led to the development of innovative processing approaches in recent years. As pointed out in the introduction, intelligent material structures require a dynamic character. This dynamic, interactive nature is present right from the point when polymer synthesis is initiated; hence, the assembly of these materials is not as straightforward as illustrated in Equation 2.1. The first step (monomer oxidation) is slow;⁵ the radical-radical coupling, deprotonation and subsequent oxidation are fast. Polymerization is believed to proceed via a radical-radical coupling mechanism,⁶ wherein the natural repulsion of the radicals is assumed to be negated by the presence of other species, such as the solvent, the counterion and even the monomer. Chain growth then continues until the charge on the chain is such that a counterion is incorporated. Eventually, as the polymer chain exceeds a critical length, the solubility limit is exceeded and the polymer precipitates on the electrode surface.

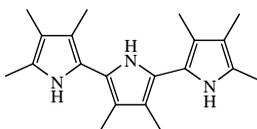


Figure 2.1 Idealized structure of polypyrrole.

A major point of contention involves where radical-radical coupling occurs and whether continued growth is in solution or from the electrode surface. At least some polymerization occurs in solution,⁷ but how much depends on the experimental conditions employed. This polymer then interacts with the bare electrode or previously deposited polymer as the reaction proceeds to produce the final structure.

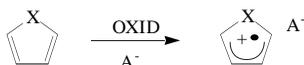
Once the initial layer of polypyrrole is deposited it becomes a reactant that determines the course of the remainder of the polymerization process. Polymerization occurs more readily (at a lower potential) on the already deposited polypyrrole than on the anode surface. This process of product becoming reactant continues until the reaction is stopped. A more detailed investigation of the polymerization process reveals the intricacies involved in producing these sophisticated dynamic structures. Thus, the overall process may be broken into several discrete steps as shown in [Figure 2.2](#). (Details are available in Reference 4.)

The electrochemical conditions, the electrode material, the solvent, the counterion and the monomer all influence the nature of the processes occurring. For example, if the applied potential is too low (under certain conditions), the rate of polymerization will be such that no precipitate eventuates. If the solvent is nucleophilic (or contains dissolved oxygen), it will react with the free radical intermediates. If the electrode material is extremely polar, at the potential required for polymerization, deposition may be discouraged. In addition the solvent, monomer, counterion and substrate interactions are all important since they dictate the solubility and/or deposition of the resultant polymer.

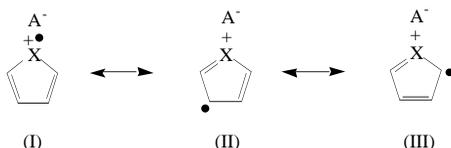
Another issue arising from closer examination of the mechanism is the question of what actually controls the rate of polymerization and hence the structure of the polymer. Again, all the parameters mentioned above play a role in determining the overall rate of reaction.⁸ The complexity arises in that the role that each plays varies depending on the stage of polymerization. For example, in the initial stages of polymerization the electrode substrate plays a critical role that diminishes once the reaction is initiated. On the other hand, the monomer may be present in excess when the reaction is initiated but due to depletion may become the rate-determining factor as the reaction proceeds.

With respect to the rate-determining step, the electrochemical reactions occurring at the cathode cannot be ignored. Particularly in a two-electrode cell, this step may become the rate-determining factor. This is the case, for example, when reduction of water is the cathodic reaction. Reactions occurring at the auxiliary electrode (the cathode) shown in [Figure 2.3](#) are usually assumed to involve reduction of the supporting electrolyte cation, dissolved oxygen or the solvent itself, unless an auxiliary reagent such as an electro-active metal ion or ferricyanide is purposefully added. The auxiliary electrode reaction will then consume this additive.

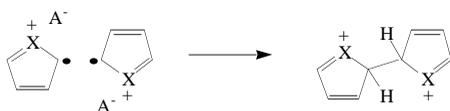
Step 1. Monomer Oxidation



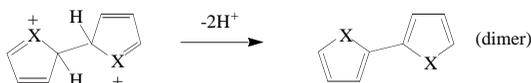
Resonance forms:



Step 2. Radical-Radical Coupling



Step 3. Deprotonation/Re-Aromatization



Step 4. Chain Propagation

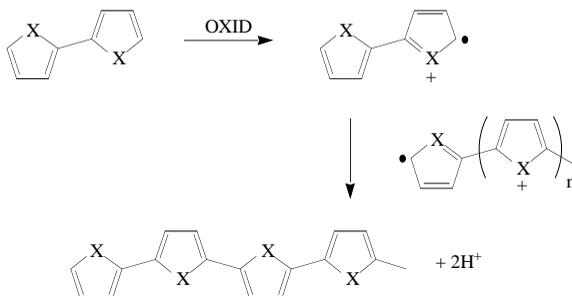


Figure 2.2 A more detailed look at polypyrrole formation.

The hydrodynamics of the electrochemical system and temperature are also important because these control the rate of transport of reactants and products to and from the electrochemical reaction zone. This, in turn, determines the polymerization efficiency. Hydrodynamics is also important in determining the form of the PPy produced. For example, using a flow-through cell and appropriate chemical environments, stable colloidal dispersions rather than insoluble films can be produced (see Cell Design).

Aspects of polymerization efficiency have been studied previously⁹ using electrochemical quartz crystal microbalance techniques, which allows the amount of polymer deposited to be weighed *in situ*. This is achieved by depositing polymer on a gold-coated quartz crystal whose oscillating

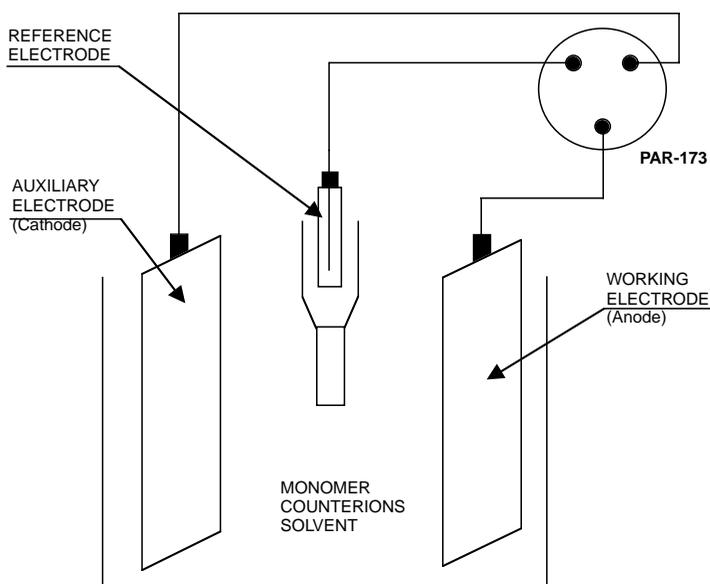


Figure 2.3 The electropolymerization cell.

frequency is continually monitored (see Chapter 1). The change in frequency can then be related to the change in mass and plots of charge (Q) vs. mass obtained. Baker and Reynolds found that the efficiency was low in the early stages of polymerization and then increased to a constant level. They also found that the final electrolytic efficiency decreased as the monomer concentration decreased, and varied depending on the electrolyte and solvent combination employed. In a sense, the electrode acts as a product collection device, interacting with appropriate components of the polymerization process. These results emphasize the competitive nature of the electrodeposition process and the fact that the polymer forms in solution then deposits onto the working electrode. Given the complexity of the polymerization process, each of the experimental properties that control it will now be considered in turn.

The polymerization environment and cell design

While the set-up required to induce electropolymerization is simple (Figure 2.3), the set-up required to deliver product of the necessary quality for real applications requires some thought and is still the subject of numerous studies. For example, in our own work,¹⁰ we have found that the use of concentric counter electrodes is essential to coat wire electrodes in a uniform fashion. In more recent work, we have verified the need for a helical wire interconnect to ensure efficient charge injection into hollow PPy fibers of micron dimensions but centimeters in length (Figure 2.4).

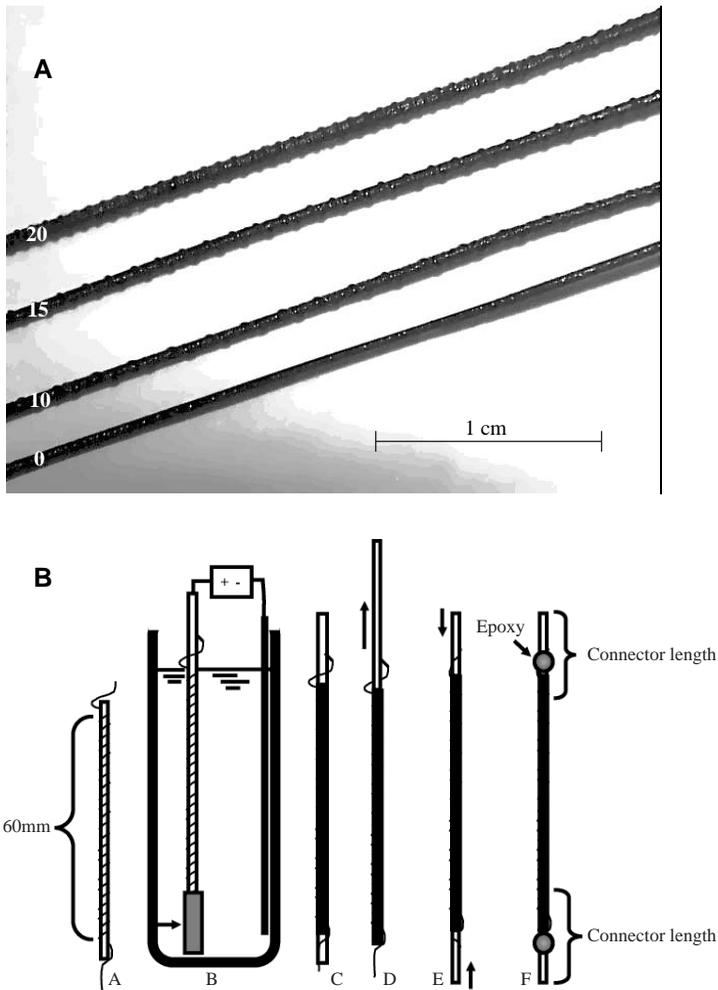


Figure 2.4 Photographs (a) of hollow polymer tubes with helical interconnect used for actuation testing. The pitch of the helix can be altered with examples shown in (a) of 20, 15 and 10 turns/cm. A hollow tube with no helix (0 turns/cm in (A)) is also shown. Schematic diagram (b) showing method of construction for these helix tubes. (a) 25- μm platinum wire is wrapped around the 125 mm wire as a spiral, (b) Polymer synthesis — the assembly is placed in polymer electrolyte solution (0.5 M Py, 0.25 M TBA PF₆ in PC) and electroplated for 24 hours at -28°C . (B) Polymer coating forms around wire and spiral, (C) 125-micron center wire is withdrawn from the polymer tube/helix, (D) two short connectors of 125 mm wire are inserted into each end, (E) 25 mm wire is pulled tight around these ends for a good electrical connection and epoxy glued to hold in place.

Most laboratory set-ups employ a three-electrode potentiostated system to ensure effective potential control and to maximize the reproducibility of the polymerization process. The positioning of the auxiliary electrode is critical in that it determines the electrical field generated, which can influence the quality and evenness of the polymer deposited. The electrode system shown in Figure 2.3 includes a reference electrode. A two-electrode cell can also be used, usually with galvanostatic (constant current) electropolymerization methods, but care must be taken to avoid degradation of the polypyrrole through poor control of the potential.

Two major considerations accentuated by the nature of conducting polymer synthesis are iR drop (potential drop due to cell resistance) effects and the hydrodynamics of the cell. As polymer is deposited on the anode, the resistance of the electrode (substrate and polymer) usually increases. The cell hydrodynamics is important in that it will regulate the movement of reactants (monomer or lower-molecular-weight oligomers) and products (higher-molecular-weight oligomers and polymers to and from the electrode). During growth, variations of the order of millivolts or slight changes in the hydrodynamics of the system may have a dramatic influence on the polymer produced.

With respect to cell design, the working electrode geometry, the anode–cathode separation and the nature of the working electrode all influence the nature of the polymer formed. The use of a thermostated cell is essential to manufacturing polymers in a reproducible fashion. Given the chemical steps involved in the polymerization process, the hydrodynamics and temperature control of the cell design are important. Not only does the temperature influence the rates of transport in the cell, it is also important in determining the extent to which unwanted side reactions occur. For example, it is known that the radicals generated during polymerization can react with oxygen to form an inferior product. At higher temperatures, such reactions would proceed more rapidly. Several workers¹¹ have shown that polymers with higher conductivity are produced from polymerizations carried out at low temperature. In our own work, temperatures as low as -28°C , using propylene carbonate as solvent, have been necessary to achieve optimal polymer conductivity.

The transport of reactants and products to and from the reaction zone is extremely dependent on the cell hydrodynamics and on whether the solution is stationary or moving. Products generated at the auxiliary electrode may also be critical, and, for this reason, the auxiliary electrode should be separated or placed downstream.

Continuous processing using electrodeposition requires that:

- A mechanically stable and conductive polymer is deposited.
- The polymer is continuously removed from the electrochemical cell.

Continuous processing cells have been described previously by Narmann.¹² The most popular approach involves the use of a rotated drum electrode. Polymer is electrodeposited onto the electrode as it passes through the cell, and then continuously stripped from the electrode as it rotates out of the cell (Figure 2.5).

In our own laboratories,¹³ we have used the fact the polymerization occurs in solution to develop a flow-through electrochemical cell to produce colloids^{14–17} or water soluble¹⁸ conducting electroactive polymers (CEPs) continuously. The use of a highly porous anode (reticulated vitreous carbon — RVC) ensures that a high-surface area is available for electropolymerization and that a flowing solution can be used to prevent polymer deposition. The use of steric stabilizers (such as polyethylene oxide or polyvinylalcohol) in the flow-through electrolyte (see use of stabilizers under Chemical Polymerization) also helps prevent deposition and promote colloid formation. Both polypyrrole and polyaniline colloids have been prepared using this approach.

The beauty of this electrochemical approach to production of colloids is that a range of dopants (A^-) can be incorporated into the polymer. For example functional dopants such as corrosion inhibitors,¹⁴ proteins¹⁵ and polyelectrolytes¹⁶ have been incorporated. Even dopants that produce chiral activity within the conducting polymer colloid have been successfully incorporated.¹⁷

Other workers² have used similar principles to enable continuous production of conducting polymer fibers in a flow-through electrochemical cell. As with the hydrodynamic system above, polymer is produced at the anode and continuously removed from the cell in the form of a fiber. Alternatively, other fibers such as kevlar or nylon can be coated using such hydrodynamically controlled polymerization systems.

The hydrodynamic aspects of cell design have been studied using a rotating electrode set-up.²⁰ As the electrode rotation speed is increased, the potential required to sustain constant current deposition increases. The hydrodynamics increases the rate of oligomer transport away from the electrode, thus preventing polymer deposition.

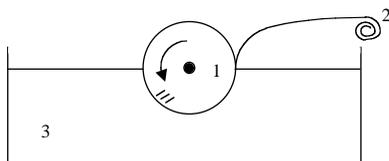


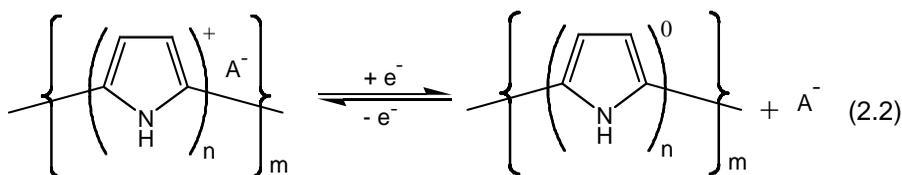
Figure 2.5 Rotary drum anode (1) used for continuous production of CEP polymer tape (2), which is continuously stripped from anode that is deposited from the electropolymerization bath (3).

Electrochemical conditions

The simplest means of inducing the polymerization process is to apply a sufficiently positive constant potential. The potential chosen will influence the rate of oxidation and, therefore, polymerization. If the rate of polymerization is too slow, oxidation of the pyrrole monomer may occur without deposition because the critical chain length may not be reached, and hence, the solubility not exceeded before the products leave the reaction zone near the electrode surface. However, the upper value of the potential is limited by a process that results in overoxidation of the polymer. This results in a less conductive and more porous polymer product^{21,22} with inferior mechanical properties. In general, due to the heterogeneity of electrode substrates (see later), constant potential growth does not result in even coatings on electrode surfaces. In addition, constant potential growth is sensitive to iR drop effects. As the polymer is deposited, electrode resistance (R) increases and the effective potential drops, thereby changing the growth characteristics of the polymer.

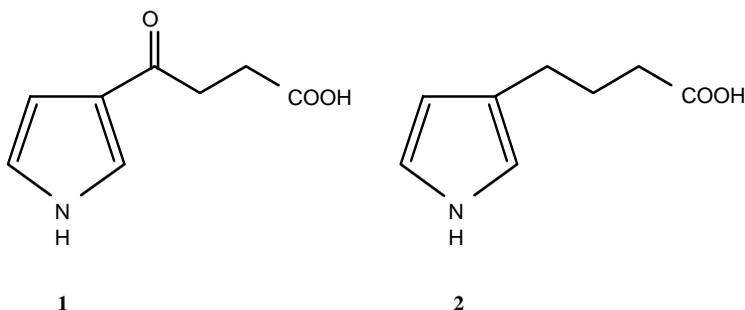
An alternative is to apply a constant current to drive the reaction. This usually results in more even film growth, although local variations in current density will produce a heterogeneous polymer. The rate of polymerization is dictated by the current density applied. Again, if the rate is too low, oxidation without deposition may occur. However, if the rate is too high, the potential may stray into the region where overoxidation of the polymer occurs.

Finally, transient potential or current waveforms can be used for polymerization. Cyclic voltammetric growth has mostly been used to carry out mechanistic studies. The use of pulsed current or potential is not a common practice. However, pulsed current methods^{23,24} have been used by Mitchell and co-workers to produce more ordered anisotropic films. The use of transient waveforms adds another dimension to electropolymer growth, because the oxidation/reduction of the polymer according to Equation 2.2 will occur during growth and the effect of this on the polymerization process must be considered.

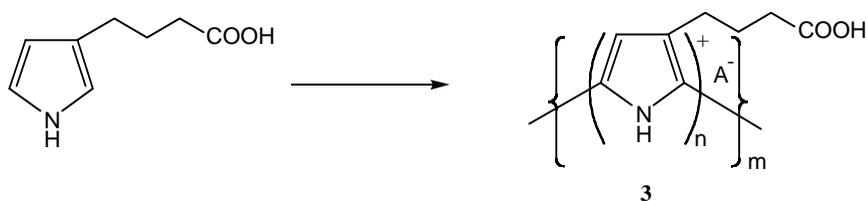


In fact, it is this oxidation/reduction process that results in the more ordered structure obtained by Mitchell and co-workers. They postulate that deposition will be regulated by the oxidation/reduction process.

Transient waveforms can also be used to modify the monomer prior to polymerization *in situ*. For example, the polymerization of monomer 1 shown below does not proceed if a constant positive potential is applied.



However, when a transient waveform is used, reduction of the above monomer to form 2 can occur at negative potentials. The polymerization of 2 proceeds according to Equation 2.3 as the working electrode is exposed to more positive potentials.²⁵



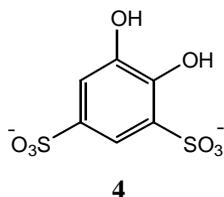
(2.3)

Electrode materials

The electrode substrate should be considered an integral part of the polymer production process,²⁶⁻²⁸ particularly in the initial stages of growth. The nature of the electrode material determines how easily the pyrrole monomer can be oxidized. It also determines the degree of adsorption of the monomer, the oligomers and finally the polymer that occurs during polymerization. Whether deposition occurs depends on the surface energy of the electrode and controls the hydrophobic/hydrophilic nature of the deposited polymer. It has been postulated that some oxide-containing electrodes undergo covalent bonding reactions with the polymer to form an extremely adherent film.²⁹

It is known that deposition on substrates where nonconductive metal oxide layers are formed at positive potentials is difficult. This includes electrodes made of stainless steel, tantalum and aluminum. However, the rate

of oxide formation is important, because we have shown that stainless steel is an ideal substrate for deposition of some polypyrroles. The rate of oxide formation depends on the solution and the electrochemical conditions employed. If the polymer can deposit before the onset of metal oxide formation, then consistent films of excellent quality can be deposited. This is aptly demonstrated with the successful electrocoating of aluminum when the catalyst Tiron (**4**, shown below) is used.²⁹



Other workers have shown that the use of specific dopants to assist in rapid deposition or metal passivation of active metals can help in this regard. For example, oxalic acid electrolytes have been used to facilitate electrodeposition of PPy on Al.³⁰

The adhesion of the polymer to the electrode surface is another consideration. For example, the polymer can be generated at an electrode such as tantalum where it will not deposit. In our laboratories,³¹ in the design of an electrochemical slurry cell to coat silica particles, we have used the fact that deposition of polypyrrole onto tantalum is difficult. The polymer generated at the tantalum anode does not deposit there, instead, it deposits on the more receptive (silica particle) surfaces in the electrochemical cell. This represents a unique polymerization process whereby the polymer is generated electrochemically in an environment that allows nonconductive substrates to be coated resulting in unique composite structures.

An interesting result obtained in 1995 shows that the substrate employed may dictate the surface (polymer or solution) properties of even relatively thick polymers.³² For example, with polymers grown from dodecylsulfate-containing electrolytes, the nature of the substrate used dictated the hydrophobicity/hydrophilicity of the conducting polymer solution interface. Polymers grown on a carbon foil substrate shown to be hydrophobic produced a more hydrophilic polymer surface. Finally, those grown on platinum, a more hydrophilic substrate, produce a more hydrophobic polymer.

These results indicate that the surfactant counterion is capable of imparting either hydrophobic or hydrophilic properties to the polymer, depending on the substrate material. This may be due to a different orientation of the surfactant counterion within the polymer for each substrate. Because the carbon foil has a much more hydrophobic surface, the surfactant counterions could be expected to align themselves more with the nonpolar end toward the substrate, and the changed end toward the solution on the carbon foil

material. This would explain the difference in surface interactions between the polymers on these two substrates.

The physical structure of the anode also plays an important role. Some workers have shown that growing through small pores (Figure 2.6) to produce fibrils can result in polymers with enhanced conductivity.³³ This is achieved by precoating the anode with a porous membrane such as a nucleopore membrane, forcing the conducting polymer to grow out from the anode through the pores. In similar studies, Mansouri and Burford have shown that the fibrils continue to grow in this form even after they leave the constraints of the membrane,³⁴ indicating that once a pattern of growth is imprinted it continues. These same authors have shown that the rate of fibril growth was solvent dependent.

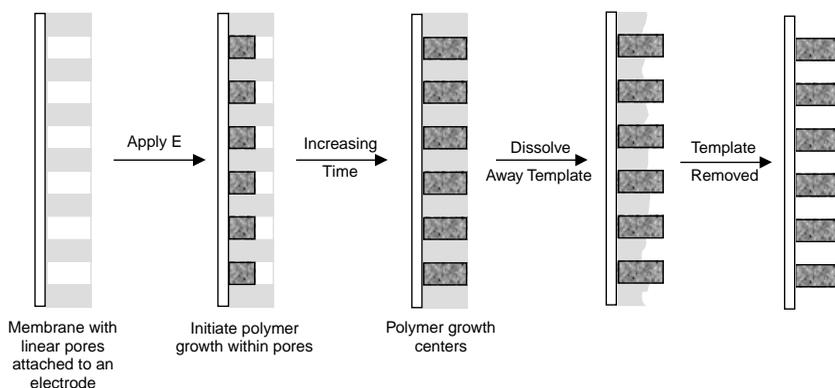


Figure 2.6 Production of highly fibrillar CEP structures. (Innis, P.C. and Wallace, G.G., *J. Nanosci. Nanotech*, 2, 441 (2002). American Scientific. With permission.)

Examples of fibrillar CEP structures obtained from work in our laboratories are shown in Figure 2.7.

Modification of the working electrode has also been used to introduce molecular templates onto the electrode surface to produce nanorods or nanowires electrochemically.

Jerome and co-workers have electrodeposited an insulating polymer polyethylacrylate onto a glassy carbon plate and used this as a template to grow polypyrrole nanowires.³⁵ Others³⁶ have shown that the use of electrodes modified with cyclodextrins for electropolymerization of polyaniline results in production of polyaniline based nanowires. Wan and Yang³⁷ have shown that the use of appropriate dopants during electropolymerization results in the growth of microtubules.

The size of the working electrode is also important. This will influence the electropolymerization process in that the conductivity decreases during deposition can be minimized, also, depletion effects are more pronounced with large electrodes. With smaller (<20 μm diameter) electrodes, electropolymerization can be carried out in low-conductivity media; also, the rate of transport to and from the electroactive center is markedly enhanced. In some

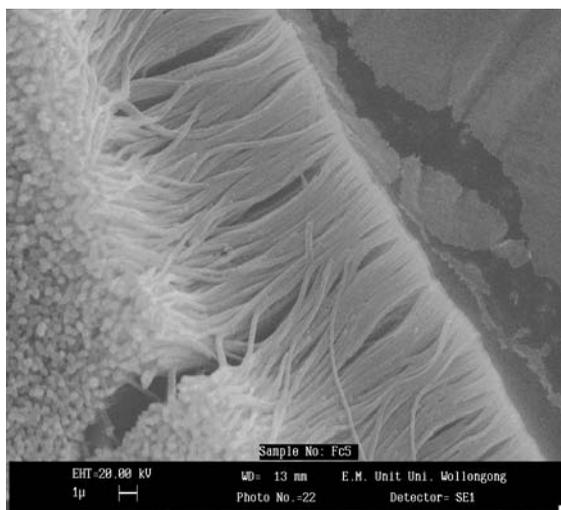


Figure 2.7 Fibrillar CEP structures. (V. Misoska, Ph.D. thesis. University of Wollongong, 2002.)

cases, this latter feature can be a problem in that the enhanced rate of transport away from the microelectrode causes increased difficulty in obtaining a polymer deposit.

The *auxiliary electrode* material should be inert, yet capable of maintaining rapid cathodic reactions to maintain the desired polymerization rate at the working electrode surface. During deposition at anodic potentials, the auxiliary electrode is exposed to (sometimes extreme) negative potentials. The increase in pH (due to the reduction of dissolved oxygen in the solution and to the reduction of water itself) may interfere with the polymerization process; hence, the positioning of the auxiliary electrode is of paramount importance. To prevent increase in pH, easily reduced species such as copper or silver salts can be added. This provides a more facile electrode reaction at the cathode and prevents electrode reactions that result in a change in pH.

When cyclic voltammetric growth or pulsed potential deposition is used, the behavior of the auxiliary electrode at anodic potentials is also important because exposure to extreme positive potentials may occur. If easily oxidized (e.g., stainless steel), the release of metal ions into solution can interfere with the polymerization process at the anode. Alternatively, generation of products from water oxidation or organic solvent oxidation can cause problems. This again emphasizes the need to control the reactions occurring at the auxiliary electrode.

The solvent

Given that some of the solvent becomes an integral part of the final product, it is more than just a reaction medium. It is a reactant and should be con-

sidered as such. The solvent will also have an effect in determining the conformational nature of the polymer. This effect is analogous to that observed with other macromolecules, such as proteins, which can fold in aqueous solution to protect their hydrophobic groups but unfold in more nonpolar solvents to expose the hydrophobic groups. The choice of solvent is critical and its role should be considered in light of the detailed polymerization mechanism.

Obviously, the solvent should be as pure as possible. Even the presence of dissolved oxygen may pose problems, as it reacts with radical intermediates and is reduced at the auxiliary electrode to form hydroxide during the polymerization process. Pyrrole is much preferred over other heterocyclics because this monomer is water soluble. Aqueous solvents are preferred to organic solvents from the point of view of cost, ease of handling, safety and the range of counterions that can be used.

The solvent should, of course, be capable of dissolving the monomer and counterion at appropriate concentrations and it should not decompose at potentials required for polymerization. If the products of such decomposition reactions are innocuous, no problems should arise. However, if necessary, other reagents (e.g., metal ions) can be added to control the auxiliary electrode reaction, as described above.

The interaction of the solvent with the electrode, the substrate, the monomer and the counterion should also be considered. Even before a potential is applied, these interactions will determine the conditions within the electroreaction zone because the degree of adsorption of the monomer and counterion will be solvent dependent. As the electropolymerization reaction proceeds, the nature of the solvent will also determine the solubility of the resultant polymer. Somewhat independently, the nature of the solvent will control the extent of interaction of these products with the electrode.

The nucleophilicity of the solvent is also important³⁸ because a more nucleophilic solvent is likely to react with the free radical intermediates. Dong and Ding³⁹ suggest that PPy grown electrochemically in aqueous solvent reacts with water molecules to produce carboxyl groups that inhibit further growth. However, the importance of water molecules in hydrating the polymer⁴⁰ has also been discussed. These workers have shown that, with an optimal amount of water (2–4% in the polymer, or one water molecule for every five to ten pyrrole rings), the water appears to participate in a favorable way in the redox reaction — decreasing the activation barrier. Interestingly, drying the polymer at 40°C for 2–3 hours reduces the water content to this level and it is extremely difficult to dry any further. With some polymeric systems,⁴¹ we have found that thin layers of polymer contain large percentages of water (see later under Counterion/Cation Effect). Interestingly, when dehydrated and then exposed to moisture, the polymers exhibit hygroscopic properties rapidly reabsorbing water from the atmosphere. In addition, the counterions incorporated during polymerization

may have solvent molecules associated with them. Where water is the solvent, hydrated counterions or cations will be incorporated.

In the case of acetonitrile, where the solvation of ions is unlikely to occur, pyrrole itself can solvate anions.⁴² This may explain why polypyrrole films formed from acetonitrile with perchlorate counterions are less porous because, with pyrrole solvating the counterion during synthesis, a denser structure would be expected. This also results in polymers that are more conductive and have lower capacitance and greater electrochemical reversibility than those grown from water. Similar differences in conductivity were observed between acetonitrile and water when dodecyl-sulfate (DS) was used as the counterion,⁴³ although the differences in conductivity were not so marked. The presence of DS probably provides some protection from the nucleophilic solvent. In other work,⁴⁴ we have shown that pyrrole can be reversibly oxidized in surfactant-containing media (i.e., the surfactant stabilizes the free radical produced). This reversibility could not be detected in the absence of surfactants.

The use of specific solvents that stabilize π segments along the polymer chain give rise to increased conductivity and stability of polypyrrole. Propylene carbonate has proven to be a useful solvent in this regard.⁴⁵ This will influence subsequent polymerization processes, because the position of a more conductive polymer leads to more efficient electrochemistry as the polymerization proceeds.

The counterion/cation effect: choice of electrolyte

Numerous workers^{46–49} have studied the effect of the counterion on the electropolymerization process. The high concentration of counterion employed means that it can have a dramatic effect on the polymerization process. The electrolyte will influence the conductivity of the solution, the polymer properties, and hence the rate of polymerization. The nature of the electrolyte salt employed can also have a marked effect on polymer-solvent interactions.

This latter phenomenon has not yet been studied in detail as far as conducting polymers are concerned. However, in other areas, the ability of particular salts to dehydrate macromolecular (in this case proteins) structures has been known for some time.⁵⁰ This dehydration can have a marked effect on the polymeric structure produced with conducting polymers and the inherent stability of the structure obtained.⁵¹

It has been shown that the concentration of counterion employed has an effect not only on the amount of anion incorporated into the polymer, but also on its structure and morphology.⁵² These differences in morphology will influence surface area and the subsequent rate of polymerization.

Other workers have carried out electropolymerization in the presence of chemical oxidants.⁵³ This results in the production of much more porous, yet mechanically stable conducting polymer materials.

For efficient polymerization, the counterion should be readily incorporated. Therefore, some studies have suggested that small size and high charge density are preferable. We have recently shown, however, that polyelectrolytes are readily incorporated.⁴¹ This affects the subsequent polymerization process because polymers with very high water contents are obtained. Formation of the open hydrophilic polymer network encourages continued growth of such structures because the polymer prefers to grow and deposit in the more hydrophobic regions.

The counterion should also be stable both chemically and electrochemically, otherwise, breakdown products may interfere in the polymerization process. If it is electroactive at potentials lower than the monomer oxidation potential, it can be incorporated using potentiostatic methods — but not with constant current techniques because the counterion will be preferentially oxidized.

The counterion may be catalytic,⁴⁷ in which case, it will have a dramatic effect on the polymerization process. For example, Tiron (**4**) (shown above) has been shown to have a catalytic effect on the electropolymerization of pyrrole, thereby enabling the process to be carried out at a more rapid rate at lower applied potentials. The ability of the counterion to ion pair, with charge oligomers produced as part of the polymerization process, will also have an effect.

The “magical” counterions in terms of conductivity and mechanical properties appear to be sulfonated aromatics,^{54–58} in particular, paratoluene sulfonate (PTS). It has been shown that the benzene sulfonates induce a degree of crystallinity,^{23,24} which results in higher conductivity that, in turn, enables the polymerization process to proceed efficiently. It has also been suggested that the sulfonated aromatics exhibit surfactant-like behavior in that the radicals are stabilized and presumably protected from unwanted side reactions with the solvent, oxygen or other nucleophiles.

The direct incorporation of biological dopants into inherently conducting polymers is providing a number of new opportunities in areas such as biosensors, bioreactors and novel surfaces for cell culturing (see Chapter 1). For example, oligonucleotides have been incorporated directly as dopants,⁵⁶ as has salmon sperm DNA⁵⁷ and even intact red blood cells.⁵⁸

The counterion employed also has a marked effect on the electropolymerization process in organic solvents. For example, the polymerization of Poly-3-carboxy-4-methylpyrrole (PCMP) proceeds differently in paratoluenesulfonic acid (PTS), tetrabutylammonium perchlorate (TBAP), tetrabutylammonium tetrafluoroborate (TBABF₄) and tetrabutylammonium hexafluorophosphate (TBAPF₆).⁵⁹ As reported by Ge and co-workers, the rate of polymerization (at constant potential) and the time required for the onset of polymer deposition varied with the counterion employed.

There is no doubt that the counterion incorporated during synthesis influences the ability of the polymer to interact with different solvents and other molecules. These “surface properties” also influence the interfacial

structure, and properties that are critically important when conducting polymers are integrated with other materials and structures.

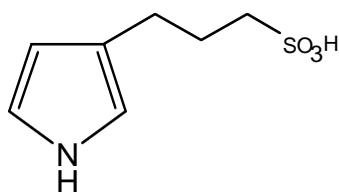
The monomer

A number of N-substituted pyrroles have been prepared previously.^{60a,b} Such substitution lowers the electronic conductivity of the resultant materials and usually results in deterioration of the polymer mechanical properties.

Pyrroles substituted in the 3 or 4 (β) position are usually preferred. It has been shown that α -substituted monomers do not undergo polymerization because these sites are required for polymer formation. Provided the substituents are not electron-withdrawing or too bulky, these monomers are easily oxidized and yield polymers with good conductivity.^{61,62}

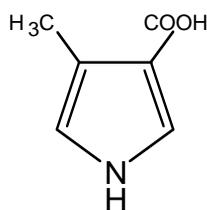
The derivatized monomers will influence the electropolymerization process in various ways. Differing functional groups will influence the solubility of the monomer, the oligomers and the resultant polymer. For example, polypyrroles can be made soluble in organic solvents by alkylation at the 3-position.⁶³ This influences the polymerization process because polymer may always be produced at the bare electrode (because there is no deposit). The production of soluble polymers provides a well-controlled means of polymerization. An indication of the achievable solubilities is given in Table 2.1.

Some functional groups will have a dramatic effect on the polymerization process since they will provide self-doping eliminating or minimizing the need for a supporting electrolyte. For example, monomers 5 and 6 shown below exhibit this phenomenon.



3-propyl-sulfonate pyrrole

5



3-methyl-4-carboxy-pyrrole

6

The ionizable $-\text{SO}_3\text{H}$ groups and $-\text{COOH}$ groups provide the charge required to dope the polymer during oxidation and polymerization. For example, in the case of 6, this results in a polymer with a very low additional counterion content. Monomer 5 can be polymerized without additional counterion.

Water-soluble polymers can also be produced by functionalizing the monomer with an alkyl sulfonate group. Havinga and co-workers⁶⁴ have shown that a polymer paste is formed from monomers such as 5, shown above.

Table 2.1

Solubility Data at 25° C for PODP¹

Polymer	Solubility (g dm ⁻³)		
	In CH ₂ Cl ₂	In CCl ₄	In Xylene
PODP-CIO ₄ (electrodeposited from CH ₂ Cl ₂)	36	52.5	57
As above (recovered from CH ₂ Cl ₂ liquor)	140	355	353
PODP-CIO ₄ (electrodeposited from THF)	3.5	13.5	30.5
As above (recovered from THF liquor)	86	497	226
PODP-CIO ₄ (electrodeposited from CH ₂ Cl ₂ /Ck ₃ CN media)	4	0	0
As above (recovered from CH ₂ Cl ₂ /CH ₃ CN media)	72	93	45
PODP-CIO ₄ (electrodeposited from THF/CH ₃ CN media)	5	1	0
As above (recovered from THF/CH ₃ CN liquor)	681	680	350
PODP-CIO ₄ (electrodeposited from CCl ₄ /CH ₂ Cl ₂ media)	10	5	1
As above (recovered from CCl ₄ /CH ₂ Cl ₂ liquor)	88	133	66

¹ PODP = PolyoctyldecylpyrroleTable adapted from Ashraf, S.A., Chen, F., Too, C.O. and Wallace G.G. *Polymer*. 1996, 37:2811.

Chemical polymerization

The number of experimental variables available with chemical polymerization is greatly reduced because no electrochemical cell or electrodes are employed. The range of dopant counterions (A⁻) that can be incorporated into the polypyrrole backbone during polymerization has also, until recently, been generally limited to ions associated with the oxidant. However, chemical polymerization remains of interest for processing purposes, first, because it may be easier to scale up this batch process, and second, it results in the formation of powders or colloidal dispersions. Furthermore, it is possible to use chemical deposition to coat other nonconducting materials.

Pyrrole polymerizations have a significant advantage in terms of flexibility over polyaniline syntheses (described later in Chapter 4) in that they can be carried out in neutral aqueous solution (i.e., no acid is required). A range of organic solvents can also be employed, the limitation being the requirement to dissolve both the pyrrole monomer and the oxidant.

Mechanism of chemical polymerization

It is usually assumed that the mechanism of chemical polymerization is similar to that described above in electropolymerization. However, work in our own laboratories⁶⁵ highlights the fact that it is difficult to duplicate the

products of electropolymerization using a chemical oxidant. Studies using 3-methyl-4-carboxy-pyrrole have demonstrated that polymers obtained with both techniques are similar in chemical composition but differ markedly with respect to polymer morphology.

Influence of polymerization conditions

The oxidant: The most widely used chemical oxidants have been ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and FeCl_3 , although hydrogen peroxide and a range of transition metal salts (e.g., of Fe^{3+} , Ce^{4+} , Cu^{2+} , Cr^{6+} , Mn^{7+}) have also been employed. The use of H_2O_2 (with Fe^{3+} catalyst) is attractive environmentally, as the only byproduct is water. For the metal-based oxidants considered by Chao and March,⁶⁶ IR spectroscopy confirmed that similar polypyrrole backbones were formed in each case.

For one-electron oxidants such as FeCl_3 , an [oxidant]/[pyrrole] molar ratio of ca. 2.3 is usually employed. Two electrons are required for the oxidation of each pyrrole unit, with the remaining 0.3 electrons being used for ca. 30% oxidative doping of the neutral PPy product into its conducting form which carries a positive charge on about every third pyrrole unit. However, with respect to polymer conductivity, Miyata and co-workers have shown that control of the redox potential in solution by adjusting the concentration of the redox couple can be used to advantage.⁶⁷ The use of binary systems (mixtures of two different oxidants) has also proven useful in this regard.⁶⁸ If the oxidizing strength is too high, the rate of polymerization is too fast, resulting in an aggregated, low-conductivity material.

The use of halogens as oxidizing agents has also been reported,⁶⁹ resulting in PPy.X products containing halide (X^-) ions as the dopant counterions. These same workers used chemical polymerization to produce PPy-poly-methylpyrrole copolymers.

Kang and co-workers⁷⁰ have also used organic electron acceptors such as 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) and chloranil. A solvent effect was observed when polymerization was carried out in DDQ, polypyrrole with the highest conductivity was produced (still only $7 \times 10^{-2} \text{ S cm}^{-1}$). Polymerization in acetonitrile gave the lowest conductivity, and in water it was slightly better. A similar solvent dependence was observed for chloranil oxidations.

The solvent: Solvent effects have also been reported for the polymerization of pyrrole using FeCl_3 as oxidant.⁷¹ The conductivities of the polypyrrole products prepared in water and alcohols ranging from MeOH to octanol were considerably higher than for the polymers prepared under the same conditions in acetonitrile, THF, chloroform and benzene.

Polymerization temperature: The vast majority of chemical polymerizations of pyrrole have been carried out between 0°C and room temperature. In one of the few systematic studies of the influence of temperature, Miyata and co-workers⁷¹ examined polymerization with FeCl_3 in MeOH solvent over the range -20°C to 60°C. Maximum conductivity was observed for the polypyrrole product synthesized at 0°C.

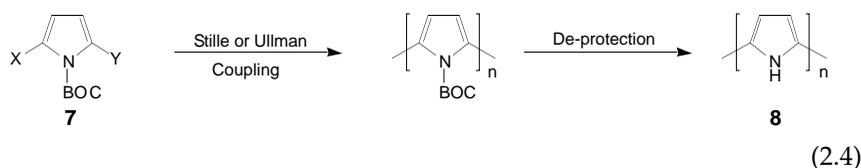
Nature of the dopant counterion (A⁻): The dopant anions (A⁻) incorporated into conducting polypyrroles are positioned interstitially between the polymer chains and, as discussed above for electropolymerization, their nature consequentially influences both the polymerization process and the properties of the resultant polymers. In initial chemical polymerization studies, the incorporated anions were limited to those arising from the oxidant employed, e.g., FeCl₃ and (NH₄)₂S₂O₈ oxidants provided Cl⁻ and HSO₄⁻/SO₄²⁻ counterions, respectively. These could, in many cases, be subsequently replaced by a range of other anions through either ion exchange or redox cycling.

More recently, it has been found that anions such as polyelectrolytes and surfactant-like anions, e.g., dodecylbenzenesulfonate (DBSA), can be inserted directly into polypyrrole products during polymerization in competition with anions arising from the oxidant. This very useful development will be discussed later in a section dealing with polypyrrole processability.

Achieving regioselective coupling with pyrrole monomers

For the formation of polypyrroles with extended π -conjugation and high electrical conductivity, it is necessary to have only 2,5'-couplings, through the preferential linking of radical cations as depicted in Figure 2.2. Unfortunately, 2,3'- and 2,4'-couplings also occur leading to structural defects (branching) in the resultant polymers. This results in diminished supramolecular order and lower electrical conductivity, as well as decreased crystallinity and the impairment of other properties.

Synthetic routes to structurally perfect oligomers of PPy, involving only 2,5'-couplings of the individual pyrrole repeat units (idealized structure 2.1), have been successfully devised. For example, 2,5-disubstituted pyrrole monomers **7** (X = Br, Y = SnMe₃) bearing a *tert*-butoxycarbonyl (BOC) protecting group on the N center have been polymerized to oligomers with 16–20 pyrrole units through a Stille coupling using organometallic reagents (Equation 2.4).⁷² Reductive Ullman coupling of 2,5-dibromo-*N*-BOC-pyrrole has similarly yielded oligomers with up to 20 pyrrole units.⁷³ A less sophisticated way to at least reduce the opportunity for unwanted 2,3'- and 2,4'-couplings is to employ the dimer 2,2'-bipyrrole as the substrate in a standard chemical polymerization.⁷⁴



In situ chemical polymerization

The above chemical polymerization routes usually precipitate the conducting polypyrroles as black powders. However, it has been found that poly-

pyrroles can also be deposited as films on the surfaces of insulating substrates by immersing the substrates in the polymerization solution. Careful control of the polymerization conditions can maximize film deposition rather than bulk precipitation,⁷⁵ as illustrated elegantly by Saurin and Armes⁷⁶ for the deposition of polypyrrole onto printed circuit boards. They employed the Fe(III) complex of 5-sulfosalicylic acid as a mild chemical oxidant rather than an Fe(III) salt and a high oxidant-to-monomer ratio. *In situ* chemical deposition has now become established as a simple and cost effective method for the deposition of thin films of polypyrrole on a wide range of substrate materials, examples of which are described below:

Deposition on glass/plastics: Kuhn, MacDiarmid and co-workers⁷⁷ have shown that *in situ* polymerization of pyrrole (0.009 M) with FeCl₃ (0.02 M) in the presence of HCl or an organosulfonic acid dopant (0.003 M) leads to the facile deposition of thin, uniform polypyrrole films on glass substrates and overhead transparencies. The conductivity of the films was highest for hydrophobic substrates. In related studies using (NH₄)₂S₂O₈ as oxidant, they found that the *in situ* deposition of polypyrrole films occurs more readily on hydrophobic surfaces, such as Si/SiO₂ and glass pretreated with octadecylsiloxane, than on related hydrophilic surfaces.⁷⁸ They exploited these different deposition rates to produce patterned microstructures of conducting polypyrroles by a microcontact “stamp” printing technique. Polypyrrole features as small as 2 μm could thereby be produced.

Polypyrrole can be similarly coated on low-density polyethylene (LDPE), while grafting of the LPDE surface with acrylic acid enhances film growth and adhesion.⁷⁹ The *in situ* oxidation of pyrrole by Fe(III) can also be used to deposit polypyrrole films on polystyrene substrates.⁸⁰ In a variation of this method, polyimide films exhaustively soaked in pyrrole (with up to 14% monomer uptake) have been coated with polypyrrole via oxidation with FeCl₃ in acetonitrile solvent.⁸¹ The resultant material shows electrical conductivity of ca. 4×10^{-2} S cm⁻¹.

Deposition on fibers/fabrics: Following pioneering studies by Kuhn and co-workers,⁸² a wide variety of textile substrates have been successfully coated with conducting polypyrroles through *in situ* chemical polymerization. These include nylon fabrics, where H-bonding between carboxyl groups on the nylon backbone and pyrrole monomers is believed to lead to a more ordered polypyrrole product.⁸³ Vapor-phase *in situ* deposition has also been employed, for example, by passing pyrrole vapor over cotton thread coated with the oxidant FeCl.⁸⁴ Typically, the surface resistance of such conducting polymer-coated fabrics decreases with greater polymer deposition.

Routes to more processible polypyrroles

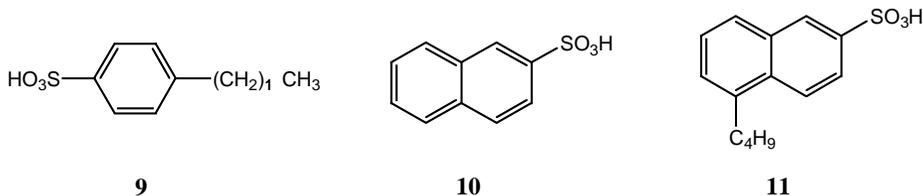
Both chemically and electrochemically synthesized polypyrroles are typically insoluble in water and organic solvents and, due to strong intermolecular and intramolecular interactions of their polymer chains, are infusible. Over the past decade, research to overcome this serious hindrance to their processibility and subsequent utilization has been intense. Several

approaches have now been developed to improve the solubility of polypyrroles, namely (1) counterion-induced solubilization, (2) colloid formation, and (3) side chain-induced solubilization. Each of these will be discussed in turn.

Counterion-induced solubilization

An important breakthrough in polypyrrole chemistry was the discovery by Lee et al.⁸⁵ in 1995 of a chemical polymerization route to an unsubstituted polypyrrole that was soluble in organic solvents. They exploited the surfactant-like qualities of added dodecylbenzene-sulfonate (DBSA) **9** as a dopant anion to solubilize polypyrrole formed during oxidation of pyrrole by aqueous $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The PPy.DBSA product, isolated as a black powder in 42% yield after 40-hour reaction at 0° C, was very soluble in *m*-cresol, and could be dissolved in weakly polar solvents such as chloroform and dichloromethane by the addition of an equimolar amount of dodecylbenzene-sulfonic acid. A film cast from chloroform solution exhibited an electrical conductivity of 5 S cm⁻¹ and its UV-visible spectrum was similar to that of electrochemically deposited polypyrrole.

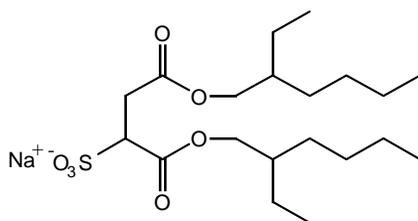
The solubilizing ability of the DBSA dopant is believed to arise from the long-chain dodecyl group's reducing the interactions between the polypyrrole chains as well as assisting solvation by the organic solvents. Subsequent studies have shown that a range of other large, surfactant-like sulfonic acids, added during polymerization of pyrrole by aqueous $(\text{NH}_4)_2\text{S}_2\text{O}_8$, can similarly cause dopant ion-induced solubilization of polypyrrole.⁸⁶⁻⁸⁸ These include dodecyl benzene sulfonic acid (**9**), β -naphthalenesulfonic acid (NSA) (**10**), 5-butyl-naphthalenesulfonic acid (BNSA) (**11**) and anthraquinone-sulfonic acid (AQSA). Freestanding films of the doped polypyrrole products may be cast from solutions in *m*-cresol, CHCl_3 , NMP or DMSO solvents, exhibiting electrical conductivities in the range 10⁻² to 1 S cm⁻¹. Marked changes in the UV-visible spectrum of PPy.DBSA, when dissolved in the above range of solvents, indicates a strong solvent dependence for the polymer chain conformation.



When camphorsulfonic acid (HCSA) is used as the sulfonic acid dopant in related syntheses, a highly conducting ($\delta = 15 \text{ S cm}^{-1}$) PPy.HCSA product is isolated, but it is completely insoluble in any solvent.⁸⁶ This latter polymer can be prepared in soluble form by analogous chemical polymerization of pyrrole in organic solvents such as CHCl_3 , THF or CH_3NO_2 . However, it is nonconductive, emphasizing the influence of the polymerization solvent on

the properties of the polypyrrole product. A similar solvent effect was observed when PPy.HCSA was prepared using H_2O_2 as the oxidant (with Fe^{3+} catalyst).⁸⁹ Kudoh has used aqueous $Fe_2(SO_4)_3$ as the oxidant to produce a similar range of surfactant-solubilized polypyrroles.⁹⁰

In a recent development, the first alcohol-soluble polypyrroles have been synthesized by the oxidation of pyrrole with aqueous $(NH_4)_2S_2O_8$ using di(2-ethylhexyl) sulfosuccinate sodium salt (NaDEHS) (**12**) as the dopant anion.⁹¹ This dopant contains both nonpolar alkyl chains and polar oxygen centers, the latter of which are believed to form H-bonds with alcohol solvents, thereby facilitating dissolution.



12

Colloidal polypyrrole dispersions

Other workers have used additives to enable the preparation of effectively "water-soluble" conductive polymer colloids. As early as 1986, Bjorklund and Liedberg⁹² observed that when pyrrole was oxidized by $FeCl_3$ in the presence of aqueous methylcellulose (Mn 100,000), a PPy.methylcellulose sol was formed that could be characterized by scanning electron microscopy. Thin films could be obtained from the sol, exhibiting a conductivity of ca. $0.2 S cm^{-1}$. Subsequently, a range of neutral water-soluble steric stabilizers such as poly(vinylalcohol), poly(ethyleneoxide) or poly(vinylpyridine) have been successfully employed to produce stable, relatively monodispersed, colloidal sols.⁹³⁻⁹⁶ Cationic and anionic polyelectrolytes have also been used.^{97,98} $FeCl_3$ has been the most common oxidant employed for polypyrrole colloid preparation. In contrast to bulk polypyrrole syntheses, $(NH_4)_2S_2O_8$ has found little application. It has been suggested that its more rapid oxidation of pyrrole monomers may lead to uncontrolled fast nucleation, causing macroscopic precipitation.

Colloidal polypyrroles prepared in aqueous solution are generally spherical. Particle size is very dependent on the synthetic conditions (stabilizer, oxidant, etc.), with sizes between 30 and 445 nm being described by Vincent et al.⁹³ The electrical conductivities of the PPy colloids are frequently a few orders of magnitude lower than those observed for macroscopically precipitated polypyrroles. This presumably arises from the insulating nature of the

attached polymeric stabilizers. Data reported by Aldissi and Armes⁹⁹ indicate that the thickness of the stabilizer is in the range of 33–36 nm. They also showed that it is possible to strip the stabilizer (PEO) after chemical polymerization and to replace it with another one. They indicated that the MWt and nature of the stabilizer, as well as the concentration and nature of the oxidant, influence particle size.

These same workers described an inverse emulsion-type polymerization process.⁹⁹ They used a conventional process in which microemulsions of water in hydrocarbon readily form in the presence of Aerosol-OT (AOT). The droplets are essentially swollen cells where radius is controlled by the water:AOT ratio. As droplets collide, hydrophilic reagents contained in them are exchanged. When pyrrole and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ dispersions were mixed, a sediment eventually appeared. However, if PVP was added at different intervals, stable dispersions of small particles could be prepared.

Armes and Aldissi⁹⁹ reported the synthesis of PPy colloids in nonaqueous solvents by the polymerization of pyrrole with FeCl_3 in alkylester solvents using poly(vinyl-acetate) as stabilizer. The same stabilizer has been similarly used to give PPy colloidal dispersions in 2-methoxyethanol and acetonitrile/methanol.¹⁰⁰ Methylacetate, methylformate and propyl-formate solvents have also been used for colloidal polypyrrole formation.^{101a,b} A greater rate of polymerization was observed than that found in water, which may account for the broader particle size of distribution in organic solvents than in H_2O . Once again, these studies highlighted the influence of the nature of the solvent on the conductivity of the PPy colloids. Solvents with more polar character gave rise to colloids with higher conductivities.

Digar et al.¹⁰² highlighted the role of the solvent in enabling the steric stabilizer to function in the colloid-forming role. At room temperature, they showed that poly(vinylmethyl ether), which does not function as a steric stabilizer in water, does so in ethanol. However, the colloids produced in an ethanol-containing solution were much lower in conductivity.

Side chain-induced solubilization

The presence of flexible alkyl or alkoxy groups in the three-ring position or the N center of polypyrrole renders the polymer soluble in organic solvents. The appropriate 3-alkyl-substituted pyrrole monomers can be synthesized by Friedel-Crafts alkylation of N-protected pyrrole, followed by Clemmenson reduction, as illustrated in Figure 2.8.¹⁰³ Electrochemical or chemical oxidation (e.g. FeCl_3) of the substituted monomer then yields the poly(3-alkylpyrrole) products.^{104,105} The enhanced processibility of these 3-alkyl and 3-alkoxy-substituted polypyrroles comes, however, at the price of reduced electric conductivity, due to steric crowding by the substituents twisting the polymer backbone from planarity. It should also be noted that, unlike analogous substituted polythiophenes where routes to regioregular polymers have been developed (see Chapter 6), these 3-substituted polypyrroles are presumably mixtures of regioisomers (head-to-tail, head-to-head, tail-to-tail, etc.).



Figure 2.8 Synthesis of alkylated pyrroles.

N-functionalized pyrrole monomers are available by the general route shown in Figure 2.9, involving reaction of pyrrole with potassium metal (in THF) to yield the pyrrol-1-ylpotassium species (7), which can be attached by a variety of alkyl and aryl halides. Chemical or electrochemical polymerization then yields the *N*-substituted polypyrroles. Although soluble in organic solvents, their electrical conductivities are, unfortunately, generally even lower than those of the 3-substituted polypyrroles. An interesting example involving a reactive substituent is the *N*-vinylpyrrole monomer, whose vinyl group can be polymerized by radical polymerization and the pyrrole units oxidatively polymerized with FeCl_3 .¹⁰⁶

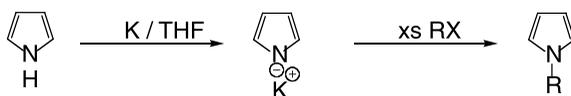
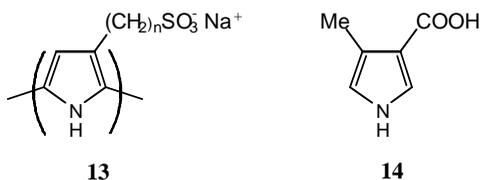


Figure 2.9 Route to *N*-functionalized pyrrole monomers.

The introduction of alkylsulfonic acid substituents onto the pyrrole rings, as in the series of 3-substituted polymers (13), results in water-soluble polypyrroles.¹⁰⁷ These polymers were obtained through either electrochemical or chemical (FeCl_3) oxidative polymerization of the appropriate substituted monomers. They are self-doped by the anionic sulfonate substituents and exhibit electrical conductivities in the range 10^{-3} to 0.5 S cm^{-1} . In our laboratories, we have alternatively synthesized (13) ($n = 4$) via an electrohydrodynamic processing technique using a flow-through cell with reticulated vitreous carbon anode and cathodes, obtaining a polymer with a MWt of ca. 10,500 and a conductivity of 0.01 S cm^{-1} .¹⁰⁸ A water-soluble carboxylic acid substituted polypyrrole (14) has also been reported, obtained by electrochemical oxidation of 3-methylpyrrole-4-carboxylic acid in CH_3CN .¹⁰⁹



Photochemically initiated polymerization

Alternative photochemical routes to polypyrrole have been described that have advantages in some applications over the conventional chemical and electrochemical syntheses. Shimidzu et al.¹¹⁰ reported that visible light irradiation of an aqueous pyrrole solution in the presence of $[\text{Ru}(\text{bipy})_3]^{2+}$ (bipy = 2,2'-bipyridine) as the photosensitizer and $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ as a sacrificial oxidant led to the deposition PPy.Cl. This powdery product exhibited a relatively low conductivity ($3 \times 10^{-4} \text{ S cm}^{-1}$) compared with PPy.Cl prepared via standard chemical or electrochemical methods. The photochemically initiated polymerization is believed to proceed via the mechanism shown in Figure 2.10, where oxidation of the pyrrole is performed by the strong oxidant $[\text{Ru}(\text{bipy})_3]^{3+}$ generated by oxidative quenching of the photo-excited $^*[\text{Ru}(\text{bipy})_3]^{2+}$ species by the sacrificial Co(III) complex. By employing the anionic polymeric membrane Nafion to absorb both the photosensitizer and the sacrificial oxidant, and irradiating with a laser at 490 nm through a photomask, Shimidzu et al.¹¹⁰ further demonstrated the ability to deposit fine (10 μm) patterns of conducting polypyrrole directly on the Nafion membrane. Other researchers¹¹¹ have similarly employed the complex $[\text{Cu}(\text{dpp})_2]^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) as photosensitizer and *p*-nitrobenzyl-bromide as the sacrificial oxidant to photodeposit conducting polypyrrole on a variety of surfaces such as paper and glassy carbon.

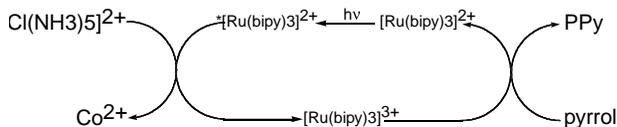


Figure 2.10 Photoelectrochemical generation of polypyrrole.

Enzyme and acid-catalyzed polymerizations

Aizawa and Wang have reported¹¹² that the copper-containing enzyme bilirubin oxidase (BOX) catalyzes the oxidative polymerization of pyrrole to give thin films of polypyrrole on substrates such as glass, plastic or platinum plates. The BOX was first adsorbed onto the matrix support from an aqueous acetate buffer solution (pH 5.5), followed by incubation with the pyrrole monomer (0.2 M) in acetate buffer (pH 6) for several hours at room temperature. The deposited polypyrrole film was reported to have similar properties to PPy made by conventional chemical or electrochemical methods.

Treatment of pyrrole with aqueous 6.0 M HCl is reported to rapidly (< 1 min) yield the trimer, 2,5-dipyrrol-2-ylpyrrolidine, in which the central heterocyclic ring is saturated.¹¹³ The use of longer reaction times (4 hours) or higher temperatures (100° C) has been shown to lead to the formation of polymeric species, which possess alternating pyrroline and pyrrolidine groups together with varying degrees of ring-opened pyrrole units.¹¹⁴ These brown polymers are nonconductive, but the presence of amine and carbonyl functional groups along their chains may prove useful for further derivatization.

The quest for extra functionality

It has proven possible to add a wide range of additional functionalities to the parent polypyrrole structure, opening up an exciting array of potential applications for these materials. Two distinct approaches to achieving this additional functionality have been successfully employed, namely:

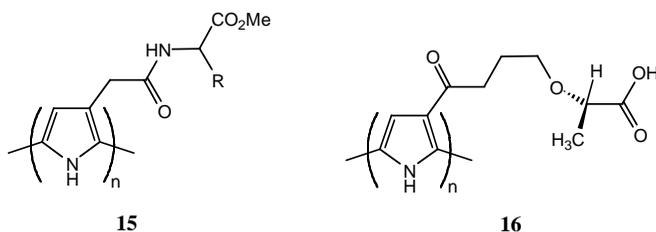
1. Covalent attachment of specific groups to the PPy backbone (either pre- or postpolymerization)
2. Incorporation of specific dopant anions (as discussed previously in this chapter)

The attachment of simple substituents such as alkyl or methoxy groups to the backbone of polypyrroles is well known to markedly enhance their solubility in organic solubility and consequently their processibility (see above). Covalent binding of more sophisticated substituents to PPy can provide a wide range of other attributes. A number of these are discussed below, with particular emphasis on the synthesis of derivatized polypyrroles with sensing capabilities.

The usual approach has been to synthesize a monomer or dimer containing the appropriate recognition group; this is subsequently oxidized to produce the conducting polymer.¹¹⁵ A drawback to this approach to functionalized polymers is that the synthesis of the initial substituted monomer may be complex and time consuming. In addition, subsequent oxidation to the desired polymer may prove difficult due to steric hindrance by the functional group, or electronic effects that shift the oxidation potential of the monomer. A significant development, therefore, is a route involving the facile modification of pre-formed polypyrroles containing good leaving groups such as N-hydroxysuccinamide.¹¹⁶ Using this approach, crown-ethers and electroactive groups such as ferrocene, as well as oligonucleotides, have been covalently attached to the pyrrole rings (e.g., [Figure 2.11](#)).^{116,117} This generic approach should be extendable to analogous polythiophenes and polyanilines.

Another significant development has been the synthesis of chiral polypyrroles. These were first prepared by Baughman et al.¹¹⁸ by the electropolymerization of pyrrole monomers bearing chiral substituents covalently attached to the pyrrole N centers. However, the chiroptical properties of these polymers were not investigated. Subsequently, Delabouglise and Garnier¹¹⁹ prepared a series of chiral polypyrroles 15 (R = CH₂OH, CHMe₂, Ph) by electropolymerizing pyrrole monomers with amino acid substituents at the 3-position of the pyrrole ring. As with other 3-substituted polypyrroles, these novel polymers exhibited lower conductivities (ca. 1 S cm⁻¹) compared with unsubstituted polypyrroles. Circular dichroism studies showed them to be optically active, and it was suggested that the presence of the chiral amino acid substituents on the pyrrole rings caused the polymer chains to preferentially adopt a one-handed helical arrangement. Recently, optically active polypyrroles containing (-)-ethyl-L-lactate as the chiral-inducing

agent (e.g., polymer 16) have been similarly electrochemically synthesized.¹²⁰ Although their circular dichroism spectra were not recorded, they were shown to possess enantioselective recognition properties (see Chapter 3).



An optically active polypyrrole (**17**) has also been synthesized by the electropolymerization of pyrrole monomer bearing a homochiral sugar covalently attached to the pyrrole nitrogen.¹²¹ This chiral polymer discriminated between (+)- and (-)-camphorsulfonate ions as potential anionic dopants in cyclic voltammetry studies.

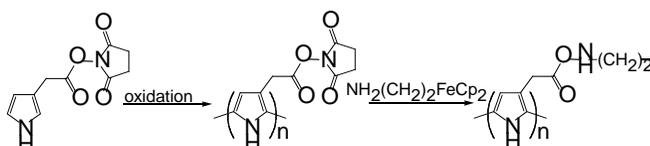
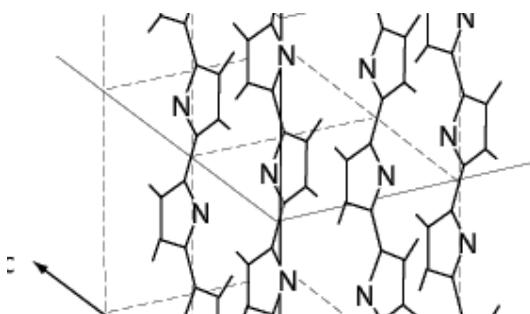
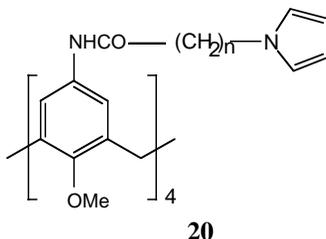


Figure 2.11 Covalent attachment of ferrocene to polypyrrole.



Other interesting recent examples of poly(3- or N-substituted pyrrole)s are the polymers (**18**) and (**19**), which contain either cyclohexylphenyl or biphenyl groups to give liquid crystalline properties.¹²² These can be prepared by either potentiostatic electropolymerization or by chemical oxidation using FeCl_3 and 1-naphthalenesulfonic acid. The products are of relatively low molecular weight ($M_n = 2,500 - 10,300$, depending on synthesis conditions) and low conductivity (10^{-4} to $10^{-7} \text{ S cm}^{-1}$ after I_2 doping). A mesophase was observed only for the lower molecular weight ($M_n < 5,000$) materials. Pyrrole monomers have also been synthesized with calix[4]arenes

grafted to the N atom of the pyrrole ring.^{123,124} Electropolymerization to give films of the corresponding N-substituted polypyrroles (**20**) was more facile for the monomer with the longer alkyl spacing arm length ($n = 4$).



Molecular Structure and Microstructure of Polypyrrole

The polymerization conditions used to prepare polypyrrole not only determine the polymer composition, but also influence the structure of the polymer from the molecular level to the microscopic level. In this section, the studies characterizing the detailed structure of polypyrrole films, coatings, particles and colloidal dispersions are reviewed. These studies provide the foundation for understanding the properties of polypyrroles, as described in Chapter 3.

Molecular Weight, Branching and Crosslinking

A key structural parameter for all thermoplastic polymer materials is the molecular weight. The molecular weight has a profound affect on physical properties such as mechanical strength and toughness and the viscosity of polymer solutions and polymer melts. Since synthetic polymers contain a distribution of molecular weights, it is most informative to measure the full distribution using techniques such as gel permeation chromatography (GPC) and to obtain the average molecular weight from such distribution.

Unfortunately, the intractable nature of polypyrrole has made molecular weight determinations virtually impossible. Methods such as GPC and other techniques including light scattering, viscosity measurements and vapor pressure osmosis all require the polymer to be dissolved completely. Since polypyrrole prepared by conventional methods does not dissolve, these analyses have not been possible.

The intractable nature of polypyrrole is a strong indication that the unsubstituted polymer is substantially crosslinked. In the case of crosslinked polymers, the molecular weight parameter becomes meaningless, and it is the density of crosslinking that is strongly correlated to physical properties such as strength, toughness and solvent-swellability. Direct evidence of chemical crosslinking in polypyrrole is rare, but ¹⁵N NMR studies have shown evidence of both α - α and α - β linkages.¹²⁵ In more recent times, theoretical methods have been used to estimate the probability of branched

structures forming during polymerization of pyrrole. These simulations give a degree of branching in the order of 20% for room temperature polymerization and show a slight dependency of branching on polymerization temperature (increasing with increasing temperature).¹²⁶ These estimates agree well with recent XPS studies of PPy/PF₆ and PPy/DBSA that show the degree of branching/crosslinking as 33% and 22%, respectively.¹²⁷ The branched and crosslinked structures are shown in Figure 2.12.

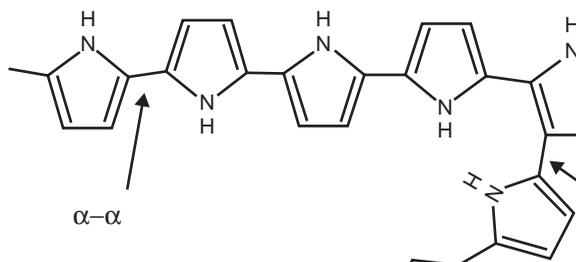


Figure 2.12 Polypyrrole chain structure showing $\alpha\text{-}\alpha$ and $\alpha\text{-}\beta$ couplings leading to chain branching and crosslinking.

Only in specific instances has it been possible to prepare soluble polypyrrole. Two approaches have been used: alkyl-substituted pyrroles (as described above) and the use of certain dopants. In the former case, it is likely that the alkyl substituents block the branching and crosslinking reactions that occur in conventional preparations of PPy. Tritium-labeled 2,2'-dimethylpyrrole was studied by Nazzari and Street,¹²⁸ and their studies showed a molecular size of between 100 and 1000 pyrrole units. More recently, it has been reported that polypyrroles soluble in alcohols and other organic solvents can be prepared using sodium bis(2-ethylhexyl) sulfosuccinate as a doping agent.¹²⁹ Solubilities of up to 11% (w/w) were obtained. Analysis of polymers formed with this dopant gave an average molecular weight of 62,000 (303 pyrrole rings) and conductivities to 12 S/cm. The dopant-induced solubility is thought to be due to the dopant's destabilizing the polymer-polymer interactions relative to the polymer-solvent interactions.¹³⁰ The large size of the dopant reduces the number of side chains and crosslinks, so the interchain interactions are weakened.¹²⁷

Turcu et al.¹³⁰ compared the optical properties of as-prepared PPy-DBSA and the soluble fraction extracted from the as-prepared polymer. The IR spectra indicated that the soluble fraction contained shorter conjugation lengths than in the as-synthesized polymer. The conjugation lengths were also sensitive to the type of solvent used, with chloroform giving longer conformation lengths and higher conductivity than m-cresol.

Crystallinity and Molecular Order

Several studies have investigated the manner in which polymer chains are arranged in the solid state for polypyrrole. The chief investigative tool in these studies is x-ray diffraction where scattering of incident x-rays occurs at specific angles related to the spacing between molecular layers in ordered crystal structures. The earliest studies by Mitchell¹³¹ and Mitchell and Geri¹³² revealed a molecular anisotropy in electrochemically prepared PPy/pTS (para-toluene sulfonate) films. The anisotropy was interpreted as being due to all *trans* coupled PPy chains lying in planes parallel to the electrode surface, but randomly oriented in the direction perpendicular to the electrode. Further studies on other dopants revealed that anisotropy was mainly observed when planar dopants were used. In such cases, the planar dopant is regarded as a template for ordering the polymer chains. In contrast, non-planar dopants, such as ClO_4^- , BF_4^- and SO_4^{2-} , produce films that appear isotropic in x-ray diffraction studies.^{133,134} The degree of anisotropy was found to increase with lower polymerization temperature,¹³² high anodic polymerization potentials,¹³² high dopant–monomer molar ratios in the polymerization electrolyte¹³⁵ and mechanical stretching.¹³⁶ In all cases, the conditions that favor an increase in molecular anisotropy also favor an increase in electrical conductivity, suggesting that the anisotropy is due to molecular orientation's favoring an increase in conjugation length.

More-detailed studies of the molecular structure of PPy/ PF_6^- (hexafluorophosphate) have recently been published. Nogami et al.¹³⁷ have reported scattering peaks due to amorphous order that is independent of the film orientation. This finding is consistent with those reported above, since the PF_6^- counterion is symmetrical and does not induce orientational order. Recent studies by Yoon et al.¹³⁸ suggested a partially crystalline structure with the polymer chain aligned along the *b*-direction and stacked along the *c*-direction in a monoclinic arrangement (Figure 2.13). Polymerization conditions that favor higher conductivity (low temperatures and low current densities) also produce a higher degree of crystallinity (up to 37%) and a larger crystallite domain length (up to 2.6nm or ~ 8 pyrrole rings). Although most of the available literature supports the planar *trans* arrangement for electrochemically prepared polypyrrole, one study suggests an alternative conformation. Davidson and co-workers¹³⁹ found clear evidence of a helical structure produced from an all *cis* coupling of pyrrole rings. These workers used dodecyl sulfate as dopant, but also argue that all published literature on x-ray diffraction of PPy is also consistent with the helical structure. Furthermore, the helical structure is identical to that proposed for poly(3-alkylthiophenes) as described further in Chapter 6.

Although molecular anisotropy has been noted in several PPy films, the overall degree of crystallinity is very low in these materials. The work by Davidson et al.¹³⁹ on thin PPy films (prepared at very short polymerization times) provides evidence of crystal formation, but the crystal growth is not maintained as the film thickens. Thus, the polymer first formed on the

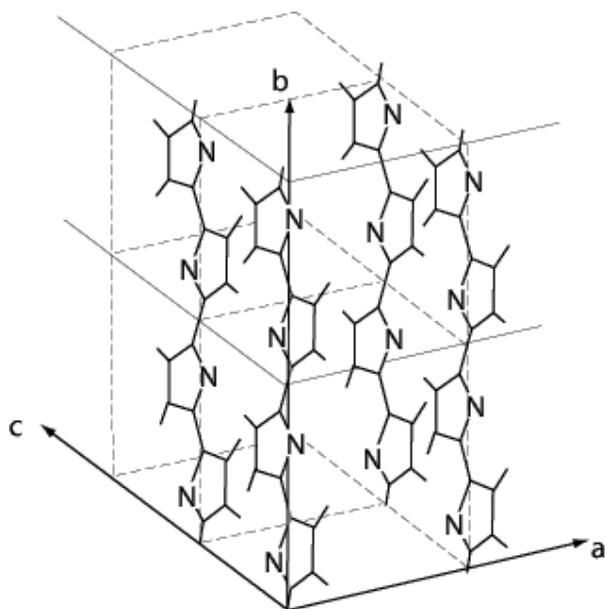


Figure 2.13 Schematic illustration of crystalline structure of PPy/PF₆.

electrode surface may have a high degree of order but does not extend into the bulk structure of thick films.

Surface Morphology and Film Density

The most readily observed structure of polypyrrole samples is the peculiar surface morphology common to all electropolymerized PPy films and coatings. The morphology consists of nodules ranging in size to hundreds of microns that, themselves, consist of aggregations of smaller particles. The structure has been referred to as a “cauliflower-” or “fractal-like” surface.

Many studies have considered the origin of the cauliflower morphology in polypyrrole and many factors have been identified as influencing the type of structure formed. For example, the type of dopant used during electropolymerization profoundly affects the surface morphology. Lemon and Haigh¹⁴⁰ reported that the nodular morphology arises from gas evolution at the working electrode during electropolymerization. Thus, the simultaneous formation of O₂ gas at the electrode surface and polymer formation results in polymer forming over the gas bubble and producing a roughened surface. The reaction occurring is suggested as:



Yoon et al.¹³⁶ have also observed large (5–10 μm diameter) pores on the electrode side of polypyrrole films prepared on unpolished platinum electrodes.

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More-recent studies have used atomic force microscopy (AFM) to determine surface morphology and surface roughness of electrochemically prepared polypyrrole films. Li and co-workers¹⁴¹ showed that the nodular surface arises very early in the electropolymerization process where “microislands” first form on the (gold) electrode surface. With longer polymerization times, the film thickness increases and the film surface consists of close-packed nodular grains of submicron diameters. Barisci et al.¹⁴² found a strong correlation between the surface potential of polypyrrole films and the nodular surface morphology. These workers concluded that the nodules are dopant-rich high conductivity regions where nuclei initially formed and around which polymer subsequently grew preferentially. This growth concept had been previously described by Yang et al.¹⁴³ and Jeon et al.¹⁴⁴ Interestingly, MacDiarmid et al.¹⁴⁵ have shown that a similar globular surface morphology is also found in chemically polymerized polypyrrole films when deposited on various substrates.

The influence of dopant type on surface morphology has been studied using AFM by Silk and co-workers.^{146,147} For thin films ($< 1 \mu\text{m}$ thick) the PPy films prepared with four different dopants (Cl^- , ClO_4^- , SO_4^{2-} , dodecyl sulfate) were indistinguishable with all consisting of globules of 100 to 300 nm in diameter and 10 to 30 nm in height. With thicker films, however, ($> 5 \mu\text{m}$ thick) clear differences were observed: the sulfate and dodecyl sulfate-doped films maintained approximately the same surface structure in thick films as in the thinner films. However, the Cl^- and ClO_4^- -doped films generated large cauliflower structures consisting of large protrusions of $\sim 2 \mu\text{m}$ in diameter and 0.5 to 1 μm in height. These protrusions showed a substructure of the smaller globules seen in thinner films. For all dopant types, the diameter of the smaller globules increased linearly with the square root of film thickness, suggesting a similar growth mechanism for all dopant types. Similar structures and similar dependence of globule diameter and film thickness had also been reported for polyaniline films, suggesting that globule formation and growth is common to both electrochemically formed polymers.

The electrode material has also been found to influence the surface morphology of electrochemically prepared polypyrrole films. In our own work, we used transmission electron microscopy (TEM) to investigate the cross-sectional structure of polypyrrole films prepared on different substrates. In all cases, the large surface globules were observed to be the caps of cone-shaped structures that extended to the electrode surface of the polypyrrole film (see Chapter 3). Interestingly, Yoon et al. showed that the cauliflower-type surface morphology could be virtually eliminated by carefully polishing the electrode surface.¹³⁸

The film densities reported for polypyrrole have been shown to be highly dependent on dopant and preparation conditions. For example, the low temperature polymerization (-40°C) of pyrrole with PF_6^- counterion produces films with a density of 1.4 g/cm^3 .¹³⁸ In contrast, the same films prepared at room temperature have much lower densities of 0.6 to 0.8 g/cm^3 .

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chapter three

Properties of polypyrroles

The assembly of polypyrroles (PPys) is an intricate process that determines the molecular and superstructure of the polymer obtained. This, in turn, influences the chemical, electrical and mechanical properties of the material. It is impossible to optimize a single property of materials such as PPy in isolation. The chemical, electrical and mechanical properties are inextricably linked.

To function as intelligent materials, conducting polymers must be capable of stimuli recognition, information processing and response actuation. As a result, they must possess appropriate chemical properties that change in response to stimuli, as well as appropriate electrical properties that allow information to be transported within the structure and switches to be actuated. The mechanical properties must also be considered, because the creation of materials with ideal chemical and electrical properties, but with inappropriate mechanical properties, will be of questionable value.

To fully optimize the material properties, the relationships between the structure and the properties must be thoroughly understood. The current state of knowledge concerning the electrical, chemical and mechanical properties of PPy structures is reviewed in this chapter.

Electrical properties — conductivity

The electrical properties of intelligent materials are important because they determine:

- The ability to transport information from one part of the structure to another
- The ability to store information
- The ability to trigger responses
- The ability to convert and store energy

Electrical conductivity in PPy involves movement of positively charged carriers or electrons along polymer chains and hopping of these carriers

between chains. It is generally believed that the intrachain hopping resistance is much greater than the interchain transport resistance.

Electron and x-ray diffraction data suggest that the polymer chains in electrochemically synthesized PPy lie parallel to the substrate electrode surface, as described in Chapter 2. This is reflected in the anisotropic nature of the conductivity of PPy.¹ The resistance along the surface of the film is known to be less than across the film. However, this anisotropy is lost with thicker films.

At a more microscopic level, the variation of the bulk conductivity observed as a function of temperature is best explained using a model consisting of highly conducting islands in a sea of amorphous less-conducting material (Figure 3.1).^{1,2}

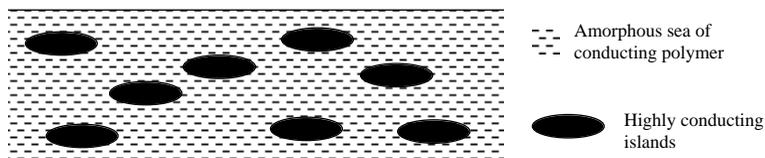


Figure 3.1 Highly conducting islands of polymer in a sea of amorphous less-conducting polymer. (Innis, P.C. and Wallace, G.G., *J. Nanosci. Nanotech*, 2, 441 (2002). American Scientific. With permission.)

Conductivity within conducting electroactive polymers (CEPs) is a complex issue. A polymer that can exhibit conductivity across a range of some 15 orders of magnitude most likely utilizes different mechanisms under different conditions. In addition to the electronic conductivity exhibited by CEPs, they possess ionic conductivity due to the solvent/electrolyte incorporated during synthesis. The experimental parameters encountered during synthesis (as listed and discussed in Chapter 2) have an effect on the polymer conductivity. In particular, the electrochemical conditions, the solvent, counterion and monomers used during synthesis influence the electronic properties of the resulting polymer.

The electrochemical conditions during synthesis can be manipulated to vary the concentration of electrons removed per unit time. This, of course, will have a dramatic effect on the resulting polymer. The polymer must be grown at potentials anodic enough to initiate polymerization, yet care must be taken not to overoxidize, because this results in less-conductive materials. Previous workers⁴ studied the effect of increased current density during growth on the conductivity of PPy/DS polymers. Over the range 2.0–8.8 mA/cm², they indicated that, initially, an increase in conductivity was observed that leveled out and then dropped off again at higher current densities. As Diaz and Lacroix pointed out,⁵ however, the optimal current density depends on the counterion/solvent system under investigation. They have shown that the quality of the films obtained deteriorated with the presence of nucleophiles during

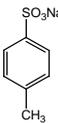
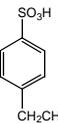
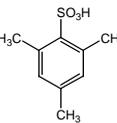
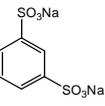
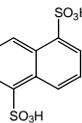
polymerization. Water itself can act as a nucleophile, attacking the pyrrole ring to form carboxyl groups that break up the polymer chain, thereby causing a decrease in conductivity and mechanical properties. The magnitude of this effect is electrolyte-dependent, because surfactants, for example, are known to stabilize the pyrrole radical⁶ even in nucleophilic solvents. Despite this enhanced stability, other workers have shown that PPy/DS has higher conductivity when grown from CH₃CN rather than water.⁷

It has been demonstrated⁸ that a more isolated cauliflower structure was observed for polymers grown from water due to hydrophobic effects. Such unevenness decreases conductivity. Aavapiriyant and co-workers⁹ also showed that the presence of small amounts of water affects the rate of growth and polymer conductivity.

The most studied of all variables is the counterion. Numerous workers¹⁰⁻¹² have shown that the counterion incorporated has a dramatic effect on the conductivity of the polymer. For a given counterion, the concentration employed also affects the conductivity of the resultant polymer.¹³ Maddison and Jenden¹⁴ even showed that counterion exchange after synthesis has an effect on the polymer conductivity. Conductivity decreases as the electron affinity of the counterion is increased. It has been reported¹⁵ that the degree of oxidation of the polymer does not vary appreciably as the counterion is varied. The trend in conductivity is related to the nucleophilicity of the counterion employed; this may be due to some sort of anion-induced localization of the radical cation in the polymer. The effect of even slight changes in the molecular structure of the counterion on the conductivity of a range of PPy's has been studied¹⁶ (Table 3.1). In some cases, the use of mixed counterion systems also has a marked effect on conductivity¹⁷ (Table 3.2).

Other workers¹⁸ indicated that anions can be exchanged after growth with minimal effect on conductivity, suggesting that the polymer superstructure is determined during synthesis, and the incorporation of other ions has minimal effect on this structure.

Table 3.1 Effect of the Counterion on the Tensile Strength and Conductivity of Polypyrrole (PP) Films

	PP/BSA	PP/PTS	PP/EBS	PP/MS	PP/BS	PP/NPS
Counterions						
Tensile strength (MPa)	17-23	70-80	60-70	36-47	40-55	40-50
Conductivity (S/cm ⁻¹)	19-20	90-110	90-110	50-70	47-70	50-70

Source: Data taken from Zhao, H., Price, W.E. and Wallace, G.G. *J. Memb. Sci.* 199487:47..

Table 3.2 Effect of Adding Dodecyl Sulfate (DS) to PPy (PP) Para-Toluene Sulfonate (PTS) Films

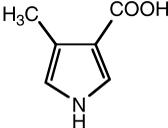
Composition of membranes	PP/PTS	PP/PTS/ DS					
Conductivity (S/cm ⁻¹)	105 ± 10	94 ± 8	82 ± 5	73 ± 7	70 ± 7	65 ± 7	40 ± 9
Tensile strength (MPa)	70 ± 6	63 ± 6	55 ± 6	24 ± 5	12 ± 3	5 ± 2	3 ± 2
Thickness (µm)	4.0 ± 0.3	4.5 ± 0.3	5 ± 0.3	5.5 ± 0.3	6.0 ± 0.3	6.3 ± 0.3	9.0 ± 0.4

Note: All films were prepared using the same electrochemical conditions. Polymerization current density: 2 mA/cm²; polymerization time: 10 minutes; amount of charge passed: 1.2 C/cm².

Source: Data taken from Reference 17.

The addition of functional groups to the pyrrole monomer influences the electronic properties of the resultant polymer. Steric effects introduced by bulky functional groups, for example, decrease the conductivity, particularly when present as *N*-substituents.¹⁹ The presence of substituents on the 3-position of the pyrrole ring has less effect, but still results in a decrease in conductivity (see Table 3.3).

Table 3.3 Effect of Substituents on Conductivity of PPyS

Typical Conductivity Range (Scm ⁻¹)		
Monomer	Dopant	
	pTS	90–110
	pTS	2

Other workers²⁰ have shown that conductivity can be improved by stretching the polymer after growth. The increase in conductivity occurred in the direction of stretching and was caused by alignment of polymer units.

The conditions used during chemical polymerization also influence the conductivity of the resultant polymer. For example, Kang et al.²¹ used simultaneous chemical polymerization (using I₂ or Br₂) at 0–4° to produce more highly conducting polymers.

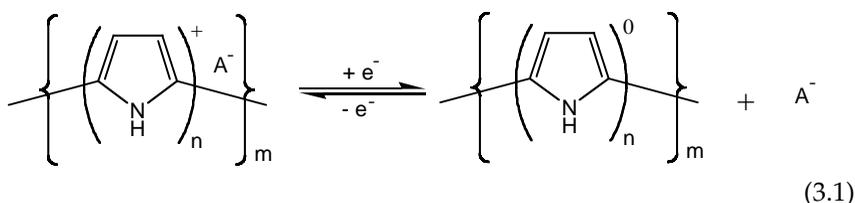
Whang and co-workers²² have shown that judicious choice of the Fe^{II}/Fe^{III} ratio, in order to manipulate to *E*^o value of the oxidizing solution, results in greatly improved conductivities.

Switching properties

The fact that these unique polymer materials conduct electricity is fascinating enough, but the ability to switch their properties *in situ* using simple electrical stimuli is intriguing. Of course, this ability is dependent on their possessing conductivity initially.

Charge can be reversibly added to or removed from a conducting polymer by cycling the material through the oxidized and reduced states. As the switch from oxidized to reduced state occurs, there is a concomitant decrease in the conductivity.

The process for PPys is often described rather simplistically as indicated in Equation (3.1):



The switch involves mass and charge transport in the film and charge transfer at the point of electrical contact (usually an inert electrode substrate). It has been shown previously²³ that reduction proceeds from the point of contact, as does reoxidation (Figure 3.2).

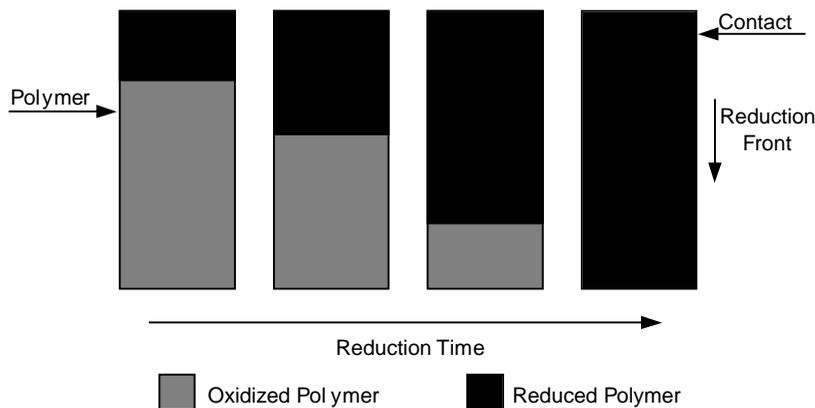


Figure 3.2 Schematic illustrating reduction of conducting polymer.

At a molecular level, it is envisaged that the reduction front percolates through the polymer material, limited (in simple cases) by the diffusion of ions out of the polymer material. The composition of the film is not uniform, but varies with time during the conversion process. Upon reoxidation, ions must be reinserted into the polymer, usually a slower process. The reoxidation is less energy efficient because the reduced polymer is less conductive.

As discussed in Chapter 1, these processes can be studied more closely *in situ* using a number of techniques (Figure 3.3). One technique allows current flow, mass changes and transitions in resistance to be monitored *in situ* as the polymer is oxidized/reduced.

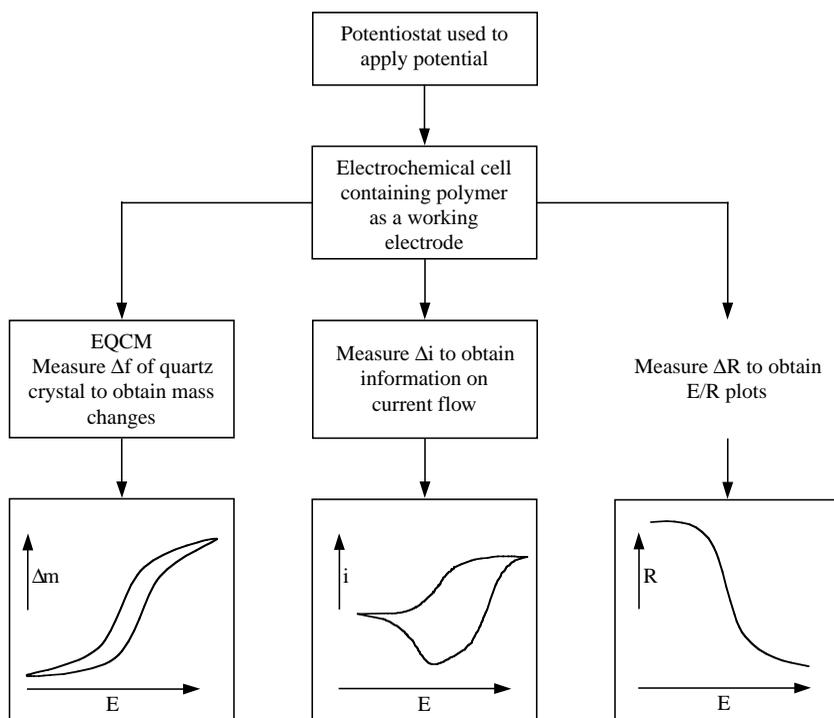


Figure 3.3 The Multidimensional Analyses Technique used to obtain Δi , Δm and ΔR as the polymer is oxidized and reduced.

A typical cyclic voltammogram and a corresponding cyclic resistogram for a well-defined polymer system are shown in Chapter 1 (Figure 1.21). The mass changes observed can be attributed to anion movement (see Equation 3.1) as the polymer is oxidized and reduced. As the polymer is reduced, a well-defined resistance transition, which is reversed upon reoxidation, is also observed. The resistance changes observed do not accompany the current flow due to oxidation/reduction, but lags behind it due to the ion exchange processes' occurring more slowly.

The following factors are important as far as the design of intelligent material systems is concerned:

- The electrical potential of the transition(s)
- The rate of the transition(s)
- Molecular events occurring during the transition(s)

Several parameters will influence the electrochemical switching process. The most important are:

- The anion or cation incorporated during synthesis
- The solvent/electrolyte system used

The effect of the anion on the cyclic voltammograms obtained during cyclic voltammetry is shown in Figure 3.4.

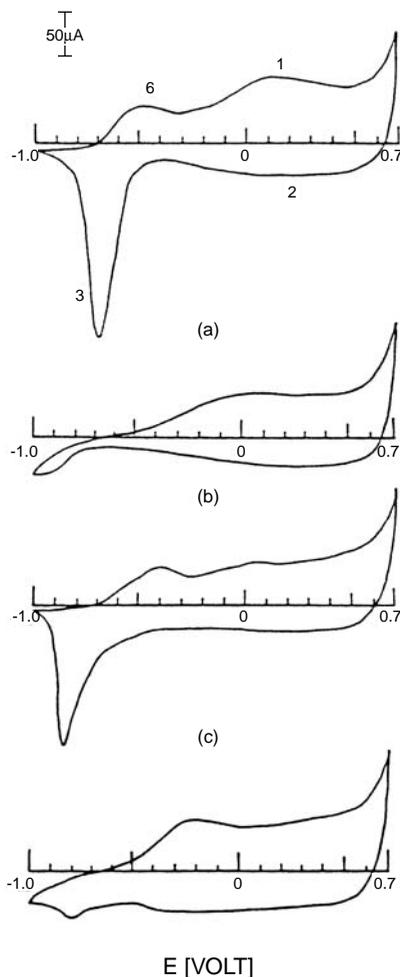
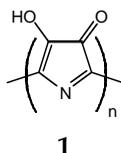


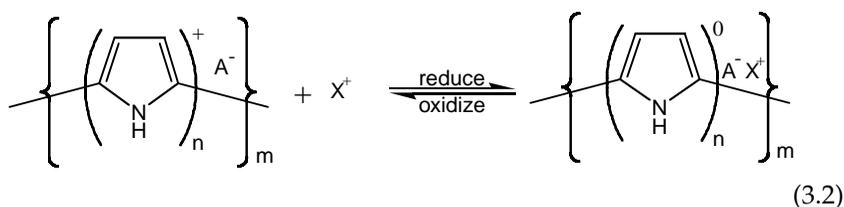
Figure 3.4 Cyclic voltammograms obtained for PPy PTS-coated electrodes: (a) 0.2 M KCl, (B) 0.2 M CaCl₂ and for PPy MS-coated electrodes, (c) 0.2 M KCl, (d) 0.2 M CaCl₂. Scan rate: 20 mV/sec. (from H. Zhao, W.E. Price and G.G. Wallace, Effect of the counterion employed during synthesis on the properties of PPy membranes, *J. Membrane Sci.*, Vol. 87, p. 51, 1994, Elsevier Science-NL, Amsterdam, Netherlands, with permission.)

These cycles can be repeated, provided the potential range is restricted. If the potential applied is too positive, overoxidation of the polymer occurs.^{24,25} This overoxidation process ultimately results in formation of the following products (**1**, shown below):



This polymeric material has inferior electrical and mechanical properties. If the potential applied is too negative, hydrogen evolution and subsequent deterioration of the polymer occur.

Using the same EQCM techniques, previous workers^{26–28} have shown that cations (X^+) are incorporated during reduction of PPys with large counterions that are not able to be removed according to:



As the polymer is reduced, anion is encouraged to leave the polymer; however, if it is slow to do so, charge compensation may be achieved by cation incorporation, the cation coming from the electrolyte in which the polymer is reduced. In some cases, where the anion incorporated during synthesis is bulky (e.g., a polyelectrolyte such as polyvinyl sulfonate) or has a bulky hydrophobic component (e.g., a surfactant molecule such as dodecylsulfate), the cation incorporation process will predominate and the polymer mass will increase upon reduction (see Chapter 1). The change in resistance, at least in solution as measured here, is much less when cation rather than anion movement predominates in the polymer oxidation/reduction process.

Although the role of the solvent during synthesis is probably more important in determining the conductivity and porosity of the polymer, because these contribute to the kinetics of switching, it may also be important in determining the electrodynamic properties. It has been shown that water will solvate polymers such as polyprrole,²⁹ and this influences conductivity and, consequently, switching. Also, other workers^{30,31} have shown that there is substantial movement of solvent in/out of the polymer during the oxidation/reduction process.

Even subtle changes in the counterion play a direct role in influencing switching characteristics. For example, it has been shown that the counterion

incorporated during synthesis affects the ion exchange selectivity series (see [Table 3.6](#)), which then influences switching characteristics. Because charge can move only in tandem with a chemical transformation, the mobility/affinity (for the polymer) of the counterion is extremely important. Visy and co-workers³² indicated that the nature of the counterion is important only when dehydrated. They observed major differences with different counterions in acetonitrile, but with other data quoted for water, no major difference was found. Others³³ have shown that the counterion incorporated during synthesis affects both the potential and the rate of the switching processes.

The effect of even subtle changes in the structure of sulfonated counterions influences the switching process.³⁴ These are evident in the cyclic resistograms ([Figure 3.5](#)) recorded during the switching of a number of PPys with different sulfonated counterions. These small differences at a molecular level are often amplified during switching. Not only do the initial steps depend on anion exchange processes, but subsequent steps during switching are influenced by the chemical (e.g., hydrophobic/hydrophilic) and physical (e.g., resistance) characteristics induced in the polymer by the inserted ions.

Salmon et al.¹⁵ showed that the nature of the monomer was important in determining the switching potential. Specifically, he found that poly-*N*-methyl pyrrole was more difficult to oxidize/reduce than PPy and that intermediate potentials were required to switch copolymers of these two pyrroles. An elegant study by Delabouglise and Garnier showed how attaching various amino acids to the polymer backbone could be used to modify the switching characteristics.³⁵

Salmon et al.¹⁵ reported that, while *N*-substituted pyrroles could be switched, it required greater potentials to do so. This was not always due to conductivity changes (e.g., *N*-phenyl [$\sigma = 10^{-3} \text{ S cm}^{-1}$, $E^\circ = 650 \text{ mV}$] and *i*-butyl [$\sigma = 2 \times 10^{-5} \text{ S cm}^{-1}$, $E^\circ = 600 \text{ mV}$]). Presumably, this was due to differing monomer/counterion affinities.

Other workers have shown that the use of copolymers of pyrrole with substituted pyrroles (*N*-methylpyrrole, in this case) can be used to alter the switching potential.³⁶ In our laboratories, studies involving a functionalized PPy³⁷ have shown that the switching characteristics are markedly affected by the counteranion incorporated during the synthesis. Obviously, this counteranion effect can be amplified by the presence of certain substituents.

Zhang and Dong³⁸ have shown the importance of the supporting electrolyte on the switching properties using *in situ* resistance and current measuring techniques. Both the potential required to trigger the switching and the rate of switching are determined by the supporting electrolyte. The solubility of the ions in the solvent used and their affinity for the polymer matrix determine the switching behavior. In some electrolytes where the anion of the electrolyte is difficult to incorporate (e.g. DS), this has a marked effect on the switching characteristics resulting in cation incorporation.

The electrolyte can also have another effect, not commonly recognized by many researchers, the chaotropic effect.³⁹ This effect, more commonly

Table 3.4 Summary and Examples of the Types of Molecular Interactions

Molecular Interaction	Example	Relative Strength	Distance Dependence	Directionality
Ionic	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{N}^+-\text{H} \\ \\ \text{H} \end{array} \quad \begin{array}{c} \text{O} \\ // \\ -\text{O}-\text{C} \\ \backslash \\ \text{R}' \end{array}$	Very strong	$1/r$	no
Ion-dipole	$\begin{array}{c} \Leftarrow \\ \text{H} \\ / \\ \text{R}-\text{N} \\ \backslash \\ \text{H} \end{array} \quad \begin{array}{c} \text{O} \\ // \\ -\text{O}-\text{C} \\ \backslash \\ \text{R}' \end{array}$	Strong	$1/r^2$	yes
Polar	$\begin{array}{c} \Leftarrow \\ \text{H} \\ / \\ \text{R}-\text{N} \\ \backslash \\ \text{H} \end{array} \quad \begin{array}{c} \Leftarrow \\ \text{OH} \\ / \\ \text{O}=\text{C} \\ \backslash \\ \text{R}' \end{array}$	Moderate	$1/r^3$	yes
Ion-induction	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{N}^+-\text{H} \\ \\ \text{H} \end{array} \quad \begin{array}{c} \Leftarrow \\ \text{H} \\ \\ \text{H}-\text{C}-\text{R}' \\ \\ \text{H} \end{array}$	Weak	$1/r^4$	no
Dipole-induction	$\begin{array}{c} \Leftarrow \\ \text{H} \\ \\ \text{R}-\text{C}-\text{H} \\ \\ \text{H} \end{array} \quad \begin{array}{c} \Leftarrow \\ \text{OH} \\ / \\ \text{O}=\text{C} \\ \backslash \\ \text{R}' \end{array}$	Very weak	$1/r^6$	no
London dispersion	$\begin{array}{c} \Downarrow \\ \text{H} \\ \\ \text{R}-\text{C}-\text{H} \\ \\ \text{H} \end{array} \quad \begin{array}{c} \Downarrow \\ \text{H} \\ \\ \text{H}-\text{C}-\text{R}' \\ \\ \text{H} \end{array}$	Very weak*	$1/r^6$	no

* London dispersion forces increase with the size and polarizability of the molecule.

\Leftarrow Permanent dipole moment.

\Leftarrow Induced dipole moment.

\Downarrow Instantaneous dipole moment.

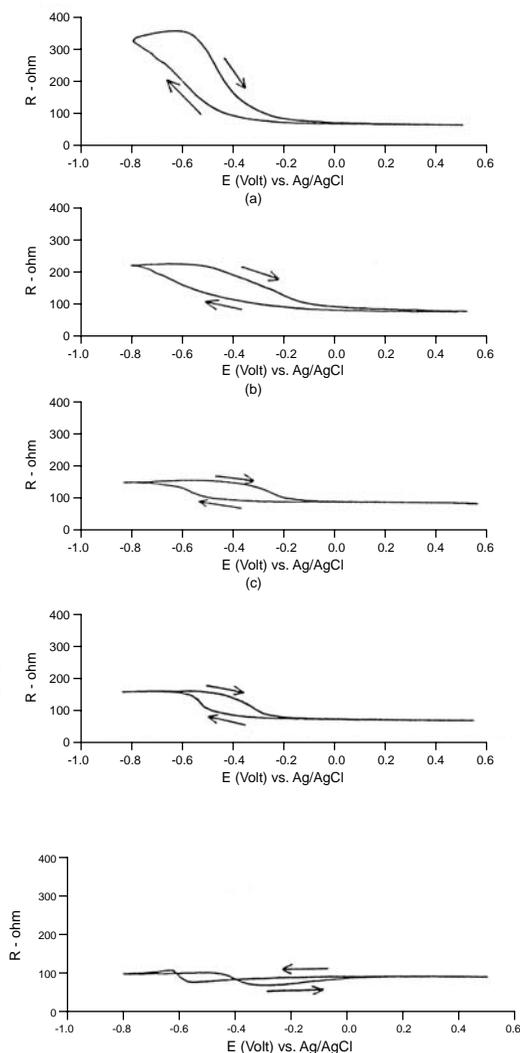


Figure 3.5 Cyclic resistograms obtained after growth (supporting electrolyte, 1 M NaCl, scan rate, 100 mV/s) for polymer containing (a) BSA, (b) PTS, (c) SBA and (d) NDS. (From A. Talaie and G.G. Wallace, The effect of the counterion on the electrochemical properties of conductive polymers, *Synth. Met.*, Vol. 63, p. 85, 1994, Elsevier Science, Lausanne, Switzerland, with permission.)

discussed in biochemical circles, is related to variations in the water structuring ability of different salts. This ability is used, for example, to dehydrate and salt out macromolecular proteins. The same effects can be expected with conducting polymers. As well as ion size effects, this can be used to explain the large shifts in switching potentials observed in different electrolytes⁴⁰

when the cation was varied, and the difference in overoxidation potentials observed in different electrolytes.⁴¹

The presence of nucleophiles during potential scanning decreases polymer stability because the polymer becomes reactive at anodic potentials.⁴² This finding was used to demonstrate the formation of covalent bonds between OH^- or CN^- and pyrrole at positive potentials.

The size of the electrode also affects switching properties. The ability to switch at high scan rates has been demonstrated previously by other workers using microelectrodes.⁴³ Conversely, use of macrostructures will be slower to switch and the degree (percentage of material affected) of switching will be much less efficient.

Chemical and biochemical properties

The chemical properties of the resultant structure determine the ability to recognize particular stimuli and respond to them appropriately. In addition, these properties determine how the conducting polymer interacts with other materials in the construction of composite intelligent material structures.

Most polymers can, and indeed do, interact with other molecules. Such molecules may be part of other larger molecular structures (important in the area of compatible materials), or they may be solvent molecules (such interaction can influence many processes including dissolution) or specific molecules in a solvent or gaseous medium.

As shown in [Table 3.4](#), all such interactions can be broken down into definable modes of molecular interactions. Organized in appropriate spatial and temporal domains, these interactions combine to give rise to chemical recognition phenomena such as complexation, enzyme or antibody/antigen interactions. In a more general sense, how these interactions are influenced by environmental stimuli determines the behavior of the polymer system.

The most common interaction of polymers involves solvents. However, only a limited number of studies have been carried out to investigate the effect of solvents on PPys. We have considered the use of dynamic-contact angle analyses and shown that Ppys' ability to interact with water is influenced by the counterion employed during synthesis and the presence of functional groups on the polymer backbone.⁴⁴ These preliminary studies have also shown that, in the process of exposing PPys to water, the polymer structure responds by becoming easier to wet. This is evident from the subsequent dynamic-contact angle scan, showing that the polymer is reluctant to shed water that has previously been incorporated. Using more conventional contact-angle measurements, we have determined that the wettability of conducting PPys is markedly affected by the counterion incorporated during synthesis ([Table 3.5](#)).

Even simple PPys (with simple counterions such as chloride or nitrate incorporated) are inherently versatile molecular structures, capable of undergoing all the interactions listed in [Table 3.5](#). Most particularly, they are strong

anion exchangers⁴⁵⁻⁴⁷ that are also capable of undergoing hydrophobic interactions. Other ion exchange groups (e.g., carboxy groups)⁴⁸ or self-doping sulfonate groups⁴⁹ can be added to the monomer prior to polymerization to modify these properties. For example, we have used the presence of the carboxy group to produce chromatographic stationary phases capable of separating small molecules or proteins by cation exchange chromatography.⁴⁸ In these cases, the cation exchange interactions took place on the carboxy groups.

A dramatic impact on chemical properties is achieved by the appropriate choice of counterion. The counterion employed during synthesis can have a marked effect on the anion exchange selectivity series of conducting polymers.⁵⁰ Table 3.6 shows the anion exchange selectivity series obtained for both PPy chloride and PPy perchlorate. As illustrated, PPy salts do not behave like conventional ion exchange resins.

The interplanar distance of neutral PPy has been reported to be 2.41 Å. If the anions are intercalated between the planes of PPy chains, as has been suggested previously, then the interplanar spacing should expand according to the size of the anions incorporated during synthesis. It appears that a small interplanar space is formed when small anions such as Cl⁻ are

Table 3.5 Contact Angles Determined for Different PPy's

Substrate	Contact Angle (°)
ITO	75.6
PPy/Cl	65.0
PPy/DS	59.7
PPy/PAA	37.8

PPy = polypyrrole

ITO = indium tin oxide coated glass

DS = dodecyl sulfate

PAA = polyacrylic acid

Table 3.6 Ion Exchange Sequence

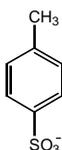
Polymer Composition	Ion Exchange Sequence
PP/Cl	Br ⁻ > SCN ⁻ > SO ₄ ²⁻ > I ⁻ > CrO ₄ ²⁻
PP/ClO ₄	SCN ⁻ > Br ⁻ > I ⁻ > SO ₄ ²⁻ > CrO ₄ ²⁻
Conventional resin	SO ₄ ²⁻ > I ⁻ > CrO ₄ ²⁻ > Br ⁻ = SCN ⁻ > Cl ⁻

used as counterions during polymerization. This small interplanar spacing makes it difficult to replace the anion within the polymer plane with a much larger anion from solution. This then affects subsequent ion exchange processes.

Results obtained from our work correlate with those predicted by the postulated hypothesis. The ionic radii of some ions used for ion exchange investigations are as follows:

Ions	Cl ⁻	Br ⁻	I ⁻	SO ₄ ²⁻	ClO ₄ ⁻	CrO ₄ ²⁻
Radii (Å)	1.81	1.95	2.16	2.30	2.36	2.40

The ion exchange sequence (in Table 3.6) on PPy.ClO₄ follows the above sequence. Therefore, CrO₄²⁻ was found to be more difficult to exchange with ClO₄⁻ compared to other ions. The selectivity toward SO₄²⁻ over CrO₄²⁻ is amazing, given the difference in size of 0.1Å. This is probably due to the large size of the CrO₄²⁻, but suggests that the polymer chains are held rigidly in place once the polymer is formed. A similar trend was noted on PPy/Cl. However, as Cl⁻ is smaller than ClO₄⁻, less Cl⁻ could be exchanged.



Paratoluene Sulfonate

2

In extreme cases, the incorporation of larger hydrophobic counterions (e.g., dodecylsulfate) results in the formation of a polymer not capable of anion exchange but quite hydrophobic in nature.^{51,52} Counterions that are intermediate in nature, e.g., paratoluene sulfonate (**2**, shown above), induce intermediate behavior because they are relatively small charged anions and also have some hydrophobic character.

Polyelectrolytes can also be incorporated as counterions during synthesis, and, because they would be difficult to remove, the anion exchange capacity is again reduced as the cation exchange capacity concomitantly increases.⁵³⁻⁵⁶

It is also possible to incorporate a range of chemically functional counterions into PPys.⁵⁷⁻⁵⁹ The fact that pyrrole can be polymerized from aqueous solutions enables a wide range of counterions to be included in the structure. In cases where a counterion with a specific activity is incorporated, the polymer may act as no more than a carrier or a means of electronic communication. Numerous examples where antibodies⁶⁰⁻⁶³ and enzymes⁶⁴⁻⁶⁸ have been incorporated have been reported. In some cases, additives (molecular carriers) have been used to facilitate incorporation of these large, low-charge density molecules.⁶⁹ For example, the interaction of anionic surfactants with proteins to produce higher-charged molecules can be used to enhance incorporation. Another novel approach to facilitating protein incorporation involves attachment to colloidal gold prior to the electropolymerization.

Using appropriate assembly techniques, the bioactivity of such components can be retained even after immobilization in the conducting polymer.

It is also possible to integrate the chemical properties of other functional molecules into the conducting polymer by direct incorporation. For example, electrocatalysts,⁷⁰⁻⁷² complexing agents,⁷³⁻⁷⁵ and polynucleotides⁷⁶ or even DNA,⁷⁷ have all been incorporated to induce the specific properties of these molecules. Chiral molecules^{78,79} and even whole cells have been incorporated.^{80,81} In our laboratories we have successfully incorporated mammalian red blood cells during electrosynthesis, using polyelectrolytes in the synthesis mixture. It is also possible to covalently attach bioactive sites to conducting polymers directly.⁸²⁻⁸⁴ The use of such approaches to attach oligonucleotides^{83,84} is particularly exciting in that it provides a platform for a new range of DNA testing technologies. A range of temperature-sensitive polyelectrolytes⁸⁵⁻⁸⁷ (**3**, shown below) have also been incorporated into conducting polymers to make the properties of the resultant materials temperature dependent.

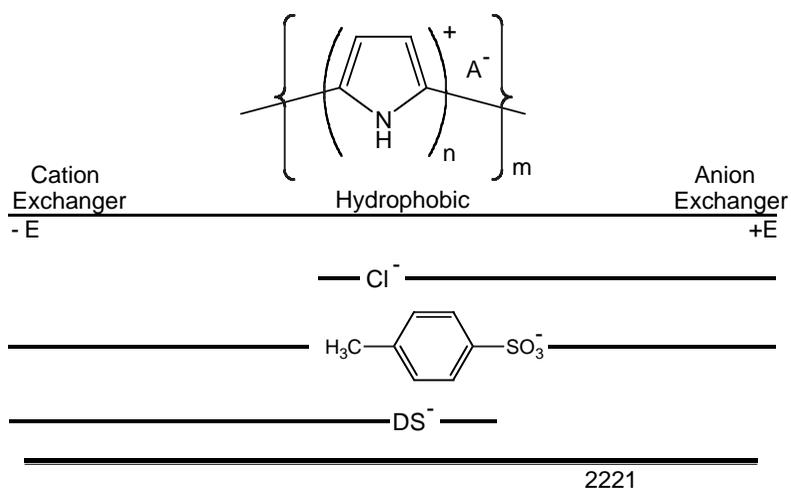
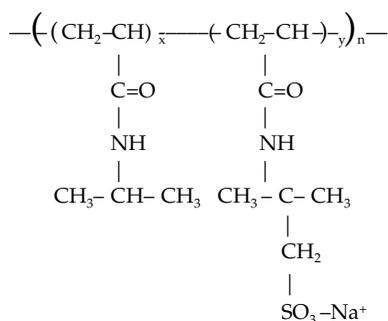


Figure 3.6 A schematic illustration of the effect of applied potential on the ion exchange properties of PPys containing different counteranions.



As far as intelligent materials are concerned, the dynamic nature of these chemical properties is important. For example, we^{60,61,88,89} have shown that the affinity for particular antibody molecules can be altered by the application of electrical stimuli. We have also shown how ion exchange properties and hydrophobic character can be adjusted.^{90,91} The potential stimuli/chemical property behavior is dependent on the counterion incorporated during synthesis, as discussed previously. As illustrated in Figure 3.5, the chemical interaction properties (cation exchange, hydrophobic and anion exchange), and the way they vary as a function of potential, is markedly dependent on the counterion (Cl⁻, PTS⁻ or DS⁻) incorporated during synthesis.

In addition, the activity of incorporated functional molecules such as proteins can be altered by application of appropriate electrical stimuli. In previous work, incorporation of proteins into phases suitable for affinity chromatography was demonstrated. It was also shown that application of electrical potential influences the Ag–Ab interaction. While the mechanism is not absolutely clear, perhaps the application of potential changes the protein conformation due to changes in the hydrophobicity of the polymer surface. Attempts to reverse the Ab–Ag interaction using applied potentials on the affinity column were unsuccessful. However, by using the same principles as sensing technology and a repetitive-pulsed potential waveform routine, reversibility of the interaction could be attained.^{60,61} The same phenomenon has been used by others more recently in development of new biosensing technologies.^{62,63}

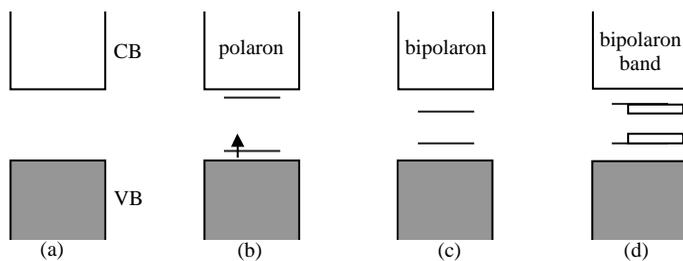


Figure 3.7 Electronic levels/bands for PPys with increasing doping.

Optical properties of PPys

1. *Electronic band structure.* Figure 3.7 shows the electronic levels or bands proposed by Bredas and co-workers⁹² for PPy, on the basis of semi-empirical theoretical calculations, as it is progressively doped from its neutral undoped state to a maximum of ca. 35% doping. In its neutral state, PPy is predicted to have a very large π – π^* (valence \rightarrow conduction) band gap of 3.2 eV. When one electron is removed to form a polaron (radical cation), two polaronic levels appear in the band gap, as shown in Figure 3.7(b). The lower of these polaron levels is half filled for such partly doped PPys (with one positive charge for every 4 to 6 monomer units), as confirmed by an ESR

signal for the unpaired electron. Further electron removal results in the formation of a spinless bipolaron and the energy levels shown in Figure 3.7(c) (together with the loss of the ESR signal). These electronic states coalesce into bipolaron bands (Figure 3.7(d)) with further doping to ca. 35% (1 positive charge for every three pyrrole monomer units). The π - π^* band gap is also predicted⁹⁰ to increase to 3.6 eV. A typical UV-visible spectra obtained for PPy-DNA is shown in Figure 3.9.

2. *UV-visible-NIR spectra: dependence on doping level and chain conformation.* A typical UV-visible spectra for PPy is shown in Figure 3.8. The UV-visible spectra of PPys and their changes with varying doping levels have, in a number of cases, been correlated with the above predictions, as first discussed by Bredas et al.⁹² For example, the change in color of neutral PPy from pale yellow to gray-black as it is electrochemically oxidized to PPy.CIO₄ is accompanied by progressive changes in the UV-visible-NIR spectrum consistent with the initial appearance of polarons and their subsequent replacement by bipolarons.⁹³ In general, highly doped PPys exhibit two characteristic bipolaron bands at ca. 1.0 and 2.6 eV (1240 and 475 nm) as well as a π - π^* band.^{94,95}

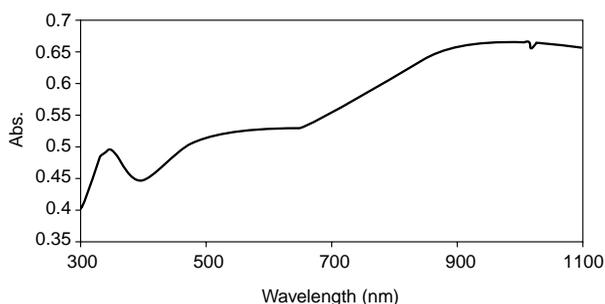


Figure 3.8 A typical UV-visible spectra obtained for PPy-DNA.

However, the position and shape of the bipolaron/polaron bands have been shown to be very dependent on environmental factors such as the deposition surface or the solvent. These changes in UV-visible-NIR spectra are believed to arise from (and to be indicative of) conformational changes in the PPy chains. For example, while conducting PPy films deposited on hydrophilic glass surfaces exhibit an absorption band at ca. 1180 nm, this band is replaced by an intense free carrier tail extending to 2600 nm for analogous films deposited on hydrophobic silanized glass.⁹⁶ By analogy with related studies of polyanilines (see Chapter 5), the presence of the free carrier tail for PPy deposited on hydrophobic surfaces is attributed to the adoption of an “extended coil” conformation by the polymer chains. This contrasts with the “compact coil” conformation favored on hydrophobic surfaces.

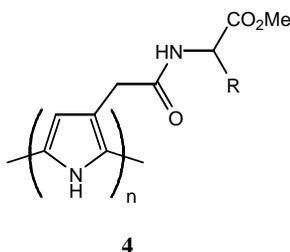
Similar marked changes in their UV-visible-NIR spectra occur for the recently discovered⁹⁷ “soluble” PPys when the organic solvent is var-

ied.^{93,98–100} For example, the bipolaron band observed at 475 nm for PPy.DBSA (DBSA = dodecylbenzenesulfonate) in chloroform solvent undergoes a large blue shift to ca. 425 nm with *m*-cresol or DMSO as solvent.^{93,96} This suggests a shorter conjugation length for the PPy in *m*-cresol and DMSO. This is consistent with the lower electrical conductivity observed for PPy.DBSA films cast from solutions in *m*-cresol rather than from chloroform solutions.⁹⁵ The intensity of the NIR bipolaron band of PPy.DBSA is also very sensitive to the nature of the organic solvent. Oh et al.⁹⁹ reported that this NIR band is more intense in relatively nonpolar solvents such as chloroform than in the aromatic solvents *m*-cresol or benzyl alcohol, and is markedly reduced in the polar solvents DMSO and NMP as well as blue shifted to ca. 850–900 nm. These spectral changes were attributed to the micelle formation by the DBSA and solvent interactions with the PPy chains. This leads to rearrangement of the polymer backbone from an “extended coil” conformation in chloroform to a “relatively compact coil” in NMP and DMSO.

Similar changes have been recently observed in the intensity and wavelength of the NIR bipolaron band of the polymer PPy.DEHS {DEHS = di(2-ethylhexyl)sulfsuccinate} in alcohol solvents of varying polarity.⁹⁸ The non-polar 2-ethylhexyl groups are believed to solvate the PPy chains more effectively in weakly polar alcohols such as *t*-butyl alcohol, resulting in an “extended coil” conformation and an intense NIR free carrier tail. In contrast, in polar ethanol or 2,2,2-trifluoroethanol solvents, this solvation is less effective, leading to the adoption of a “compact coil” conformation and markedly less intense NIR absorption.

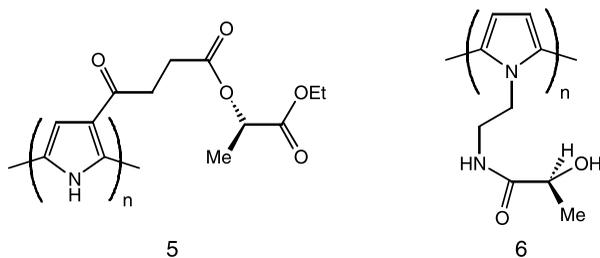
Chiroptical properties of optically active PPys

The first reported circular dichroism (CD) study of chiral PPys was by Delabouglise and Garnier¹⁰¹ on the polymers **4** (R = CH₂OH, CHMe₂, Ph), in which a series of amino acids are covalently bound at the 3-position of each pyrrole ring. They exhibit a circular dichroism band at ca. 470 nm associated with the absorption band at 460 nm. This optical activity is believed to be induced by the presence of the chiral amino acid substituents, leading to the adoption of a one-handed helical structure by the PPy chains.



More recently, Pleus and Schwientek¹⁰² prepared a series of related chiral PPys bearing (–)-ethyl L-lactate as the chiral functional group located at

either the pyrrole ring 3-position or the ring N center, e.g., polymers **5** and **6**. Although no circular dichroism studies were carried out on the PPy films, cyclic voltammograms recorded in the presence of (+)- or (-)-CSA⁻ revealed them to be enantioselective. Preferential doping of the chiral PPy by the (-)-CSA⁻ anion occurred, as indicated by the substantially higher charge passed when cycling the potential in the presence of this enantiomer rather than (+)-CSA⁻. Similar enantioselectivity between the (+)- and (-)-CSA⁻ ions is exhibited by optically active films of the polymer **6**, which has a glucose derivative covalently bound at the pyrrole N centers.¹⁰³



Very significantly, recent studies by Pleus et al.¹⁰² have revealed that the conducting films **4** and **5** can be employed as chiral electrodes for the enantioselective electroreduction of acetophenone and 4-methylbenzophenone to their corresponding alcohols. Enantioselectivities as high as 58% could be achieved.

Mechanical properties of PPy

To be functional, any material must possess adequate mechanical properties to withstand the stresses and strains that occur during service. For example, standalone membranes must be sufficiently stiff to maintain their shape and sufficiently strong to resist rupture when subjected to pressure gradients. Similarly, coatings are subjected to high stress resulting from different thermal expansion between coating and substrate. Thus, the coating material must show high ductility, so that it is able to expand and contract without cracking or delaminating. Membranes and coatings are just two of the many potential applications for CEPs, but they demonstrate the key importance of mechanical properties.

It is widely recognized by researchers in this field that the mechanical properties of PPys vary widely from strong, tenacious materials to extremely brittle ones. As a consequence, it is necessary to understand how the mechanical properties are affected by the chemical structure, the processing conditions and the conditions of use (service environment). The ultimate aim is to develop and understand causal relationships between the structure of the PPy and the mechanical properties. Such relationships would enable the deliberate manipulation of the structure (e.g., by controlling the processing conditions) to produce desired mechanical properties.

This section reviews the published work on the mechanical properties of PPy. Most of this work, which is discussed first, has been conducted on dry films. Some recent work on PPy adhesion to electrode materials is also presented, along with the results of investigations into environmental effects on mechanical properties.

Dry state mechanical properties

Several investigators have specifically studied the mechanical properties of PPy, while numerous others have reported such properties as incidental to other findings. The most commonly reported values are the Young's modulus (E , a measure of material stiffness), the tensile strength (σ_B) and the percentage of elongation at break (ϵ_B , a measure of ductility or brittleness). All tests described in Table 3.7 have been conducted in tension, using thin films as samples (apart from Bloor et al.,¹⁰⁴ who used 1 mm-thick plates).

The most pertinent feature in Table 3.7 is the vast range of mechanical properties that have been reported for PPy. It is apparent that the composition of the polymer (e.g., counterion type) and the polymerization conditions have a significant effect on the polymer properties. However, the relationships are not straightforward. For example, Wynne and Street¹⁰⁵ have shown that acetonitrile solvent yields PPy films with very good mechanical properties, whereas Sun et al.¹⁰⁶ and others have reported the opposite. It is clear that systematic analyses are required to elucidate the determinants of the mechanical properties of PPy.

Most of the previous work has been empirical in nature. However, these studies have been important in demonstrating those factors that influence the mechanical properties. For example, mechanical properties of PPy films have been observed to improve as the polymerization temperature decreases. Sun et al.¹⁰⁶ have observed that the tensile strength of PPy.pTS increases as the synthesis temperature decreases. Similarly, Hagiwara and coworkers^{107,108} have observed the elongation to break of PPy.CIO₄ and PPy.PF₆ films, respectively, increase upon decreasing polymerization temperature. Sun et al.¹⁰⁶ attributed the differences in mechanical properties to changes in the molecular structure of the polymer (e.g. conjugation length or molecular weight) caused by the decreasing reaction temperature.

The applied potential and current density used during electropolymerization have also been found to be significant variables. A steady decrease in the tensile strength of PPy.pTS films has been observed as the applied potential during polymerization was increased.¹⁰⁹ Other workers¹¹⁰ have also reported a decrease in the Young's modulus of PPy.pTS with increasing applied potential during electropolymerization. No specific explanation has been offered for the behavior. However, it has been suggested¹⁰⁹ that the change in the mechanical properties may be associated with a decrease in the density of the films as the potential of polymerization was increased, with a "more open, mechanically less durable material" being produced. Hagiwara et al.¹⁰⁸ observed an increase in the elongation to break of PPy

Table 3.7 Summary of Mechanical Properties of PPys

Polymerization Conditions*	E(GPa)	θ_B (MPa)	ϵ_B (%)	Variables Studied	Reference
Vitreous carbon and platinum ACN + 0.5% water. Various counterions $E_{app} = 3-6$ V CD = 0.51-7.44 mA/cm ²		18-55	7-27	E_{app} and CD during polymerization <i>Action of water during polymerization</i> Different counterions	Buckley et al. ¹⁰⁹
Carbon electrode Water or ACN + 0.7% water pTS $E_{app} = 3$ V CD = 0.016 mA/cm ² $T = 0^\circ$ C	1.2-3.5	35-76	16-50	Plasticizing effect of residual solvent Effect of polymerization solvent	Wynne and Street ¹⁰⁵
Platinized electrodes PC (with and without water) pTS ⁻ CD = 0.3-3.2 mA/cm ²	3.3-4.1	34-65	2.6-6.0	1 mm plates prepared CD during polymerization varied Plasticizing effect of water	Bloor et al. ¹⁰⁴
Various solvents PTS $E_{app} = 0.8-1.3$ V		8-59	7-17	Effect of large additions of water to ACN solvent Effect of solvent additives	Hiaz and Hall ¹¹¹
Stainless steel Water Various counterions CF = 1.3 mA/cm ²		17-68	1-10	Various counterions	Wettermark et al. ¹¹⁵
Titanium ACN + 1% water or ACN + PC + 1% water PTS- $E_{app} = 0.7-1.1$ V CD = 0.7-3.5 mA/cm ² $T = 20$ or -40° C	0.9-4.3	2-59	2-24	Reaction temperature Aging Added plasticizers	Sun et al. ¹⁰⁶

Table 3.7 Summary of Mechanical Properties of PPys (Continued)

Polymerization Conditions*	E(Gpa)	θ_B (MPa)	ϵ_B (%)	Variables Studied	Reference
Titanium PC = 1% water PTS ⁻ $E_{app} = 1.0V$ CD = 0.3–1.0 mA/cm ² $T = 0$ or 25° C	1.0–2.7	36–43	3–26	Aging	Cvetko et al. ¹¹⁴
Carbon and platinum PC + 1% water PF ₆ ⁻ Various E_{app} and CD Various T			670–180**	Effect of polymerization conditions on elongation of films	Hagiwara et al. ¹⁰⁸

* Where reported the polymerization conditions are summarized: working electrode; solvent; counterion; applied potential (E_{app}) if potentiostatic growth; current density (CD) if galvanostatic growth; polymerization temperature.

**Tested at 150° C.

pTS⁻ = p-toluene sulfonate

ACN = acetonitrile

PC = propylene carbonate

films as the potential was increased during polymerization. This was also accompanied by variations in film density.

The solvent used during electropolymerization also affects mechanical properties. For example, Wynne and Street¹⁰⁵ observed that the incorporation of a small amount of water with acetonitrile as the polymerization solvent improves the mechanical properties of the PPy.pTS films. This result was attributed either to differences in the composition or in molecular weight. However, the latter was not determined, and minimal differences were reported in the former. In contrast, others¹¹¹ have shown that large additions of water to acetonitrile result in a substantial decrease in strength. It has also been noted that PPy.pTS films formed from propylene carbonate were superior to those formed from acetonitrile solvent in terms of mechanical properties, but again, reasons were not suggested.¹¹²

Several researchers have observed that PPy films can be plasticized by solvents such as water, leading to a decrease in brittleness.^{103,105,106,109} Wynne and Street¹⁰⁵ showed that PPy.pTS reversibly absorbs moisture, causing plasticization of the films. Sun et al.¹⁰⁶ have noted that the loss of moisture from PPy/pTS films with time leads to embrittlement, while the incorporation of phthalate plasticizers into the films improved ductility. Similarly, several workers^{113,114} have used surfactants as counterions, resulting in a good plasticizing effect.

By far the most important processing variable for mechanical properties is the type of counterion used (Table 3.7). The effects of various counterions incorporated into PPy films on the mechanical properties have been studied by several workers.^{109,112,114} For example, Cvetko et al.¹¹⁴ observed that the pTS⁻ counterion produced flexible films, whereas all other counterions investigated produced brittle films. These other counterions included BF₄⁻, AsF₆⁻, ClO₄⁻, HSO₄⁻, BrC₆H₄SO₃⁻ and CF₃COO⁻. Our own studies (Tables 3.1 and 3.2) have also demonstrated the dramatic effect the choice of counterion has on tensile strength.

Buckley et al.¹⁰⁹ have further investigated the effects of counterion structure on the mechanical properties of PPy films by using variations on the pTS⁻ structure, for example, C₆H₅SO₃⁻, CH₃CH₂C₆H₄SO₃⁻, and CH₃(CH₂)₁₁C₆H₄SO₃⁻. pTS⁻ again showed the best results. Buckley et al. have demonstrated that the current density used during polymerization may have a more significant effect, because the p-dodecylbenzenesulfonate counterion gives very similar mechanical properties to the pTS⁻ when a similar current density is used. These workers suggested that the wide variations in properties reported might be attributed to differences in polymerization conditions.

The key to understanding the properties of PPy films is to develop an understanding of the relationship between the structure of the polymer and its mechanical properties. Unfortunately, few studies have been devoted to gaining such an understanding. This is due, in part, to the intractable nature of PPy films, which makes structural characterization difficult.

Molecular weight of the PPy is one variable that has sometimes been quoted as a possible explanation for differences in the mechanical properties of PPys prepared in different ways. Wynne and Street¹⁰⁵ suggested that the change in mechanical properties of PPy.pTS with changing solvent may be due to different molecular weight polymers being produced. Others¹⁰⁶ have also proposed that differences in molecular weight might account for the different mechanical properties observed in PPy.pTS films prepared at different temperatures. Unfortunately, the molecular weights of the polymers were not determined in these studies; consequently, it is not possible to confirm these assertions.

Buckley et al.¹⁰⁹ noted a correlation between the composition of the PPy, in terms of the ratio of counterion to monomer and the tensile strength of the films. These workers observed that the concentration of counterion intercalated with the polymer depends on the potential applied during polymerization. However, they noted that the change in mechanical properties could also be due to changes in the density of films.¹⁰⁹ Thus, the effect of counterion content or polymerization potential on the mechanical properties of the films remains unknown.

Crosslinking is likely to significantly affect the mechanical properties of the polymer — the greater the degree of crosslinking, the more brittle the material. Unfortunately, there have been no reports on the effect of polymerization conditions or counterion type on the degree of crosslinking produced in the polymer. Consequently, it is not known to what extent crosslinking

varies as a result of differing conditions and to what extent the crosslinking affects the mechanical properties.

Numerous x-ray diffraction studies have been conducted on PPy films to characterize the degree of molecular order. It has been noted¹¹⁵ that the degree of alignment increased as the applied potential and temperature of polymerization decreased. As reported above, the mechanical properties of PPy films were observed to improve under such conditions. Thus, there may be some correlation between molecular order and the mechanical properties of PPy films.

A greater degree of order has been observed when the films are mechanically stretched.^{107,108} The stretching is believed to orient the molecular chains in the direction of the applied stress. However, the effects of stretching on the mechanical properties have not been reported.

Several studies have shown that electrochemically prepared films have an inhomogeneous nodular (or "cauliflower") structure.¹¹⁶ A number of studies have reported the morphology of PPy films as a function of various processing variables; however, little is known of the mechanism of formation of the nodular structure or the effect of this structure on mechanical properties.

Qian and Qui¹¹⁷ have observed that the morphology of the PPy film depends on the type of counterion used. For example, ClO_4^- , BF_4^- and PF_6^- yielded films with high concentrations of voids, while PPy/PTS films consisted of densely packed nodules. Other workers have noted a dependence of the density of the PPy films on the polymerization conditions.^{108,109} Thus, the change in film morphology may explain the effect of counterion type and polymerization conditions on the mechanical properties, as surveyed above.

One study in our laboratories investigated the direct link between PPy film morphology and the mechanical properties.¹¹⁷ Observation of the fracture surfaces of the films showed a roughened surface with cone-shaped features (Figure 3.9), similar to those observed in TEM micrographs of the film cross sections.¹¹⁸ It was concluded from this study that the cone boundaries are points of weakness within the film that allow easier crack propagation. Thus, films with less prominent boundaries should show improved fracture resistance.

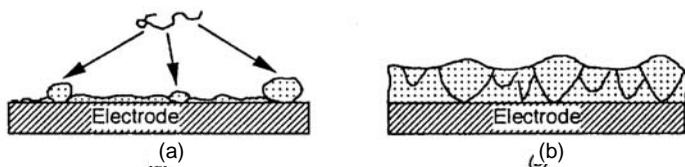


Figure 3.9 Fracture surface of PPy.pTS.

In the basis of these reports, it seems that the relationship between the morphology of PPy films and the mechanical properties needs to be further

assessed. Once this relationship is known, the effects of smaller-scale variations in structure can be determined.

Environmental effects on mechanical properties

Some information is available about the environmental effects on the mechanical properties of PPy. For most intelligent polymer systems, the mechanical properties need to be stable with time in the service environment. However, some systems may require mechanical actuation properties of the polymer; indeed, such actuation may need to occur in response to environmental changes. For these reasons, it is informative to study the effects of the environment on the mechanical properties.

Two aspects of the mechanical properties of PPy in different environments have been studied in our laboratories^{119,120} — the effects of different salt solutions and the effect of an applied potential. The latter was achieved using the experimental set-up shown in Figure 3.10. In both cases, the Young's modulus, elongation at break and tensile strength were measured. In addition, in the latter, the mechanical actuating behavior of the PPy was also examined. The actuating behavior of conductive polymers has also been studied by other workers and was reviewed in Chapter 1.

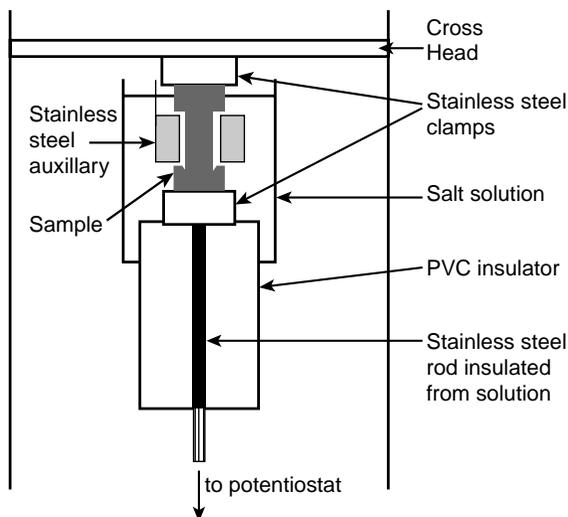


Figure 3.10 *In situ* cell for mechanical testing. (M. Ghandhi et al., Film substrate and mechanical properties of electrochemically prepared PPy, *Polymer*, Vol. 36, No. 25, p. 4762, Elsevier Science, Oxford, England, with permission.)

Figure 3.11 (a) and (b) shows the effect of different aqueous environments on the mechanical properties of PPy.pTS. It is clear that the films become more ductile in chloride solutions and potassium hydroxide solution. Little change in properties is noted in air, water, sulfuric acid or potassium sulfate.

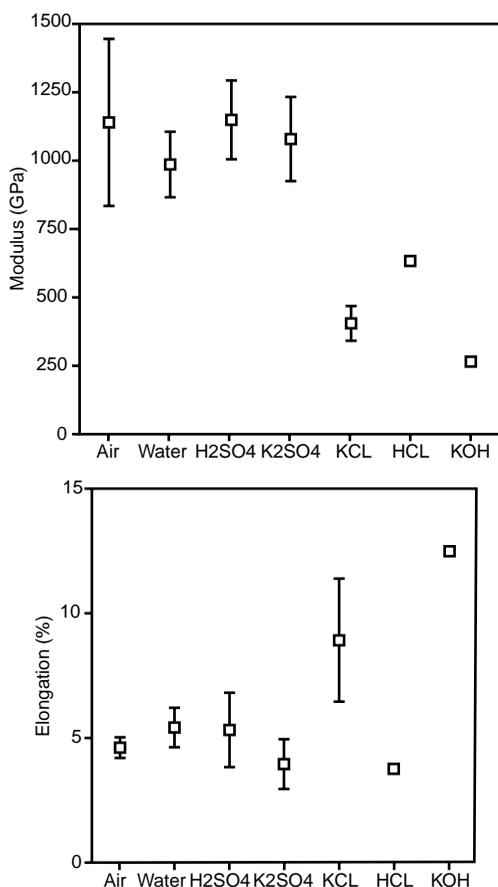


Figure 3.11 (a) Young's moduli of PPy.pTS films tested immediately after immersion in various aqueous environments. The modulus in air is included for comparison. (b) Elongation at break of PPy.pTS films tested immediately after immersion in various environments. The elongation in air is included for comparison. (Data from References 119 and 120.)

The reasons for these changes are not clear at present, although it is known that alkaline solutions have a degradative effect on PPy.¹¹⁹ These processes are likely to cause a reduction in the molecular weight or crosslink density of the polymer, and hence, increase its ductility. The sensitivity of the polymer to environmental conditions demonstrates the importance of determining its behavior in the actual service environment.

When electrical potentials are applied, equally dramatic changes in mechanical properties have been observed.¹²² That is, negative potential induced a much higher plasticity in the PPy.pTS samples. When tested without an applied potential, the samples showed classical brittle behavior with an elongation at break of 10%. However, when the polymer was reduced, the

elongation to break increased to approximately 20%. The electrolyte solution influenced the changes in mechanical properties, with divalent cations requiring a more negative potential to induce ductility. This correlates with the ease of ion transport into the polymer. Application of positive potentials was found to have a minimal effect on the mechanical properties compared with the dry-state behavior. The effect of an applied potential (in different electrolytes) on the tensile strength is shown in Figure 3.12.

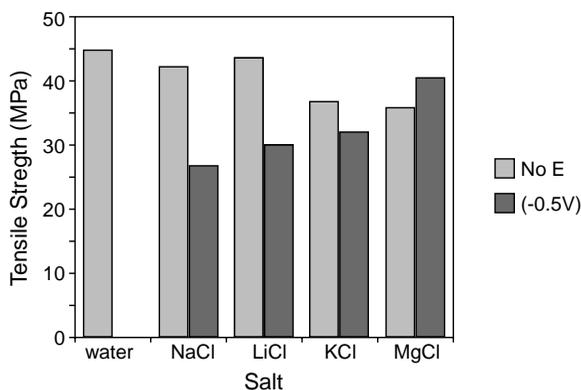


Figure 3.12 Effect of applied potential on tensile strength.

The changes in force within a PPy:pTS film held at a constant strain and subjected to cyclically varying potential have been studied (Figure 3.14). Such changes are caused by contraction or swelling of the polymer, which can be correlated with ion flow out of or into the polymer.

Conclusions

Obviously, the way in which CEPs such as PPy are assembled has a dramatic effect on their chemical, electrical and mechanical properties. This information can be used to advantage by those involved in material design from the molecular level. Factors influencing electrical and chemical properties continue to be studied, adding more information to the already massive databank — these are not simple systems.

Fully understanding the importance of the mechanical properties of a material for its successful application requires that the mechanical properties of PPys be further studied. Literature reports confirm that the properties of PPys vary widely and are related to composition, processing and conditions in a complex way. Thus, the study of the mechanical properties must be conducted at a fundamental level — by developing structure–property relationships. This, however, requires a greater understanding of the structure of PPys, both at the molecular and the supramolecular level.

A further aspect that has not been described in great detail is the effect of service environments on the mechanical properties of the PPys. All tests

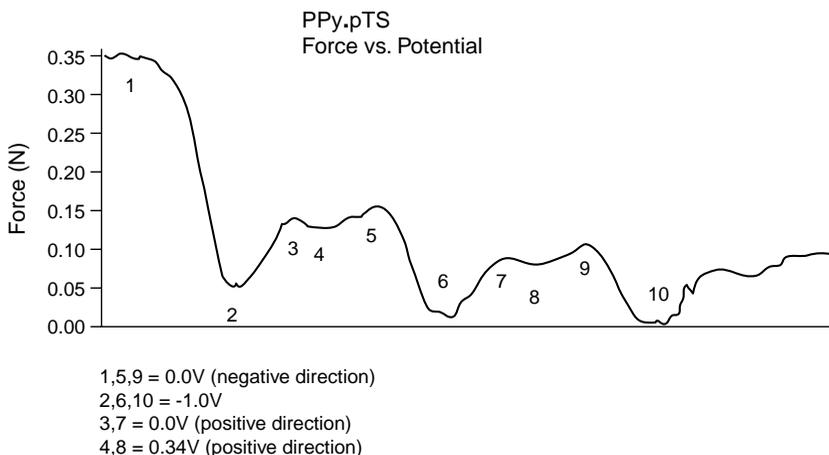


Figure 3.13 Changes in force recorded for a stretched PPy film subjected to a cyclically varying potential.

have been conducted in controlled laboratory conditions, and only a few studies have considered the effects of aging on the mechanical properties. If PPy's are to be confidently used in service, their performance must be addressed at various temperatures, under varying strain rates and cyclic loads, in contact with various liquid or gaseous media and under the influence of applied electrical fields.

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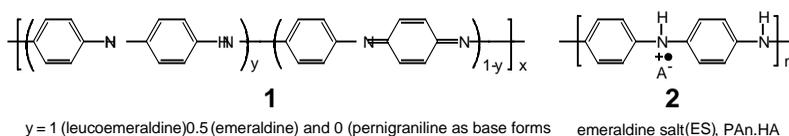
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chapter four

Synthesis and structure of polyanilines

Polyanilines (PAns) have been known for more than a century, since the synthesis of the so-called "aniline blacks" that enjoyed an early use as cotton dyes in the 1860s. Systematic studies^{1,2} of their properties prior to World War I led to the proposal by Green and Woodhead² of an aniline octamer structure and the existence of several oxidation states. Only sporadic studies of polyanilines were undertaken over the following 70 years, until investigations by MacDiarmid et al. in the mid 1980s,^{3,4} and, in particular, the discovery of electrical conductivity for its emeraldine salt form, led to an explosion of interest in this fascinating polymer.

Polyaniline is now accepted to have the general polymeric structure shown as **1** below. It differs from most other inherently conducting polymers, such as polypyrroles (PPys) (Chapters 2 and 3) and polythiophenes (Chapter 6), in that it possesses three readily accessible oxidation states. These range from the fully reduced ($y = 1$) *leucoemeraldine* state to the half oxidized ($y = 0.5$) *emeraldine* form to the fully oxidized ($y = 0$) *pernigraniline* state. Emeraldine is the state with the highest conductivity. There is also an over-oxidized form of pernigraniline.



Polyaniline also differs from PPys and polythiophenes in that the N heteroatom participates directly in the polymerization process (PAn is a "ladder" polymer that polymerizes head-to-tail) and also participates in the conjugation of the conducting form of the polymer to a greater extent than the N and S heteroatoms in PPy and polythiophene.

In addition, PAN is unique among inherently conducting polymers in that it can be rapidly converted between base and salt forms by treatment with acid or base. These reversible redox and pH switching properties (see Chapter 5 for details), together with the electrical conductivity of its emeraldine salt form **2**, its ease and cheapness of synthesis, and its good environmental stability, have led to its becoming the most extensively studied conducting organic polymer over the past decade, and a wide range of potential applications are currently being developed.

Polyanilines are most commonly prepared through the chemical or electrochemical oxidative polymerization of the respective aniline monomers in acidic solution. However, a range of polymerization techniques have now been developed, including:

- Electrochemical polymerization
- Chemical polymerization
- Photochemically initiated polymerization
- Enzyme-catalyzed polymerization
- Polymerization employing electron acceptors

Electrochemical polymerization

The electrochemical cell arrangement described for production of PPy (see Chapter 2) is applicable to the electropolymerization of polyaniline. The polymerization cell design is of equal importance for the preparation of polyaniline as for PPys. All the requirements of the cell design apply, and the same versatility of the form of assembly can be attained, although, in practice, polyaniline has not been investigated as extensively in this regard. The only additional requirement of a polymerization cell for polyaniline is that the electrode and construction materials should be stable in acid media.

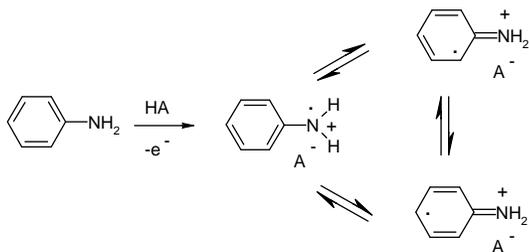
Electrochemical polymerization is routinely carried out in an acidic aqueous solution of aniline. This low pH is required to solubilize the monomer and to generate the emeraldine salt as the only conducting form of polyaniline. Constant potential or potentiodynamic techniques are generally employed because the overoxidation potential for polyaniline is very close to that required for monomer oxidation.

The appearance of defects due to overoxidation of the polymer have been proposed, but the exact nature of the overoxidation is not known. One theory is that crosslinking occurs,⁵ while another describes the opening of the chain after the formation of a paraquinone.⁶

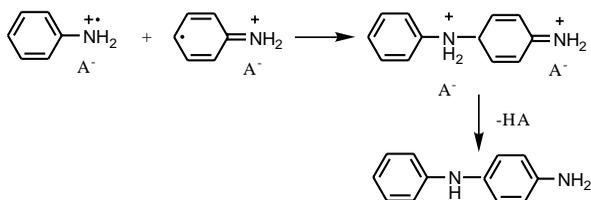
A short-term increase of the applied potential to 0.9–1.1 V (vs. Ag/AgCl) during potentiostatic deposition has been reported to give more adherent films.⁷

Mechanism of electrochemical polymerization. The generally accepted mechanism for the electropolymerization of aniline is an E(CE)_n process, as presented in Figure 4.1.^{8–10} Formation of the radical cation of aniline by

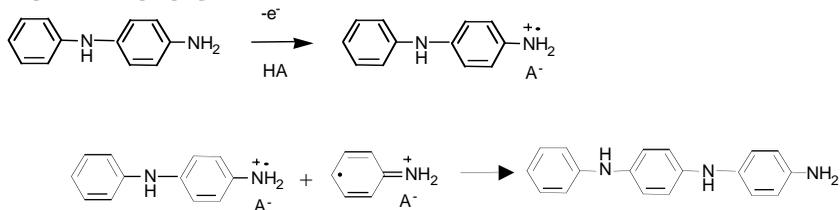
Step 1. Oxidation of monomer



Step 2. Radical coupling and rearomatization



Step 3. Chain propagation



Step 4. Oxidation and doping of the polymer

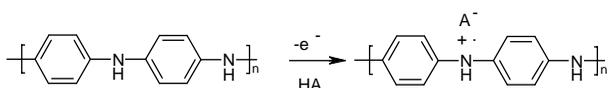


Figure 4.1 Electropolymerization of aniline. (Innis, P.C. and Wallace, G.G., *J. Nanosci. Nanotech*, 2, 441 (2002). American Scientific. With permission.)

oxidation on the electrode surface (step 1) is considered to be the rate-determining step. This is followed by coupling of radicals, mainly *N*- and *para*-forms, and elimination of two protons. The dimer (oligomer) formed then undergoes oxidation on the electrode surface along with aniline. The radical cation of the oligomer couples with an aniline radical cation, resulting in propagation of the chain. The formed polymer is doped by the acid (HA) present in solution (step 4).

The growth of polyaniline has been found to be self-catalyzing;^{11,12} the more polymer deposited, the higher the rate of polymer formation. A mechanism for this has been proposed, involving adsorption of the anilinium ion

onto the most oxidized form of polyaniline, followed by electron transfer to form the radical cation and subsequent reoxidation of the polymer to its most oxidized state.¹²

Electrode materials

A variety of working electrodes can be used, including platinum or gold plates, glassy carbon, reticulated vitreous carbon and indium-tin-oxide (ITO)-coated glass.

As with PPys, the electrode substrate plays a critical role in determining the extent of polymer deposition and the nature of the deposit formed. In extreme conditions, the surface chemistry of the electrode can be so incompatible that no polyaniline will deposit — in fact, surface treatments of ITO exploit this phenomenon in micro contact printing to allow patterns of conducting polymers to be produced on the substrate.¹³ Others have shown that the inherent conductivity of the underlying substrates can have a dramatic effect on the conductivity of the resulting polymer deposited.¹⁴

For some applications, especially in the area of corrosion protection, electropolymerization of polyaniline onto active substrate is of interest. Lacroix and co-workers¹⁵ achieved this by first coating mild steel with a very thin PPy layer and then electrocoating polyaniline on top of this. Others have electrodeposited polyaniline-PPy composites on aluminum¹⁶ or steel¹⁷ surfaces using oxalic acid electrolytes. A number of ring-substituted anilines have also been directly electrodeposited on active iron substrates using an oxalic acid electrolyte.¹⁸ To create novel nanostructures, polyanilines have been recently deposited on aligned carbon nanotubes¹⁹ or into the interstitial spaces of inverse opals^{20,21} to create novel ordered 3-D networks (Figure 4.2). Molecular templates (such as cyclodextrin) have also been added to electrode surfaces to facilitate electrodeposition of nanostructures.²²

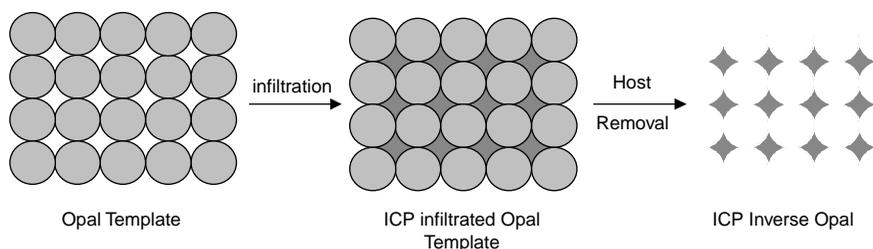


Figure 4.2 Schematic showing approach used to produce highly ordered inverse opal structures with conducting polymers.

Others²³ have used an STM tip to produce polyaniline nanowires by electrodepositing between an SEM tip and another substrate, then stretching the polyaniline wire to create nanostructures.

The solvent

Electropolymerization of aniline is almost always carried out in strong acids. The aniline monomer is soluble in water only under acidic conditions. The conducting form of polyaniline occurs only in acidic conditions, as the polymer is doped by protonation as well as oxidation.

Even within strong acids, however, the anion employed can have a marked effect on the properties of the polyaniline obtained.²⁴ PAnS grown from oxyacids have a sponge-like structure. Those grown from HCl form a spaghetti-like structure because, as with PPy, the anion used influences the rate of polymerization.

However, a limited number of publications have described polymerization from organic solvents (e.g., acetonitrile); in all cases, thin films of low conductivity were produced. Others have used acetonitrile²⁵ with dodecylbenzenesulfonate as the dopant anion to facilitate solubility of the aniline.

The electrolyte

The electrolyte is normally the acid (HA) added to aqueous solution to provide a sufficiently low pH. The dopant A^- incorporated into the polymer is usually the conjugate base from this acid. As with other CEPs, the nature of the anion is critical in determining the morphology,²⁶ conductivity²⁷ and subsequent switching characteristics of the polymer. It also plays a critical role during growth, because some oligomers/polymers (e.g., those containing HSO_4^-/SO_4^{2-}) are inherently more soluble, which delays the onset of precipitation onto the electrode surface.²⁸

It has been shown that addition of polyelectrolytes to the solvent can result in the incorporation of these larger molecules as dopants even when the acid is in excess.²⁹ Others have shown that the addition of inert salts (e.g., LiCl, CaCl₂) to the acid electrolyte can result in significant increases in molecular weight — up to 160,000 g mol⁻¹.³⁰

A significant development in polyaniline chemistry was the report^{31,32} of the first optically active polyanilines, prepared through the electrochemical polymerization of aniline in the presence of the chiral dopant acids (IS) (+)- or (IR) (-)-10-camphorsulfonic acid (HCSA). Films of the emeraldine salts PAn.(+)- HCSA and PAn.(-)-HCSA can be readily deposited on ITO-coated glass electrodes using either potentiostatic (0.8–1.1 V vs. Ag/AgCl), potentiodynamic (sweeping the potential from -0.2 to 1.0 V), or galvanostatic (applied current density of 0.5 mA cm⁻²) methods. These films exhibit strong circular dichroism bands in the visible region (see Chapter 5), indicating the induction of chirality into the PAN backbone by the (+)- and (-)-HCSA dopants.

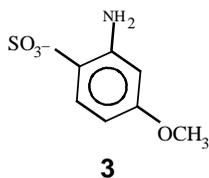
Analogous electrochemical oxidation of the monomer, 2-methoxyaniline in the presence of (+)- and (-)-HCSA, has provided a similar route to optically active poly(2-methoxyaniline), POMA. HCSA, films.³³

The converse approach to inducing chirality into conducting polymer chains, namely the incorporation of an *optically active cation*, has also been

successfully employed in our laboratories to produce the first optically active water-soluble sulfonated polyaniline. Poly(2-methoxyaniline-5-sulfonic acid) (PMAS) has been prepared in optically active form through the electropolymerization of 2-methoxyaniline-5-sulfonic acid in the presence of (*R*)-(+)- or (*S*)-(-)-1-phenylethylamine.³⁴ The optical activity and electroactivity of the chiral sulfonated polyanilines are retained when immobilized on poly(4-vinylpyridine) (see Chapter 5).

The monomer

A tremendous range of monomer derivatives of aniline has been investigated,³⁵⁻⁴¹ with many of them forming polymers with properties significantly different from those of polyaniline. In most instances, the conductivity, electroactivity and other electrochemical attributes of the resultant polymers have been studied. The electronic properties have also been investigated.⁴² However, the chemical properties of these substituted polyanilines have not been investigated to any great extent. Other workers^{43,44} have attached sulfonate groups to polyaniline after polymerization to make the polymer water soluble. Alternatively, the functionalized aniline **3** containing a methoxy and sulfonate group has been used to produce water-soluble conducting polyanilines electrochemically.⁴⁵ Using a flow-through electrochemical method, accurate control over the molecular weight and, hence, conductivity, can be obtained. It is also possible to produce copolymers with aniline using this approach.



Colloids

Using a flow-through electrochemical cell, we have developed an electrohydrodynamic route to polyaniline colloids (rather than the more traditional chemical oxidation route) including dispersions with novel functionality. For example, we recently reported the first optically active PAn colloids, obtained through the electropolymerization of aniline in the presence of poly(styrene-sulfonate) as an electrosteric stabilizer and (+)-HCSA (HCSA = 10 camphor-sulfonic acid) as the chiral inducing agent.⁴⁶ Chiral PAn colloids have also been synthesized using the core-shell technique, in which PAn.(+)-HCSA/SiO₂⁴⁷ and PAn.(+)-HCSA/PU nanocomposites (PU = polyurethane)⁴⁸ are generated through the electropolymerization of aniline onto the surface of small silica (20 nm) and PU (40 nm) particles in aqueous dispersion. In the case of the PAn.HA/PU dispersions, the film-forming properties

of the polyurethane (PU) component assist the subsequent formation of uniform, strongly adhering conducting polymer films.

The first successful synthesis of a polyaniline/PPy copolymer was achieved by the (galvanostatic) electropolymerization of mixtures of aniline (0.5 M) and pyrrole (0.1–1.0 M) in acetonitrile solvent in the presence of CF_3COOH as acid and tetraethylammonium tetrafluoroborate as supporting electrolyte. Differential scanning calorimetry and FTIR measurements confirmed that the electrically conducting product was a mixture of polyaniline, PPy and a random polyaniline/PPy copolymer.⁴⁹

The presence of small amounts of thiophene monomer (25–75 mM) in acetonitrile solutions of aniline (250 mM) has been reported to accelerate the electrochemical formation and conductivity of PAn homopolymer. This was attributed to catalysis by thiophene cation radicals. When higher concentrations of thiophene (>100 mM) were used in the monomer feed, increasing amounts of a polyaniline/polythiophene copolymer were shown to be present in the product.⁵⁰

Chemical polymerization

Chemical synthesis has the advantage of being a simple process capable of producing bulk quantities of CEPs on a batch basis. To date, it has been the major commercial method of producing polyanilines, several companies producing bulk powders, dispersions and coated products.

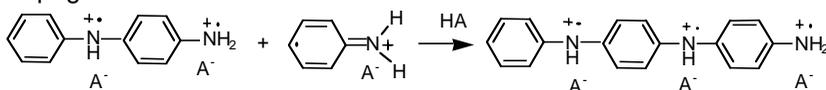
For chemical polymerization, the oxidizing force is supplied by a chemical oxidant in the solution. The most widely employed chemical oxidant has been aqueous ammonium persulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, leading to the incorporation of $\text{HSO}_4^-/\text{SO}_4^{2-}$ as the dopant anions (A^-) in the PAn.HA product. Acidic conditions ($\text{pH} \leq 3$) are usually required to assist the solubilization of the aniline in water and to avoid excessive formation of undesired branched products.⁵¹ An $(\text{NH}_4)_2\text{S}_2\text{O}_8$ /aniline molar ratio of <1.2 is usually employed. Because the $\text{S}_2\text{O}_8^{2-}$ anion is a two-electron oxidizer (acceptor), this suggests that a little over two electrons are removed from each aniline monomer during polymerization.

Mechanism of chemical polymerization

The chemical polymerization of aniline by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is believed to proceed, in its initial stages, by a mechanism similar to that described earlier for electrochemical polymerization.^{52–54} The first involves formation of the aniline radical cation. In the second step, coupling of *N*- and *para*-radical cations occurs with subsequent rearomatization of the dication of *p*-aminodiphenylamine (PADPA). It is then oxidized to the diradical dication. Although “head-to-tail” (i.e., *N*-*para*) coupling is predominant, some coupling in the *ortho*-position also occurs, leading to defects in conjugation in the resultant polymer.

A significant variation from the electropolymerization route occurs in the subsequent chain propagation and product formation steps (Figure 4.3). The initial polymer product has been confirmed from spectroscopic studies^{55,56} to be the fully oxidized *pernigraniline salt* form of polyaniline, which is not surprising in view of the high oxidizing power (1.94 V vs. standard hydrogen electrode (SHE)) of ammonium persulfate. When all oxidant is consumed, the remaining aniline in solution reduces the pernigraniline to form the final product, the green emeraldine salt (step 4). Color changes during the reaction reflect the described steps: during the second step the solution is pink due to PADPA; during the third step the solution becomes deep blue due to formation of protonated pernigraniline; and, in the final step, green emeraldine salt precipitates.

Propagation of chain



Reduction of Pernigraniline Salt to Emeraldine Salt

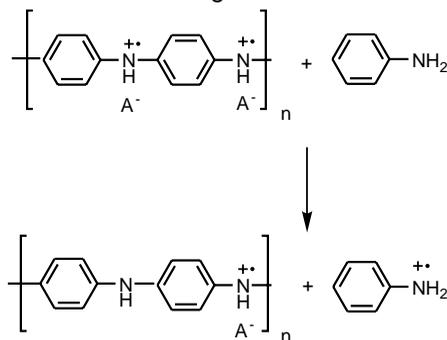


Figure 4.3 Chemical polymerization of aniline.

The properties of polyanilines, such as electrical conductivity, morphology, molecular weight and stereoregularity, are sensitive to the polymerizing conditions employed. On the basis of extensive studies, the influence of various polymerization conditions on the properties of emeraldine salts (PAN.HA) are summarized In Equation 4.4.

Polymerization temperature

Chemical polymerizations of aniline with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were initially performed at room temperature. However, later studies showed that the PAN obtained was of relatively low molecular weight and contained significant defect sites such as undesirable branching due to *ortho*-coupling.^{57,58} Subsequently, the most widely employed temperature for chemical polymerization

of aniline monomers has been ca. 1–5°C, as described by MacDiarmid et al.,⁵⁹ providing PAN, whose emeraldine base forms have molecular weights (M_w) of 30,000–60,000 g mol⁻¹.

For industrial applications, it is desirable to have PAN with high molecular weights (M_w ca. 100,000) and low polydispersity ($PD < 2.0$). The use of low temperatures down to –30 or –40°C (achieved through the addition of salts such as LiCl and CaF₂) has led to PAN with much higher molecular weights (up to 400,000).^{60–63} It was revealed through ¹³C NMR studies of the leucoemeraldine base forms of the PAN products (obtained by subsequent reduction) that the most structurally regular PAN were obtained at –30°C.⁶¹ However, these reactions generally require more than 48 hours to complete and the polydispersity is relatively high ($PD > 2.5$). Researchers at DuPont Technologies have recently reported that the best results are achieved by polymerization at 0°C in the presence of higher concentrations of LiCl or NaCl (5–10 M); under these conditions polymerization is complete within 3 hours with a higher yield (80%) and superior polydispersity ($PD < 2.0$).⁶⁴

Nature of the acid (HA)

The nature and concentration of the protonic acid (HA) employed in aniline polymerization with S₂O₈²⁻ have been reported to have a significant effect on the physicochemical properties and molecular weights of the PAN.HA emeraldine salt products.⁵¹ The polymerization reaction time using HClO₄ as the dopant acid was also observed to be ca. twice as long as with HCl, HNO₃ or H₂SO₄, which may be associated with a more compact morphology for the PAN.HClO₄ products.⁶⁵

Nature of the oxidant

A wide range of other chemical oxidants has also been successfully employed for the polymerization of aniline monomers. Although the standard electrode potential for FeCl₃ is low (0.77 V) compared with (NH₄)₂S₂O₈, it has proven to be a particularly useful oxidant, resulting in polyanilines with $M_n > 20,000$. Maximum yield and molecular weight of the PAN.HCl emeraldine salt product are reported⁶⁶ to occur without added acid. The optimum reaction temperature (35°C) is higher than that found above for (NH₄)₂S₂O₈ (≤ 0°C), which may arise from the slower electron transfer rate of FeCl₃. The polymer product has electrochemical properties similar to PAN produced with (NH₄)₂S₂O₈.⁶⁶ Solid state ¹³C NMR studies of the corresponding emeraldine bases (obtained by alkaline de-doping) similarly show the FeCl₃ and (NH₄)₂S₂O₈-derived polymers to be very similar. The use of FeCl₃ also enables polymerization to be carried out in polar organic solvents such as methanol, rather than water.

Other chemical oxidants that have been examined include ceric ammonium sulfate,⁶⁷ potassium dichromate,^{67,68} potassium iodate⁶⁸ and hydrogen peroxide,^{68,69} although it is reported that optimal conductivities are obtained when (NH₄)₂S₂O₈ is used as oxidant.⁵¹ It has been suggested⁶⁸ that the poly-

merization process is less dependent on the oxidation potential of the particular oxidant (see Table 4.1) than on the degradation processes. Hydrogen peroxide oxidation of aniline gives only low conversion, but the addition of catalytic amounts of FeCl_2 ($\text{Fe}^{2+}/\text{aniline} = 1/500$) results in good yields of PAn.HCl, with a conductivity (7 S cm^{-1}) similar to that formed using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidant.⁶⁹ KIO_3 is also reported to be an effective and convenient oxidant for the preparation of polyaniline.

Table 4.1

Oxidant	E^0 (V, vs. SHE)
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	1.94
H_2O_2	1.78
$\text{Ce}(\text{SO}_4)_2$	1.72
$\text{K}_2\text{Cr}_2\text{O}_7$	1.23
KIO_3	1.09
FeCl_3	0.77

Nature of the solvent

Chemical polymerization of aniline and substituted anilines has generally been carried out in aqueous solution. Addition of 0.2–0.6 (v/v) acetone, THF or ethanol to the reaction mixture was found to slow down the polymerization of aniline by $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{HCl}$, with reaction times varying in the order $t_{\text{acetone}} \sim t_{\text{THF}} > t_{\text{ethanol}}$.⁷⁰ The yields of emeraldine salt products (ca. 65%) and the electrical conductivities of the products (ca. 10 S cm^{-1}) were similar in each case to those obtained without added organic solvent, but their molecular weights were lower. Similarly, Kuramoto et al.^{71,72} have polymerized the dodecylbenzenesulfonic acid (DBSA) salt of aniline (dissolved in chloroform) with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (in a small amount of water). A homogeneous green/black suspension was obtained from which the PAn.DBSA emeraldine salt product could be readily isolated by the addition of excess methanol or acetone was obtained.

Polyaniline has also been prepared in acetonitrile and chloroform solvents using $\text{Fe}(\text{ClO}_4)_3$ and tetrabutylammonium periodate as the oxidant, respectively.^{73,74}

Achieving regioselective coupling with aniline monomers

For the oxidative formation of PAn with extended π -conjugation and high conductivity, the regioselective head-to-tail *para*-coupling of the initially formed radical cations is required, as depicted in Figures 4.1 and 4.3 above. However, the coupling of the *N*-centered radical cation with the *ortho*-sited radical also occurs to a limited extent, resulting in branched PAn chains. The extent of such *ortho*-coupling has been estimated by ^{13}C NMR spectroscopy to be ca. 5% for chemically synthesized emeraldine base.⁶¹ This undesired coupling can be reduced by the use of aniline monomers bearing blocking substituents in the *ortho*-position. However, these are generally less readily

oxidized than the parent aniline, and the emeraldine salt products less conducting due to twisting of the PAn chains from planarity caused by steric interactions by the ring substituents (*vide infra*).

Template-guided synthesis

Employing a polyelectrolyte to bind to and preferentially align the aniline monomers prior to polymerization (e.g., by $S_2O_8^{2-}$) has shown promise in facilitating the desired head-to-tail coupling of the aniline substrates. During polymerization, the anionic polyelectrolytes such as poly(styrenesulfonate) and poly(acrylate)⁷⁵⁻⁷⁷ also provide the required counterions for charge compensation in the doped PAn products. This can lead to water-soluble or water-dispersed emeraldine salt products. These water-soluble PAn have found use as photoresist materials when crosslinked with various light-sensitive entities.⁷⁶

Comparison of chemically and electrochemically prepared PAn films

Until recently, it has been generally considered^{78,79} that PAn prepared by the alternative chemical and electrochemical routes have similar chemical structures, although differences in morphology were noted and there was disagreement in the literature as to which route produces material of the higher molecular weight.^{80,81} From a comparison of the circular dichroism spectra of chemically and electrochemically prepared PAn.(+)-HCSA films (see Chapter 5), we have recently found the first unequivocal evidence that these polyanilines possess different structures/conformations for their polyaniline chains.⁸²

In situ chemical polymerization

The above chemical polymerization routes (e.g., employing $S_2O_8^{2-}$ as oxidant) typically deposit the PAn.HA emeraldine salt products as bulk powders. However, it was noted by MacDiarmid and Epstein as early as 1989 that PAn salts can also be deposited as films on a variety of substrates by immersing the substrate in the polymerization mixture.⁸³ In fact, during standard chemical polymerization, one often observes the deposition of a thin, extremely adherent green emeraldine salt film on the walls of glass reaction vessels, as well as the bulk precipitation of PAn.HA powder. By judicious manipulation of the polymerization conditions, such as reagent concentrations/ratios and modification of the substrate surface, one can maximize the surface deposition as opposed to polymer precipitation.⁸⁴ This phenomenon has been developed into a widely useful *in situ* polymerization technique for the preparation of PAn films on a variety of insulating surfaces such as glass and plastics, as well as on fibers and fabrics.

Deposition on glass/plastics

In situ polymerization of aniline is generally carried out in aqueous $(NH_4)_2S_2O_8/HCl$. The glass support is typically removed from the reaction

mixture during the polymerization at the stage when a blue/violet film of pernigraniline salt has formed on its surface. This film is then reduced to the green emeraldine salt product by reaction with a separate aniline/HCl solution.⁸⁵ Alternatively, the glass support can be left immersed in the reaction mixture until the polymerization is complete.⁸⁶

The *in situ* deposition of conducting polyaniline films was found by MacDiarmid et al.⁸⁷ to occur more readily on hydrophobic surfaces, such as Si/SiO₂ and glass pretreated with octadecylsiloxane (OTS), than on related hydrophilic surfaces. They exploited these different deposition rates to produce patterned microstructures of PAN by the microcontact "stamp" printing of patterned hydrophilic films of OTS on hydrophilic glass substrates prior to the aniline polymerization. Conducting PAN features as small as 2 μm in lateral dimension could be produced with this method. In collaboration with Alan MacDiarmid using this *in situ* route, we have prepared optically active PAN.(+)-HCSA and PAN.(−)-HCSA films on glass by replacing the HCl in the polymerization solution by (+)- or (−)-camphorsulfonic acid.⁸⁸

Not surprisingly, in view of the above preference for hydrophobic surfaces, PAN can also be deposited by the *in situ* method on supports such as low-density polyethylene (LDPE).⁸⁹ Modification of the LDPE surface by grafting with acrylic acid promotes the growth and adhesion of the PAN films. Conducting PAN coating can be similarly deposited on poly(vinylchloride) and poly(methylmethacrylate) surfaces through chemical oxidative polymerization.⁹⁰

Deposition on fibers or fabrics

An important development, pioneered by Kuhn and co-workers,^{91,92} has been the deposition of conducting polyanilines onto fibers and fabrics. Not only hydrophobic fibers such as polyesters and polypropylene, but also hydrophilic cotton can be coated with PAN with this *in situ* polymerization method. PAN/nylon-6 composite films have also been prepared by adsorbing aniline onto thin nylon-6 films and then treating with aqueous (NH₄)₂S₂O₈.⁹³ The composite films exhibited a low percolation threshold, requiring just 4% PAN for electrical conductivity.

Vapor phase deposition

Vapor phase deposition of conducting polyaniline films on cotton fibers has also been achieved by impregnating the thread with (NH₄)₂S₂O₈ oxidant and then exposing the surface to aniline vapor.⁹⁴ Polyacrylamide films coated with conducting polyaniline (σca. 10⁻⁵ S cm⁻¹) have been similarly prepared.⁹⁵

Deposition in nanoscale matrices

An elaboration of this technique, incorporating the concept of template-guided synthesis, is the use of nanoporous matrices such as zeolites and polycarbonates as a template within whole pores to perform the chemical polymerization of aniline monomers. For example, Wu and Bein⁹⁶ have

prepared nanofilaments of conducting emeraldine salt in the 3 nm-wide channels (pores) of the aluminosilicate host, MCM-4l, through initial adsorption of aniline vapor into the dehydrated host followed by oxidation with $(\text{NH})_2\text{S}_2\text{O}_8$.

Photochemically initiated polymerization

Kobayashi et al.^{97,98} recently reported the photochemically initiated polymerization of aniline by irradiation with visible light of either bilayer or single-layer films containing $[\text{Ru}(\text{bipy})_3]^{2+}$ (as initiator) and methylviologen (MV^{2+}) as sacrificial oxidant. Irradiation of the $[\text{Ru}(\text{bipy})_3]^{2+}$ near its absorption band at 452 nm leads to the generation of the triplet excited state $^*[\text{Ru}(\text{bipy})_3]^{2+}$ species. Electron transfer between the $^*[\text{Ru}(\text{bipy})_3]^{2+}$ and MV^{2+} generates the strong oxidant $[\text{Ru}(\text{bipy})_3]^{3+}$ responsible for the oxidation/polymerization of aniline to polyaniline.

These studies focused on the deposition of PAn on bilayer or single-layer electrodes for image formation and use in molecular electronics, rather than bulk PAn synthesis. Using appropriate masks, these photochemical routes were shown to have exciting potential for the generation of patterns of CEPs on substrates (with definitions as low as 2 μm). It was, however, observed that small amounts of aniline dimer (e.g., 10^{-3} M) were necessary in the aniline monomer (0.3 M) substrate solution to achieve photopolymerization. This was attributed to the lower oxidation potential of the dimer compared with aniline, with the dimeric radical cation formed in the initial oxidation step then reacting with aniline monomer to give an even more readily oxidized trimer, eventually leading to PAn.

We have independently explored the use of both $[\text{Ru}(\text{bipy})_3]^{2+}$ and $[\text{Ru}(\text{phen})_3]^{2+}$ as polymerization photoinitiators for the bulk synthesis of emeraldine salts. Significantly, we found⁹⁹ that, by employing the cobalt (III) complexes $[\text{CoCl}(\text{NH}_3)_5]^{2+}$ and $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]^{3+}$ as the sacrificial oxidants rather than methylviologen, aniline can be readily photopolymerized to PAn.HNO₃ and PAn.HCSA (HCSA = camphor-10-sulfonic acid) salts *without* the need to add aniline dimer. Facile polymerization of substituted PAn could be similarly achieved, e.g., yielding poly(*n*-butylaniline).HNO₃ and poly(2,5-dimethoxyaniline).HNO₃ salts. We have also employed this photoinitiated route as a novel and simple method to incorporate conducting PAn.HA salts into fabrics.

Enzyme-catalyzed polymerization

Considerable interest in the use of enzymes such as horseradish peroxidase (HRP) as catalysts for the synthesis of polyanilines and PPys with oxidants such as peroxide, has recently been shown.^{100,101} Although this method has the advantage of being environmentally benign (the H_2O_2 oxidant is converted into water), early studies produced polymers with low molecular weight and extensive chain branching. Samuelson et al.^{102,103} have largely

overcome these problems for the HRP-catalyzed synthesis of PAN through an elegant approach using polyelectrolytes such as polystyrenesulfonate (PSS) as templates in the reaction mixture to induce more structural order during polyaniline growth. The PSS plays three roles in this approach:

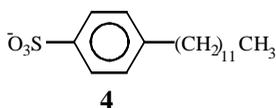
1. Serving as a template that aligns the aniline monomers prior to polymerization so as to promote the desired head-to-tail coupling
2. Providing the counterions for doping the synthesized PAN to the conducting emeraldine salt form
3. Imparting water "solubility" to the PAN.PSS product

Another advantage of this enzyme-catalyzed route to colloidal PAN salts is the considerably higher pHs that can be employed compared with the previous chemical and electrochemical polymerization methods. Horseradish peroxidase immobilized on chitosan powder as a solid support has also been found to catalyze the H₂O₂ oxidation of aniline to a similar PAN.PSS product, opening up the prospect of enzyme reuse and the design of enzyme reactors for PAN synthesis.¹⁰⁴

The mild (pH 4.3) conditions for these HRP-catalyzed syntheses have led to the similar employment of more-delicate biological polyelectrolytes such as DNA as the aligning templates.^{105,106} In this case, electrostatic interactions between the DNA phosphate groups and protonated aniline monomers prior to polymerization are believed to provide the preferential alignment leading to *para*-directed coupling of the aniline units. As discussed in Chapter 5, binding of the DNA to polyaniline in the PAN.DNA product leads to a remarkable reversible change in the conformation of the DNA chains.

Polymerization using electron acceptors

Kuramoto et al.^{71,72} developed a novel route to conducting emeraldine salts through the reaction of the dodecylbenzenesulfonic acid salts **4** of aniline or 2-methoxyaniline with the strong organic electron acceptor dichlorodicyanobenzoquinone (DDQ) in chloroform solvent. The PAN.DBSA product was isolated by the addition of excess methanol and acetone to the polymerization mixture, simultaneously removing oligomers and other organic by-products. In contrast, the weaker organic electron acceptors chloranil and TCNQ showed no oxidative polymerization activity. These researchers more recently extended this approach to the synthesis of optically active polyanilines with the polymerization of aniline and its substituted analogues 2-methoxyaniline, 2-ethoxyaniline and *o*-toluidine with DDQ in mixed chloroform/THF solvent.^{107,108}



Miscellaneous polymerization methods

Plasma polymerization of aniline in the absence of a solvent or a chemical oxidant, giving neutral undoped PAN, was first described in 1984.¹⁰⁹ This method has recently been further developed^{110,111} with Cruz et al., for example, describing the deposition of PAN film using RF glow discharges between stainless steel electrodes and 0.02–0.08 atmosphere pressures. The aniline monomer reacts with electrons in the plasma and the polymer deposits on the reactor wall after growth.

Very recently, acidic (0.6 M H₂SO₄) aniline solutions have been reported to undergo slow (10 days) spontaneous polymerization on platinum or palladium foil surfaces, providing a novel “electroless polymerization” route to polyaniline.¹¹² X-ray photoelectron spectroscopy and FTIR spectral studies suggest that the deposited PAN materials are in the rarely reported *nigraniline* oxidation state, intermediate between the well known emeraldine and pernigraniline states.

Routes to more processible polyanilines

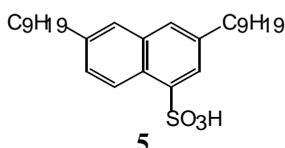
Emeraldine salts prepared by the above chemical (and electrochemical) oxidative routes are typically amorphous infusible solids that are insoluble in both organic solvents and water. These intractable characteristics have hindered the development of applications for PAN and considerable research has been carried out over the past decade to develop routes to more readily processible polyanilines.

Approaches that have proven successful in enhancing processibility include (a) emulsion polymerization and (b) the synthesis of colloidal polyanilines. The former leads to PAN soluble in organic solvents, while the latter provides effectively “water-soluble materials.” An alternative approach (c) has been side chain functionalization, involving the polymerization of ring or *N*-substituted aniline monomers bearing either alkyl/alkoxy groups (to enhance solubility in organic solvents) or sulfonate/carboxylate groups (to induce water solubility). These approaches are discussed below.

Emulsion polymerization

In initial emulsion polymerization studies,^{113,114} oxidation of the aniline monomer was carried out in xylene/water or chloroform/water emulsions containing dodecylbenzene sulfonic acid (DBSA). PAN.DBSA polymers with high MWts with a higher degree of crystallinity were obtained, and the polymers exhibited a fibril structure. These differences in properties were attributed to the fact that the higher solubility of the PAN product in the emulsion sustained the polymerization reaction.¹¹⁴ Further applications of this synthetic route include the preparation of a PAN.chlorophyll material, which exhibits good solubility in organic solvents such as chloroform, benzene and THF.¹¹⁵

However, the PAN products were not easily recovered and generally were isolated by breaking the emulsion, e.g., by adding acetone, to precipitate the emeraldine salt. A major development with this method was therefore the discovery by workers at Monsanto¹¹⁶ of a direct synthesis of an emeraldine salt that is highly soluble in organic solvents. The method uses a reverse emulsion procedure involving initial formation of emulsion particles consisting of a water-soluble organic solvent (e.g., 2-butoxyethanol), a water-insoluble surfactant-like dopant (dinonylnaphthalenesulfonic acid, DNNSA) **5**, aniline and water, using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidant. As the reaction proceeds, the mixture changes from an emulsion to a two-phase system, with the PAN product remaining in the organic phase. This solution is typically diluted with toluene and has been sold commercially under the tradename PANDATM.



The PAN.DNNSA emeraldine salt is highly soluble (it is not a dispersion) in nonpolar organic solvents such as xylene and toluene, a common solvent used in many paints. It has a molecular weight (M_w) > 22,000 and an electrical conductivity of $10^{-5} \text{ S cm}^{-1}$. Interestingly, treatment of a PAN.DNNSA film with methanol or acetone leads to a marked (5 orders of magnitude) increase in conductivity, which is believed to arise from extraction of excess DNNSA dopant, causing an increase in polymer crystallinity.

Colloidal polyaniline dispersions

The most commercially successful method of producing processible forms of CEPs has been the aqueous colloidal dispersion route pioneered by Vincent and Armes¹¹⁷⁻¹¹⁹ (see two recent reviews by Armes¹²⁰ and Wessling¹²¹). Unlike the methods discussed above, which all require extensive derivatization of the aniline monomer, dispersions are readily formed from unsubstituted aniline and are readily manufactured in bulk quantities.

The major route to colloidal (effectively “water-soluble”) PAN has been through the chemical oxidation ($\text{S}_2\text{O}_8^{2-}$) of the monomer in the presence of polymeric steric stabilizers and electrosteric stabilizers (polyelectrolytes), such as poly(vinylalcohol), poly(*N*-vinyl pyrrolidone), poly(ethylene oxide), poly(styrene sulfonate), dodecylbenzene sulfonate and dextran sulfonate. It has been found that the stabilizer can act simultaneously as a dopant, imparting new functionality to the polymer or additional compatibility for the final application.

Colloid formation during chemical synthesis occurs due to the formation of small growing PAN particles in aqueous solution adsorbing the stabilizer onto their outer layers, typically through hydrogen bonding. The adsorbed outer layer then stabilizes the particle and prevents coalescence. Typical particle sizes range from 60 to 300 nm¹²² and are strongly dependent upon the type of stabilizer, oxidant type and concentration, monomer concentration, temperature, etc., and they can exist as either discrete particles or group together as conglomerate structures. Recently, colloidal PAN.HCl/DBSA dispersions containing 10–20 nm particles and PAN.HCl/PVA (PVA = polyvinylalcohol) dispersions with particles as small as 5 nm have been reported,^{123,124} the latter in mixed DMSO/water solvent.

We have shown that such colloids are electroactive and can be electrodeposited.¹²⁵ However, the electrodeposited films are not coherent and “redissolve” once the negative potential is removed. Optically active colloidal polyaniline nanocomposites of the type PAN.HCSA/polyacrylic acid have also recently been synthesized using the chemical oxidation route, by the oxidation of aniline with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the presence of (+)- or (-)-HCSA as the dopant acid and polyacrylic acid as the steric stabilizer.¹²⁶

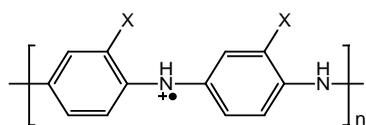
Alternatively, the *core-shell approach* has been employed to generate aqueous dispersions (or nanocomposites) in which emeraldine salts are deposited on the surfaces of nanoparticles such as silica^{127,128} or TiO_2 ¹²⁹ during polymerization. The resultant core-shell structures often group together as conglomerate structures described as having a raspberry-like morphology.¹³⁰

A detailed ¹H NMR kinetic investigation¹³¹ of the polymerization of aniline in DCl/D₂O solution has revealed no significant differences between the rates of dispersion polymerization using a poly(ethylene oxide)-based stabilizer and standard precipitation polymerization in the absence of any stabilizer. However, faster polymerization of aniline was observed in the presence of 20 nm silica particles leading to PAN-silica nanocomposites. In contrast, slower polymerization occurred in the presence of surfactant micelles to form surfactant-stabilized PAN particles, presumably due to the high solution viscosity.

Substituted polyanilines

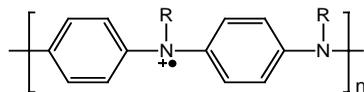
Alkyl- and alkoxy-substituted PAN.

A wide range of alkyl- and alkoxy-substituted polyanilines of the general types **6** and **7** have been synthesized by the chemical or electrochemical oxidation of appropriately substituted aniline monomers.^{41, 132–135} Such substitution imparts solubility in organic solvents upon the emeraldine salt products that is markedly improved over the parent (unsubstituted) PAN.HA salts. The poly(2-methoxyaniline) (POMA) species, in particular, has been the subject of extensive studies.^{132–134} This species has the additional attractive feature of being soluble in water after being wet with acetone.



(X= R, OR)

6



7

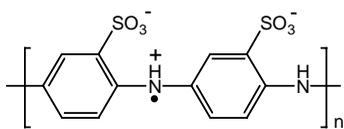
The substituted polyaniline products often have much lower molecular weights than the parent, unsubstituted PAN, although M_w values as high as $400,000 \text{ g mol}^{-1}$ have been obtained for POMA by controlled chemical polymerization at -40°C .⁶⁰ This improvement in processibility for substituted polyanilines is also generally gained at the expense of a large decrease in electrical conductivity due to twisting of the polymer chains from planarity by the bulky substituents.

Oxidative polymerization of substituted aniline monomers is frequently more difficult than that of aniline itself. A potentially useful recent development is therefore the report¹³⁶ of a chemical biphasic procedure permitting the polymerization of a large variety of *N*- and *o*-alkylanilines in moderate yields without modification of conditions. The polymerization mixture is composed of two nonmiscible solvents (hexane and water), an organic acid (methanesulfonic acid) and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidant. Another highly significant advance has been the synthesis of the novel poly(aniline boronic acid), which can be readily converted into a range of other substituted PANs, including previously inaccessible polymers (*vide infra*).¹³⁷

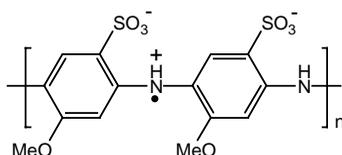
Sulfonic acid-substituted PAN.

Considerable interest in the polymerization of sulfonated aniline monomers in the hope of producing water-soluble sulfonated polyanilines has also been shown. Attempts to polymerize *o*- or *m*-aminobenzenesulfonic acid by both chemical and electrochemical means have generally been unsuccessful, which has been attributed to steric and electronic deactivation by the electron-withdrawing sulfonic acid substituent.^{138,139} However, Young et al.¹⁴⁰ have reported that *o*- and *m*-aminobenzenesulfonic acid can be successfully synthesized by a novel high-pressure (19 kbar) procedure using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidant in the presence of 5.0 M LiCl and 5% FeSO_4 , yielding the fully sulfonated self-doped polyaniline **8** (SPAN).

The related fully sulfonated polymer, poly(2-methoxyaniline-5-sulfonic acid) **9** (PMAS) can be prepared under normal atmospheric pressure by the oxidation of 2-methoxyaniline-5-sulfonic acid with aqueous $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the presence of ammonia or pyridine (to assist dissolution of the substituted monomer).¹³⁹

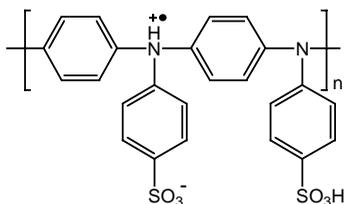


8 (SPAN)

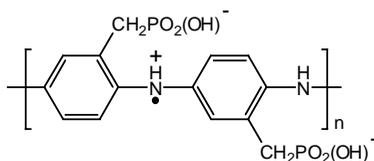


9 (PMAS)

The self-doped polymer, poly[*N*-(4-sulfophenyl)aniline] **10**, bearing a sulfonated substituent on each of its N centers, has been similarly prepared by oxidizing the relevant monomer with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in aqueous HCl.^{141,142} Phosphonic acid substituents can also be utilized to generate self-doping polyanilines, as illustrated by the oxidation ($\text{S}_2\text{O}_8^{2-}$) of the monomer *o*-aminobenzylphosphonic acid to give the novel polymer **11**.¹⁴⁴ Its low conductivity (ca. $10^{-3} \text{ S cm}^{-1}$) may arise from H-bonding between the $\text{PO}_2(\text{OH})^-$ substituents and NH^+ radical cation sites on the polymer chain, causing significant charge-pinning.



10



11

Postpolymerization modification — enhancing functionality

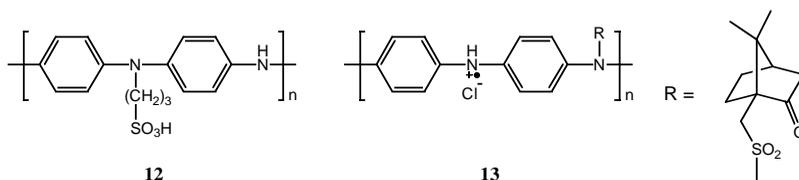
An alternative approach to increasing the solubility and hence the processibility of PAN has been a variety of *postpolymerization* methods. Such modifications have also been pursued to introduce added functionality to PAN, allowing their use in a range of applications such as chemical and biochemical sensors. The postpolymerization modifications typically involve either (a) chemical reactions on preformed emeraldine base (EB), leucoemeraldine base (LB) or pernigraniline base (PB) leading to covalent binding of groups to the aniline rings or N centers, or (b) doping of preformed emeraldine base (EB) with agents such as Brönsted acids (HA), Lewis acids and metal complexes, or organic electron acceptors. These various approaches are summarized below.

Covalently substituted polyanilines

In addition to their direct synthesis from sulfonated aniline monomers (described earlier), a number of water-soluble self-doped sulfonated polyanilines can also be prepared by postpolymerization methods. Most widely investigated has been the synthesis of the ring-substituted SPAN (Structure 8). Treatment of emeraldine base with fuming sulfuric acid gave a SPAN product with ca. 50% of the aniline rings sulfonated.¹³⁸ Subsequently, it was found that up to 70% of the aniline rings could be sulfonated by similar treatment of leucoemeraldine base, giving a polymer with enhanced electrical conductivity (ca. 1 S cm^{-1}).¹⁴⁴ The substitution of amino and alkylthio groups onto the aniline rings of PAn has similarly been achieved through the treatment of emeraldine base (or pernigraniline base) with alkyl amines and alkylthiols.¹⁴⁵

Deprotonation of the amine centers in emeraldine base by treatment with NaH in DMSO, followed by reaction with 1,3-propanesulfone, provides a route to the water-soluble self-doped polymer **12**, in which a $-(\text{CH}_2)_3\text{SO}_3\text{H}$ group is covalently attached to ca. 50% of the N centers along the polymer chain.¹⁴⁶ The use of the fully reduced leucoemeraldine base (LB) as substrate should lead to a higher degree of N-substitution. This has been confirmed in a related study, where subsequent treatment of the deprotonated LB with alkyl halides has provided a general route to poly(N-alkylanilines), with alkyl chains varying in length from butyl to octadecyl.¹⁴⁷

In our laboratories, we have used a related approach to covalently attach chiral camphorsulfonate groups to N centers of PAn by the reaction of EB with (1S)-(+)-10-camphorsulfonyl chloride in NMP/pyridine.¹⁴⁸ The optically active product **13**, isolated as the HCl salt, is believed to preferentially adopt a one-handed helical conformation for its polymer chains. This provides the first example of chiral induction in a PAn species through a covalently attached group. A significant advantage for **13** over the chiral PAn.HCSA salts described earlier is that it consequently retains its optical activity upon alkaline dedoping in solution to its EB form.

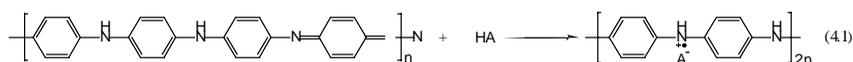


A factor hindering the expansion of polyaniline chemistry to date has been the lack of a generic route to variously substituted derivatives. An exciting development in this respect is the recent synthesis of the novel poly(aniline boronic acid).¹³⁷ Aromatic boronic acids are versatile chemical precursors undergoing a wide range of transformations, which provides a facile route to a range of substituted PAns that are difficult to synthesize

directly from their respective monomers. This approach has been successfully demonstrated for the synthesis of poly(hydroxyaniline) and for poly(halogenoaniline).¹³⁷

Doping of EB with Brönsted acids, HA

Polyaniline is unique among inherently conducting polymers in that it can be converted into a conducting form by a nonredox acid-doping process exemplified by the doping of emeraldine base with Brönsted acids (HA) to yield electronically conducting PAN. HA emeraldine salts (Equation 4.1). A wide variety of acids can be employed, ranging from inorganic acids such as HCl, HNO₃, H₂SO₄, H₃PO₄ and HBF₄ to organic sulfonic and carboxylic acids.



In an important discovery in the early 1990s, Cao et al.¹⁴⁹ found that organic solvent solubility can be imparted to conducting PAN salts by the incorporation of surfactantlike dopant acids (HA). For example, by doping emeraldine base (EB) with large bifunctional protonic acids such as camphor-10-sulfonic acid (HCSA) or dodecylbenzenesulfonic acid (DBSA), it is possible to solubilize fractions of these polymers in their fully doped state into solvents such as *m*-cresol, chloroform, toluene and xylene. This solubilization is caused by the hydrocarbon “tail” in the dopants, while the sulfonate (SO₃⁻) “head” forms an ionic bond with radical cation NH^{•+} sites on the PAN chains. There is some debate as to whether this approach produces true “solutions” or forms dispersions in organic media. In practical terms, the result is the same: solution-processible unsubstituted conducting polymers in the doped state.

Films of the PAN.HCSA and PAN.DBSA polymers can be cast from these solutions; the properties of the films are very dependent on the solvent used.^{150,151} This is attributed to the solvent’s ability to produce either a rod-like (more highly conducting) or coil-like (less conducting) polymer structure (see Chapter 5). The solubility of these polymers in organic solvents has also facilitated the preparation of conducting blends of PAN with various insulating polymers.^{149,152} The blends can exhibit a very low percolation threshold, believed to arise from the formation of an interpenetrating network morphology.¹⁵³

It has recently been shown that acid doping of emeraldine base can also be carried out in the solid state,¹⁵⁴ e.g., the mechanical blending of stoichiometric amounts of solid emeraldine base and HCSA or picric acid leads to electrically conducting PAN.HA salts.

Water-soluble emeraldine salts can also be prepared by this acid-doping technique. For example, doping of emeraldine base with phosphonic acid

containing poly(ethyleneglycol)monoethyl ether (PEGME) as a hydrophilic tail gives a mildly conducting PAN that is soluble (or dispersible) in water.¹⁵⁵

With the water-soluble poly(*o*-methoxyaniline) (POMA), Mattoso et al.¹⁵⁶ have reported the *self-assembly* of multilayer conducting polymer films by depositing alternating layers of the POMA cation and polyanionic dopants such as poly(styrenesulfonate) and poly(vinylsulfonate) onto a glass substrate. This concept has been further developed with POMA by employing the anion of poly(3-thiopheneacetic acid) as the polyanionic dopant, giving novel self-assembled films in which both the cationic and anionic components are electroactive polymers.¹⁵⁷

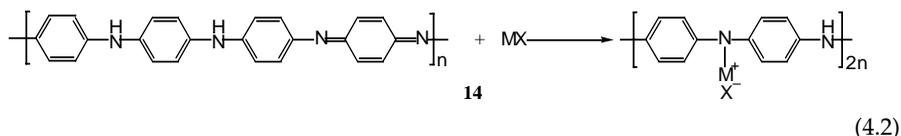
We have employed a related approach in generating films containing alternating layers of the anionic water-soluble sulfonated polyaniline PMAS **8** and the polycation, poly(vinylpyridine).¹⁵⁸ The analogous self-assembly of multiplayer films of the sulfonated polyaniline SPAN **8** and the light-sensitive polycation, diazoresin, has also recently been described.¹⁵⁹

Incorporation of chiral dopant anions or cations

The synthetically facile acid-doping approach (Equation 4.1) has also been successfully employed by us and others to produce optically active polyanilines. The addition of the chiral dopant (+)- or (-)- camphorsulfonic acid (HCSA) to EB in organic solvents such as *N*-methylpyrrolidinone rapidly generates optically active PAN.HCSA salts in solution, where the PAN chains are believed to adopt a one-handed helical arrangement (see Chapter 5).^{160,161} Optically active PAN.HCSA films can be cast onto glass from these solutions. We have observed similar, but less rapid (hours), chiral induction by doping the EB forms of the ring-substituted polymers poly(2-methoxyaniline) (POMA) and poly(σ -toluidine) with (+)- and (-)-HCSA.^{162,163} Optically active polyanilines can also be similarly produced by employing other chiral dopant acids such as (+) – or (–) – tartaric acid and *O,O'*-dibenzoyl derivatives.¹⁶⁴

Doping of EB with Lewis acids

Solutions of EB can be also readily doped with a range of metal salts and Lewis acids in a process (Equation 4.2) reminiscent of the Brønsted acid doping of EB described above. In a fashion similar to protonic doping, binding of the metal ions to imine N sites on the EB chains is believed to occur, leading to conducting PAN products of the general type **14**.

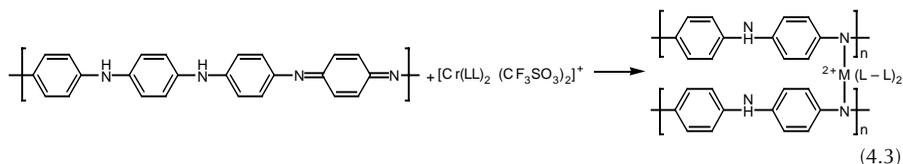


Considerable attention has been paid to the doping of EB with LiCl and other lithium salts because of the significance to lithium ion rechargeable

batteries.¹⁶⁵⁻¹⁶⁷ The coordination of transition metal ions such as Zn(II) and Pd(II) to polyaniline N centers has also been described by several research groups.^{165,168-170} For the reaction of Pd(II) species with EB, a redox reaction involving partial oxidation of the PAN to its pernigraniline state and concomitant reduction of Pd²⁺ to Pd⁰ is reported to accompany the complexation reaction.¹⁷¹ The Pd-containing PAN species have significant catalytic activity for a range of reactions (see Chapter 5). Similar doping and redox processes have been suggested during the related reaction of CuCl₂ with EB in NMP solvent.¹⁷²

Complexation (doping) of EB with classic Lewis bases such as AlCl₃, GaCl₃, SnCl₄ and FeCl₃ solubilizes PAN in acetonitrile and nitromethane, solvents that will not dissolve EB or its protonated PAN.HA emeraldine salts.¹⁷³ This improved solubility is attributed to metal doping at *all* the PAN basic sites, eliminating H-bonding between adjacent polymer chains that is one of the major contributors to poor PAN solubility (see Chapter 5).

The generation of octahedral transition metal (TM) complexes of PAN through related reactions of EB with complexes containing readily removable ligands should have considerable advantages over the above doping with simple metal salts. These include a variety of fixed geometric (*cis* or *trans*) and chiral configurations, distinctive redox/ spectroscopic properties associated with their metal-ligand interactions, and their potential use as probes for the nature and site of metal binding to PAN. To this end, we have doped EB in CHCl₃ solvent with the Cr(III) complexes *cis*-[Cr(L-L)₂(CF₃SO₃)₂]⁺ (L-L = 1,2 diaminoethane; 1,10-phenanthroline or 2,2'-bipyridine) and *cis*- and *trans*- [Cr(cyclam)(CF₃SO₃)₂]⁺ containing readily replaced triflate ligands, as summarized in Equation 4.3.¹⁷⁴ In the *cis*-[Cr(phen)₂(CF₃SO₃)₂]⁺ case, strong support for coordination of Cr(III) to imine N sites on the polymer chains came from photoluminescence studies on the related reaction with the aniline tetramer.



Doping of EB with organic electron acceptors

"Pseudodoping" of EB by a range of organic acceptors has also been reported by Kang et al.,^{175,176} producing charge transfer complexes with conductivities as high as 0.1 S cm⁻¹. On the basis of the maximum conductivity achieved, the complexing/"doping" ability of the organic acceptors with EB decrease in the order: TCNE ~ *o*-chloranil > DDQ > *o*-bromanil > *p*-fluoranil > *p*-chloranil. With *o*-chloranil, x-ray photoelectron spectroscopic (XPS) studies show the formation of Cl⁻ ions and positively charged N centers on the PAN chains

and a concomitant decrease in imine N sites. This indicates that the charge transfer interaction between the electron acceptor and EB must proceed further than simple formation of a charge transfer complex, consistent with pseudodoping of EB. Similar charge transfer interactions are observed between *o*-chloranil or *o*-bromanil with the EB forms of the substituted PAns, poly(2-chloraniline), poly(3-chloroaniline) and poly(2-ethylaniline).¹⁷⁷ However, XPS data reveal less extensive charge transfer, presumably due to steric hindrance associated with the aniline ring substituents.

Ion implantation

Ion implantation has recently been employed as an alternative doping method to convert neutral nonconducting polyaniline into a conducting form. For example, bombarding PAn with high-energy (24 keV) I⁺ ions is reported¹⁷⁸ to cause a 12-orders-of-magnitude increase in the conductivity of the polymer.

Structure of Polyaniline

Polyanilines formed by both the chemical and electrochemical processes have been extensively studied to establish structure–property relationships. In this section, the structural studies of polyaniline are reviewed and the influence of structure on properties is considered in Chapter 5. The description of polyaniline structure is complicated by its complexity. As described above, polyaniline can exist in six different forms (the salt or base forms of leucoemeraldine, emeraldine and pernigraniline). In addition, the protonated forms of polyaniline also have counter-anions intimately associated with the positively charged polyaniline chains. Finally, it has also been observed that polyanilines may contain considerable amounts of solvent molecules.

Molecular Structure and Conformation

Polyaniline formed by either the electrochemical or chemical process give essentially linear chains with predominantly para head-to-tail couplings. As reviewed above, variations to the linear structure have been introduced by substitutions on the benzene ring. Only the unsubstituted polyanilines are described in this section, as fewer structural studies have been reported on substituted polyanilines.

Molecular Weight

A small number of studies have investigated the molecular weight of polyaniline as prepared by standard methods. In early work, MacDiarmid and Epstein¹⁷⁹ reported that the normal gel permeation chromatography (GPC) techniques could be used to determine molecular weight distributions of polyaniline. The emeraldine base form of the polyaniline was dissolved in

NMP with 0.5wt% LiCl to prevent gelation. Using narrow polystyrene standards, the PAn molecular weight was estimated to be 64,452 (M_w) and 25,283 (M_n), giving a polydispersity of 2.55. The molecular weights could be increased (to $M_w=440,000$; $M_n=127,000$; PDI=3.5) by cooling the reaction solution to -9°C (in the presence of LiCl) to precipitate anilinium hydrochloride and to minimize the concentration of free aniline in the solution. These authors also compared the molecular weights obtained from GPC (using polystyrene standards) and that obtained from light scattering of leucoemeraldine solutions. The leucoemeraldine was obtained by reducing the emeraldine base using hydrazine and the molecular weight by light scattering was found to be approximately one half of that estimated using GPC.

More recently, Mattes and co-workers¹⁸⁰ have investigated the effect of polymerization temperature on the molecular weight of chemically synthesized polyaniline. Using polystyrene standards, the molecular weights (M_w) increased from 31,000 to 235,000 as the polymerization temperature decreased from 0°C to -40°C . LiCl was used during polymerization, while the emeraldine base was dissolved in NMP using 2-methylaziridine as an antigelation agent.

Mattes et al. also determined the Mark-Houwink constants for polyaniline emeraldine base in NMP. The Mark-Houwink equation relates the intrinsic viscosity (solution viscosity at infinite dilution) to the polymer molecular weight:

$$[\eta] = KM_w^\alpha$$

where $[\eta]$ is the intrinsic viscosity and K and α are the Mark-Houwink constants. By relating the intrinsic viscosity of the four different emeraldine base samples to their weight average molecular weight (determined from GPC using polystyrene standards) the Mark-Houwink constants were determined to be $K = 1.2 \times 10^{-4} \text{ dl g}^{-1}$ and $\alpha = 0.77$. These values are in the range expected for flexible chain conformations.

The importance of using LiCl to prevent polymer aggregation has been demonstrated by Angelopoulos et al.¹⁸¹ in GPC studies. These workers noted that without LiCl the GPC chromatogram showed a bimodal distribution. The high MW peak, however, disappeared when LiCl was added to the solution, suggesting that the high MW peak was due to polymer aggregation. NMP can H-bond to the polyaniline, but this solvent does not sufficiently solvate the polymer to disrupt all PAn interactions. Thus, additives such as LiCl must be added to prevent PAn H-bonding interactions.

Chain Conformation

A number of studies have considered the nature of the polyaniline conformation in solution— effect of solvent/dopant/oxidation state. As described in Chapter 5, the polyaniline can form either tight coils or expanded chains,

depending on the nature of the solvent used. This behavior is typical of polymers in either “poor” or “good” solvents, but has a significant impact on the electronic properties of conjugated polymers, as described in the next chapter for polyaniline.

Bulk Structure

Nanoscale Heterogeneity

There is considerable evidence and widespread acceptance that PAN forms a heterogeneous structure in its emeraldine salt form. The evidence comes mainly from electronic transport studies in which the temperature dependence of conductivity fits a charge hopping model.¹⁸² It is proposed that small domains of highly ordered polymer are surrounded by less ordered material and that electron transport is dominated by the slow conduction through the latter. In the ordered regions, it is suggested that the polymer chains lie flat, allowing a longer conjugation length as the π orbitals can overlap. In the amorphous regions, the chains are more twisted, causing less overlap of π orbitals and shorter conjugation lengths.

Recently, a number of studies have provided direct evidence of the heterogeneous structure of polyaniline ES. In our own work (see [Figure 1.27](#)),¹⁸³ we have used a variant on the scanning tunneling microscope to probe the electronic structure of ES. In this technique (called current-imaging tunneling spectroscopy, CITS) the I-V characteristics of the polymer are mapped with nanometer resolution. For polyaniline ES, it was found that small (20 to 80 nm) domains having metallic-like I-V curves were surrounded by an insulating matrix. The structure fit very well with the description provided by conductivity modeling.

Crystallinity, molecular order and conformation in solid state

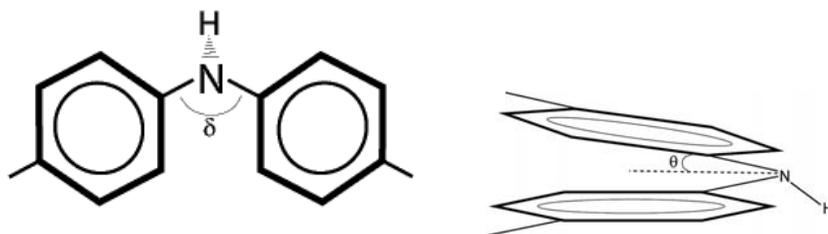
The exact nature of the structure of the ordered phase in PAN is still subject to ongoing research. The elucidation of such structure is complicated by the various means of producing ES films or coatings — direct electropolymerization or through acid doping (protonation) of the emeraldine base. The latter technique has the advantage of the EB's being highly soluble, and good quality films and coatings can be cast from the solution. Subsequent treatment of the EB films gives the emeraldine salt. It has been known for some time that certain dopants render the PAN emeraldine salt soluble. Thus, it is also possible to form films and coatings by direct casting from ES solutions. However, as described above, the nature of the solvent used for the ES can profoundly affect the conformation of the PAN in solution; these conformational differences are also carried over to the cast films. The following sections review the structural studies of solution cast and electropolymerized polyaniline in both the EB and ES forms.

Pouget et al. gave an exhaustive study to PAN crystallinity in 1991¹⁸⁴ and this work remains the main reference point for more recent studies. Pouget

and co-workers report two forms of crystallinity in the emeraldine salt form of PAN, and that these two structures are produced by different processing methods. The so-called ES-I structure is produced by direct polymerization of aniline in acid to produce the doped PAN ES, either using chemical oxidants or electrochemically. Deprotonation of the ES-I produces an amorphous emeraldine base (denoted EB-I) and re-protonation of EB-I once again generates the ES-I structure. A new crystallographic structure is produced, however, when EB-I is dissolved in solvents such as NMP and cast as a film. Now the emeraldine base is crystalline with a degree of crystallinity $\sim 50\%$. This structure is denoted EB-II. When EB-II is doped with HCl, it produces the ES-II structure, again with a degree of crystallinity of 50%, but fundamentally different from the ES-I structure. Curiously, when ES-II is deprotonated, it produces an *amorphous* EB, the re-protonation of which gives the ES-II structure (not ES-I). More-specific descriptions of these crystal structures and a summary of more recent studies are given in the following sections.

Solution Cast Emeraldine Base.

The emeraldine base form of PAN can be either crystalline or amorphous, depending on its preparation conditions. The crystalline form (EB-II) has a degree of crystallinity of up to 50% and a crystallite size of 5 to 15 nm.¹⁸⁴ The crystal structure has been indexed as an orthorhombic lattice with the polymer chains oriented in the c direction. The lattice parameters enable an estimate of the ring-N-ring angle (δ) about the amine nitrogen as between 131° and 141° . Furthermore, modeling of the structure enables an estimate of the ring tilt angle (θ), where the phenyl rings are tilted out of the plane defined by the N atoms by $+30^\circ$ and -30° for alternating rings. The chain structure is represented in Figure 4.4 and the proposed¹⁸⁴ orthorhombic structure is shown in Figure 4.5.



.Figure 4.4 Chain angles δ (bond angle ring-amine N-ring) and θ (ring torsional twist) defined.

More-recent studies have examined the effect of solvent on the structure of EB films cast from solutions. For example, Ou and Samuels¹⁸⁵ found that EB films cast from NMP solution were partially crystalline, as evidenced by

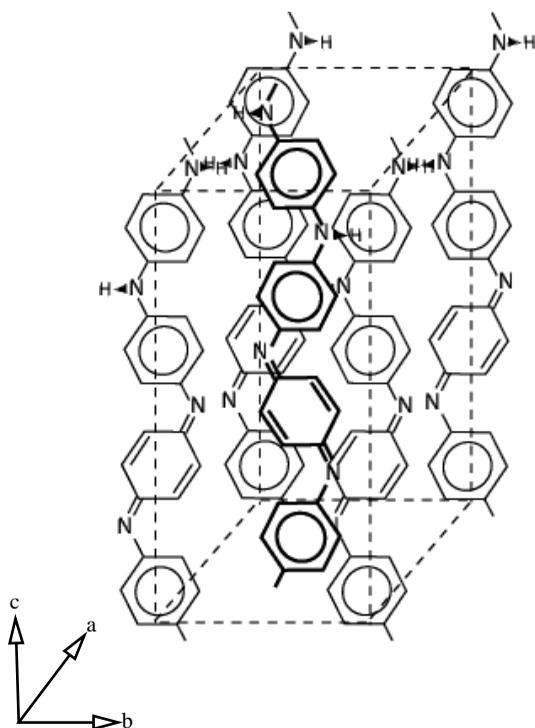


Figure 4.5 Proposed EB-II orthorhombic crystal structure for emeraldine base.

shoulders appearing above the amorphous band in x-ray diffraction studies. However, when the EB was cast from a solution in *N,N'*-dimethyl propylene urea (DMPU), no evidence of crystallinity was observed. Whereas the NMP solutions were unstable (undergoing gelation due to the formation of H-bonded networks between the PAn chains), the DMPU solutions were stable, probably because the DMPU can itself H-bond to the PAn. The implication of these observations is that the structure formed in solution is likely to become nucleation sites for crystallization upon solidification by solvent evaporation. Disrupting the solution structure reduces the number of nucleation sites and effectively prevents crystallization. Contrasting results have been reported by Angelopoulos et al.,¹⁸¹ who showed that crystallinity was observed only in films cast from low concentrations of EB in NMP (<10 wt%). These results were interpreted as the solution network in higher concentrations actually impedes crystal formation upon solvent evaporation.

There is more general agreement that increased crystallinity of EB can be induced by mechanically stretching the films or fibers. Ou and Samuels estimate the crystallinity for undrawn EB to be 11 to 15% and increases to 20 to 30% with a draw ratio of 3.5. Mechanical drawing also results in a high degree of anisotropy, with the crystallites oriented in the draw direction.

XRD studies by Fischer et al.¹⁸⁶ confirm the increase in crystallinity with drawing of EB fibers. The increase in crystallinity was attributed to the nucleation of new crystallites, rather than by growth of existing crystals. These workers also noted an orientation effect of the amorphous phase, so that highly drawn ($L/L_0 = 4.5$) EB has an amorphous phase analogous to the nematic liquid crystal structure.

Emeraldine Salt from Protonation of Emeraldine Base.

Protonation of the emeraldine base can produce two types of ES crystal structures. The structures are denoted ES-I (from protonation of amorphous EB-I) and ES-II (from protonation of EB-II).

The ES-II structure, like the EB-II structure from which it is formed, is likely to have an orthorhombic lattice. Model calculations show the ring tilt angle to be close to 0° , accounting for the higher conductivity of the ES compared with EB. The formation of the ES-II structure by doping the EB-II can be visualized by a shift of the middle chain in Figure B by $b/2$ and $c/2$ and insertion of dopant ions between the (a,c) layers.¹⁸⁴

The ES-I structure is less well defined, but likely involves a tilting of the chains with respect to the (a,b) basal plane. There are similarities between the EB-II structure and the ES-I structure in terms of d-spacings, and a model ES-I structure can be derived from the EB-II structure by inserting a dopant ion in the channel delimited by four adjacent chains.¹⁸⁴ A compact structure is obtained by assuming that the dopant sits in the hollow of the polymer chain zigzag. Good agreement of calculated and experimental XRD spectra is obtained by assuming such a structure, although some subtle differences remain unexplained.¹⁸⁴ The model structure assumes a ring tilt angle of 0 to 15° and a chain twist angle (of the chain with respect to the c axis) of 20 to 30° .

Solution Cast Emeraldine Salt.

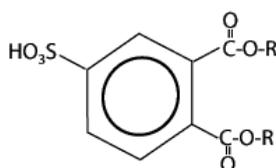
Emeraldine salt films can be prepared directly from solutions when particular counterions are used to impart solubility. The most extensively studied system is the camphorsulfonic acid-doped ES as cast from a m-cresol solution. Lunzy and co-workers have considered the crystal structure of camphorsulfonic acid-doped polyaniline (PAN-CSA) as cast from m-cresol.¹⁸⁷ Although presenting a clear crystal structure with a degree of crystallinity of 25%, the unit cell structure has no resemblance to the structures formed by the emeraldine base.

In fact, Minto and Vaughan¹⁸⁸ argue that the PAN-CSA crystal structure is a variation of the ES-I crystal structure described above. The interactions between the phenyl rings in the CSA and the polymer produce a more planar structure of the polymer chains compared with the ES-I structure (ring tilt angle up to 15°). The planar arrangement also reduces the interchain separation from $a = 0.426$ nm for ES-I (HCl doped) to $a=0.35$ nm for PAN-CSA. Furthermore, Minto and Vaughan describe a liquid-crystal-like order in the

amorphous phase of PAN-CSA due to ordering and solvation by residual *m*-cresol solvent. Finally, the unstretched films examined by Minto and Vaughan were found to show a preferred orientation of the polymer chains parallel to the substrate.

More-recent studies have shown the consistency of the crystal structure of PAN-CSA to be variable and highly dependent on the conditions of film preparation. Djurado and co-workers¹⁸⁹ have speculated that the influence of chain branching during polymerization may play a role in the nature of the crystal structure formed.

Pron and co-workers¹⁹⁰ have investigated the crystal structure of other soluble emeraldine salts. In these studies, the solubility of the ES was induced using dialkyl ester sulfonate dopants (**14**) where R = *n*-pentyl, *n*-octyl, *n*-dodecyl or other alkyl chains:



14

The general model of the crystal structure proposed by Dufour et al.¹⁹¹ is drawn schematically in [Figure 4.6](#). In this structure, the alkyl chains separate the ordered polyaniline chains and the separation of the latter depends upon the alkyl chain length. In fact, detailed analysis suggests that the alkyl chains are interdigitated, as shown in the figure. Similar structures have been proposed for dodecylbenzenesulfonic acid doped PAN 191.

Electropolymerized Emeraldine Salt.

The crystal structure of electropolymerized PAN ES has been shown to conform to the ES-I structure, at least for simple counterion such as Cl⁻. Zhu et al.¹⁹² used STM/AFM to obtain high resolution images of both electrochemically grown and solution cast PAN films with different dopants. They found a high degree of molecular ordering with extended PAN chains stacked in parallel rows and separated by a distance that correlated with dopant size. The interchain separation was found to be 0.4 nm for Cl⁻-doped ES, close to the expected chain separation for the ES-I crystal structure. The interchain distance increased to 0.7 nm for ClO₄⁻ dopants and 1.4 nm for *p*-toluene sulfonate-doped ES. These separations were found to closely agree with molecular mechanics calculations.

Influence of Water and "Secondary Dopants" on PAN crystallinity. An increase in crystallinity of PAN emeraldine salt has been reported by the incorporation of secondary plasticizing agents. Pron et al.¹⁹⁰ have shown that

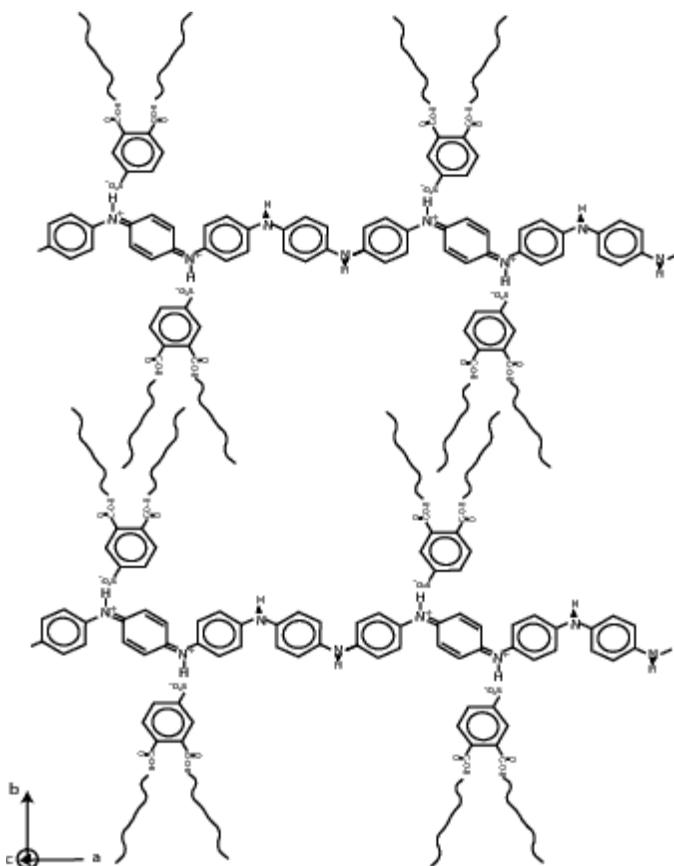


Figure 4.6 Layered stacking of ES chains with *n*-alkyl diester dopants separating the chains in the *b* direction.

the incorporation of an “external” plasticizer enhances the crystallinity of dialkyl ester-doped PAN. The use of dioctylphthalate or tritolyl phosphate was shown to increase the intensity of WAXD scattering peaks and to also increase the electrical transport properties. With about 30wt% of external plasticizer added (with respect to the PAN base), it is estimated that one plasticizer molecule is associated with 13.5-14 PAN repeat units. The analysis of the XRD peaks show that the plasticizer does not enter the crystalline domains and must, thus, remain in the amorphous regions. The plasticizer, therefore, is believed to enhance the crystallization of the PAN by allowing greater chain flexibility during the latter stages of film casting.

Morphology and Density

The film morphology of electrochemically prepared polyaniline has been shown by many workers to be fibrillar in nature and often quite porous. In

contrast, solution-cast films are flat and featureless with little porosity. The factors influencing the morphology of electropolymerized PAN are reviewed below.

Armes and co-workers have investigated the structure of both PAN colloid particles (stabilized with polyvinylalcohol) and electrochemically prepared PAN films. In both cases, the fundamental morphology was nanoparticles of up to 20nm in diameter. Colloid particles were “rice grain” shaped. Thick films showed submicron-sized features that appear to be aggregates of the smaller particles.

Several other studies have indicated that the PAN film morphology changes during the polymerization process. Abrantes et al.,¹⁹³ for example, used ellipsometry techniques to investigate the thickness and properties of PAN/SO₄ films prepared potentiodynamically. These workers found clear evidence of a less dense structure forming at longer polymerization times. Desilvestro and Scheifele¹⁹⁴ have reviewed some of the early structural studies on PAN. They report that SEM and ellipsometry studies have shown that thin (< 150nm) PAN films prepared electrochemically are compact, with densities of ~1.45 g/cm³. Thicker films become very porous with a granular or fibrous surface structure. Films of many tens of microns thick can have porosities in excess of 80%.

Based on studies of polymerization of aniline in a number of supporting electrolytes, Desilvestro and Scheifele¹⁹⁴ have proposed the following growth mechanism for electrodeposited PAN. An induction period occurs initially in which a dense layer of globular morphology is deposited. Polymerization then proceeds from localized globules leading to fibrils of roughly uniform diameter. Further deposition occurs at the active ends of fibrils and at branch points (which occur to be evenly distributed). Partial thickening of the fibrils also occurs during further polymerization. Porosities were consistently reduced when faster polymerization occurred (e.g., potentiodynamic polymerization, higher aniline concentrations).

A number of studies have investigated the effect of counterion on PAN film morphology. In our own studies, we have commonly observed a powdery deposit for electrochemically prepared PAN (see Chapter 5). Comparing small counterions, Duic et al.¹⁹⁵ found a correlation between film morphology and conductivity. Fibrous morphologies were produced by using four acids, with the diameter of the fibrils decreasing with different anions: HSO₄⁻ > NO₃⁻ > Cl⁻ > ClO₄⁻. The rate of polymerization (under identical potentiodynamic conditions) followed the same order and is possibly related to specific anion adsorption on the electrode promoting a higher concentration of the anion at the polymerization site. The Cl⁻ ion promotes less branching of fibrils than the oxyacids and the lower degree of branching may account for the lower conductivity (10⁻³ S/cm) of the PAN-Cl compared with the PAN prepared from oxyacid electrolytes (1 to 8 S cm).

Hwang and Yang have compared the morphology and porosity of PAN prepared with polyelectrolytes. As with other workers, Hwang and Yang found that HCl produces a porous fibrous network with fiber diameters ~

100 nm. The addition of poly(acrylic acid) produced extended long needles of polyaniline loosely connected together. Other polyelectrolytes, such as poly(vinylsulfonate) and poly(styrenesulfonate) produce more globular surface structures.¹⁹⁶ Yang has advanced the hypothesis that the morphology is determined by H-bonding interactions between the anilinium ions and the polyelectrolyte chains to produce so-called "double strand" polyaniline.

The morphology of *in situ*-deposited PAN emeraldine salt using chemical oxidants produces a very similar morphology to thin electrodeposited films. For thin films (60 nm thick), AFM studies reveal densely packed granular features of 50 to 100 nm in size giving smooth films.¹⁹⁷ Thicker films are much rougher, with granular features up to 200 nm in diameter.

The growth mechanism of *in situ*-deposited films proposed by Stejskal et al.¹⁹⁸ has similarities to that described above for electrodeposited PAN. It is important to note that the *in situ* method produces both a surface coating and the normal powdery precipitate from the bulk of the solution. It is proposed by Stejskal that aniline radical cations adsorb on the substrate surface during an "induction period" before bulk polymerization is observed. The adsorbed species initially promote the formation of a dense film on the substrate surface. Once this film has formed, further growth occurs on the PAN surface in a manner similar to the growth of localized globules that occurs in the electropolymerization. The surface roughness of *in situ* PAN films may be further increased by the incorporation of PAN precipitates from the bulk solution into the surface film.

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chapter five

Properties of polyanilines

As with polypyrrole (PPy), the electrical, chemical and mechanical properties of polyaniline are inextricably linked. In addition, polyaniline has spectacular optical and chromic properties that distinguish it from other conductive electroactive polymers (CEPs). The current state of knowledge concerning properties of polyaniline is reviewed in this chapter.

Electrical properties

Conductivity

Polyaniline has an electronic conduction mechanism that seems to be unique among conducting polymers, because it is doped by protonation as well as undergoing the *p*-type doping described for PPy. This results in the formation of a nitrogen base salt rather than the carbonium ion of other *p*-doped polymers.¹ Many of the unusual properties of polyanilines arise because of the A-B nature of the polymer configuration, whereas most other conducting polymers are of the A-A type. Furthermore, the B component is the basic N heteroatom, which is involved with the conjugation in polyaniline (PAn) more than the heteroatoms in PPy and similar polymers. Therefore, the conductivity of PAn depends on both the oxidation state of the polymer and its degree of protonation.

Polyaniline can exist in a range of oxidation states. The one that can be doped to the highly conducting state is called “emeraldine.” It consists of amine (–NH–) and imine (=N–) sites in equal proportions. The imine sites are protonated² by acids HA to the bipolaron (dication salt) form. However, this undergoes a further rearrangement to form the delocalized polaron lattice, which is a polysemiquinone radical-cation salt. The structures at each stage of this process are shown in [Figure 5.1](#).

Although theoretical calculations have predicted that the bipolaron state is energetically more favored than the polaron,² it is widely agreed that polarons are the charge carriers responsible for the high conductivity in polyaniline.^{3–7} It has been proposed that the presence of coulombic interactions,

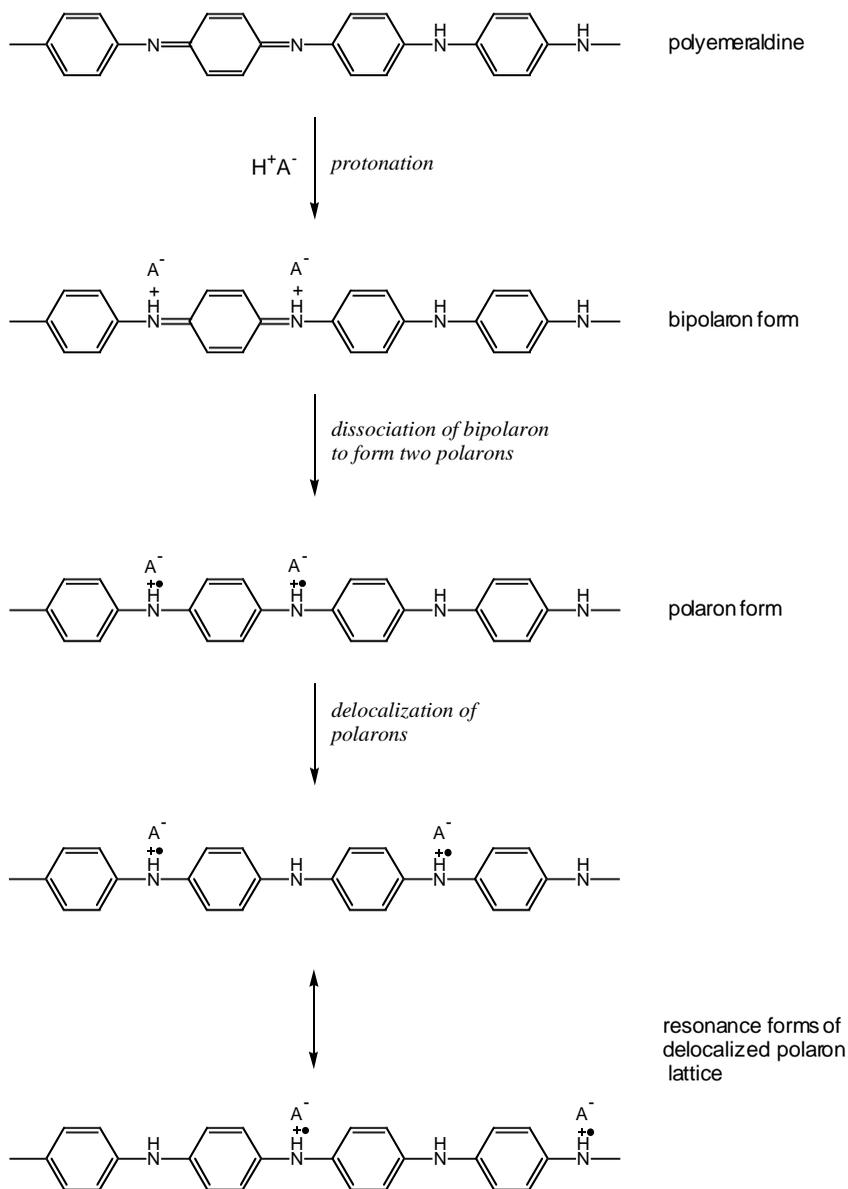


Figure 5.1 The doping of EB with protons to form the conducting emeraldine salt (PAn.HA) form of polyaniline (a polaron lattice).

dielectric screening and local disorder in the polyaniline lattice act to stabilize the delocalized polaron state.⁸ It has also been shown that bipolaron states do exist in polyaniline, but they are few in number and are not associated with the conducting regions of the polymer.⁸

The conductivity of PAN.HA emeraldine salts is dependent on the temperature⁹ as well as humidity and hence, polymer water content.^{10,11} In general, attachment of functional groups decreases the conductivity, whereas the formation of copolymers between aniline and functionalized aniline results in polymers with intermediate conductivity. In addition, the preparation conditions,^{12,13} particularly as they relate to the formation of structural defects¹⁴ and the polymer morphology,^{15,16} influence conductivity. It has also been reported that the conductivity of PAN is dependent on the solvent it is cast from or exposed to. This phenomenon has been referred to as “secondary doping.”^{17,18} The solvent causes a change in the polymer conformation that results in increased conductivity.

However, the most significant dependence of the conductivity of PAN is upon the proton doping level.¹⁹ The maximum conductivity occurs when polyaniline is 50% doped by protons, to give the polaron lattice structure shown in Figure 5.1. Under these conditions, the conduction mechanism is similar to that for the other polymers described, with the polaron states overlapping to form mid-gap bands. The electrons are thermally promoted at ambient temperatures to the lower energy unfilled bands, which permits conduction.²⁰

Even so, the occurrence of a charge exchange phenomenon is necessary to produce the conductivity levels observed, even in 50% doped polyaniline, because of the presence of structural defects other than those caused by inadequate protonation of the nitrogen sites. It is proposed that this involves interchain or intrachain proton exchange as well as electron transport. This explains the observed dependence of conductivity on the ambient humidity, as the presence of water within the polymer lattice would facilitate this proton-exchange phenomenon.¹⁶

At doping levels higher than 50%, some amine sites are protonated, and at levels lower than this some imine sites remain unprotonated. In both instances, delocalization of the charge carriers over the polymer backbone is disrupted, thereby reducing the polymer conductivity. When significant proportions of these nonconducting phases occur, polyaniline behaves in a manner equivalent to a conducting system in which metallic islands are dispersed throughout a nonconducting media. In such a system, transport of the charge carriers occurs through “charge energy-limited tunneling” involving long-range hopping. This is similar to that which occurs in granular conduction models, except that it occurs on a molecular scale in polyaniline. This complex relationship between the conductivity of polyaniline and the chemical nature of its environment has resulted in great efforts to characterize these phenomena and, particularly recently, to find applications where these unusual properties are of benefit. Further discussion of this aspect appears in the section on the switching properties of polyaniline.

Recently, much interest has been shown in enhancing the order and consequent conducting properties of conducting polyaniline salts via *post-polymerization* treatment with an appropriate “secondary dopant.” In particular, much attention has focused on the influence of *m*-cresol **1** solvent or

vapor on the properties of the emeraldine salt PAN.(±)-HCSA obtained by doping emeraldine base (EB) with racemic (±)-10-camphorsulfonic acid.^{21–23} Such emeraldine salt films cast from such doping reactions in DMSO, DMF, *N*-methylpyrrolidinone and chloroform solvents are considered to possess a “compact coil” conformation of their polyaniline chains.^{23,24} These tightly coiled chains exhibit a characteristic localized polaron band at ca. 800 nm in their UV-visible spectra and show relatively low electrical conductivities (typically 0.1–1 S/cm). In contrast, emeraldine salts cast from similarly doped solutions in *m*-cresol solvent have been assigned an “expanded coil” conformation on the basis of their markedly higher electrical conductivities (150–200 S/cm) and strikingly different absorption spectra.^{23,24} Most diagnostic is the replacement of the high wavelength (ca. 800 nm) polaron band by an intense, broad free-carrier tail absorption in the near infrared (1000–2500 nm).

Meta-cresol vapor has also been shown to have a major effect on the properties of PAN.(±)-HCSA salts. Exposure to *m*-cresol vapor of films originally cast in the “compact coil” conformation causes a change to an “expanded coil” arrangement for the polymer chains and a large (ca. two orders of magnitude) increase in electrical conductivity.^{23,25} Once again, associated with these changes is the disappearance of the localized polaron band in the visible absorption spectrum at ca. 800 nm characteristic of the “compact coil” conformation and its replacement by a strong, broad free-carrier tail in the near infrared region.

In both the liquid and gas phases, the *m*-cresol is considered to act as a “secondary dopant” for the polyaniline chains, leading to the above conformational changes. Theoretical studies^{26,27} suggest that the effects associated with *m*-cresol arise from a synergistic combination of interactions between the *m*-cresol, HCSA and the polyaniline chains. These involve H-bonding between the phenolic OH group of the *m*-cresol and the carbonyl group of the HCSA and π -stacking of phenyl rings in the secondary dopant and the polyaniline chain.

Other phenolic compounds have also been shown to cause similar changes in conformation and physical properties of PAN.HCSA salts.²⁴ Most of these, like *m*-cresol **1**, are highly corrosive and toxic, limiting their desirability for processing and enhancing the electrical conductivity of polyanilines. However, we have recently found that the structurally related molecules thymol **2** and carvacrol **3**, which are much less toxic than *m*-cresol, can also function as effective secondary dopants for PAN.(±)-HCSA films and increase the electrical conductivity by up to two orders of magnitude.²⁸

The UV-vis spectrum for PAN (±)-HCSA obtained by doping EB with racemic HCSA in carvacrol is shown in Figure 5.2. The presence of a strong free-carrier tail absorption in the near infrared confirms substantial conversion of the emeraldine salt to an “expanded coil” conformation.

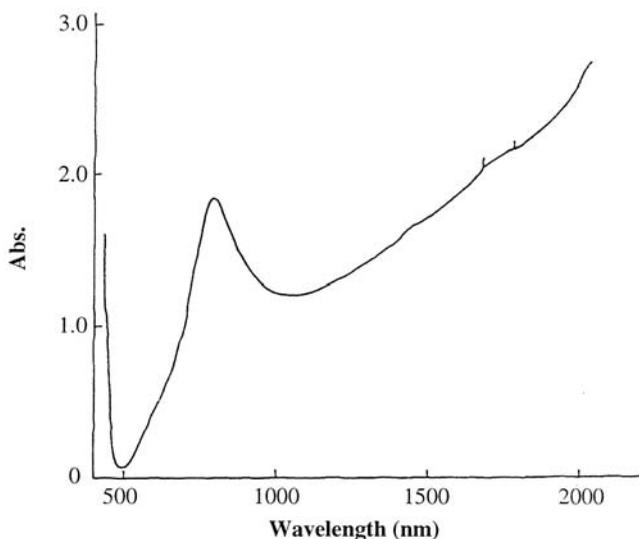
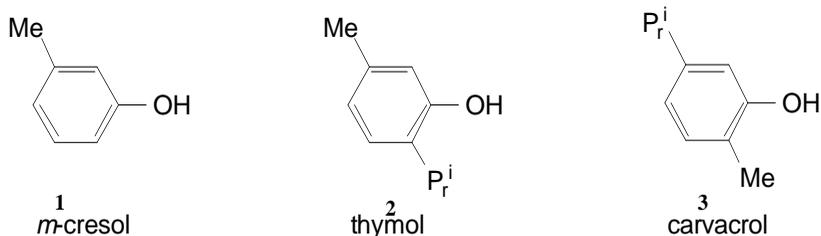


Figure 5.2 UV-visible spectra obtained after doping EB with (\pm)-HCSA in carvacrol.



Switching properties

Polyaniline is an interesting material that undergoes two distinct redox processes as well as pH switching between unprotonated and protonated states (Figure 5.3).²⁹ The redox processes are readily observed using cyclic voltammetry (Figure 5.4). The most conductive form of the polyaniline is the emeraldine salt form that occurs between approximately +0.20 and +0.60 V vs. Ag/AgCl. At less positive potentials, the fully undoped form (leucoemeraldine) is much less conductive, as is the fully oxidized form (pernigraniline) at higher potentials.

The doping reaction is the same as that which occurs during the polymerization process, and the dedoping reaction is the reverse process. Many

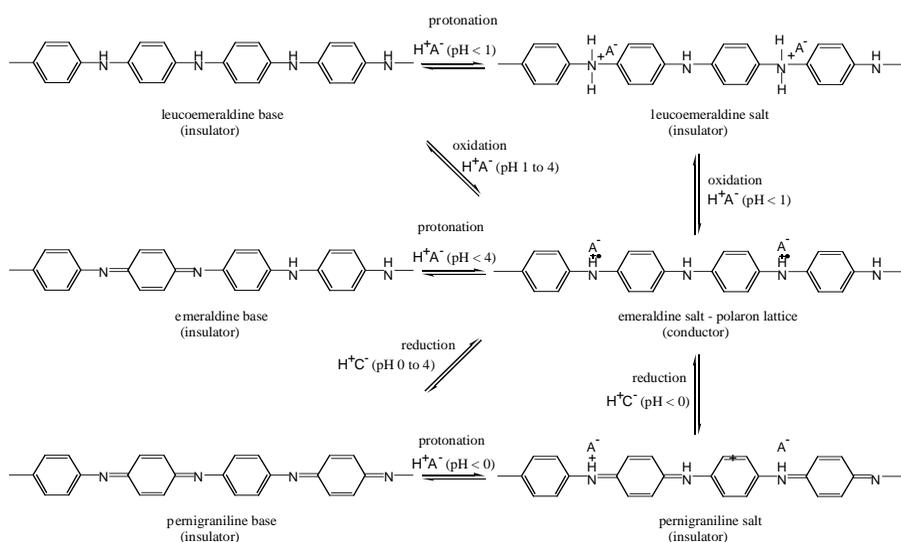


Figure 5.3 The protonation and redox reactions between the various forms of polyaniline.

of the side reactions that can occur during polymerization can also be a problem during doping, particularly those involving overoxidation.

Polyaniline can be “switched” by the addition of acids and bases that protonate and deprotonate the base sites within the polymer. This leads to the dependence of the polymer states, and thus the reactions, upon the pH of the solutions. IN solutions of pH greater than 4, polyaniline loses it electroactivity entirely because the emeraldine salt, the only conducting form of the polymer, is dedoped to form the insulator emeraldine base (EB).

If the PAN polymer is exposed to potentials greater than the second oxidation process, a third voltammetric response appears upon cycling the potential. This is due to oxidation/reduction of a degradation product.³¹ In fact, insoluble degradation products are formed, probably due to chain scission by hydrolysis of amine groups to form benzoquinone and acrylamine terminations.

Polyaniline has been shown to exhibit similar redox behavior in both aqueous and nonaqueous media.³¹ However, in organic solvents, the second (more positive) oxidation response is irreversible, due to the lack of protons in such media.

Thus, polyaniline undergoes transitions between various states. Therefore, its chemical properties are varied and can be controlled by application of a potential or an acid or base. Not only do the conductivity and chemical properties of polyaniline change, the color of the polymer also changes between each of these states (Figure 5.4).^{32,33} These chromatic changes in polyaniline have led to an interest in its use for display devices, redox and pH indicators and other applications.

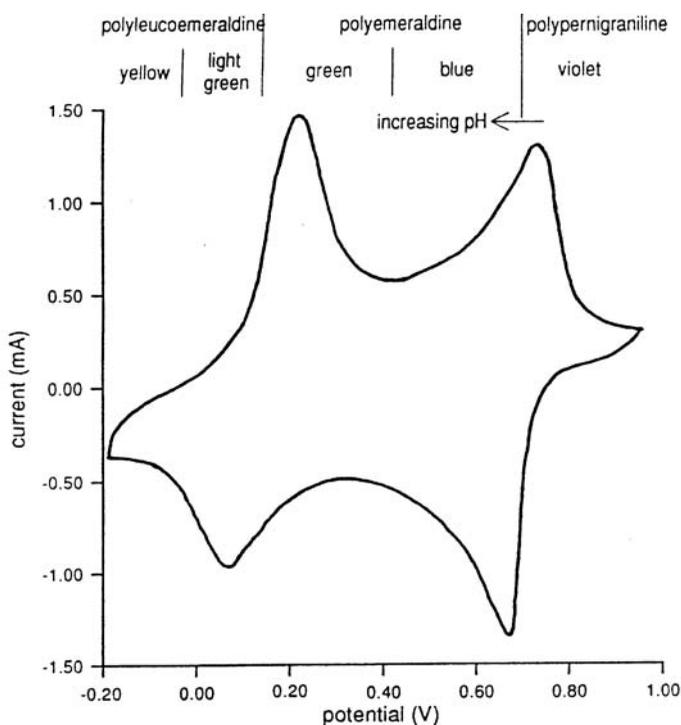


Figure 5.4 Cyclic voltammogram of polyaniline (HCl) on a glassy carbon electrode; 1 M HCl(aq); 50 mV/s; the potentials at which structure and color changes occur and the change in the potential of the second redox reaction with pH are shown as well. The second oxidation peak moves to a less positive potential with increasing pH.

The electrochemical switching of polyaniline can be readily monitored by cyclic voltammetry. However, because of the dependence of the switching on the protonation level of the solution, the peak potentials vary with the pH. A signature voltammogram for polyaniline at pH of 0 is shown in Figure 5.4, including the potentials at which structural and color changes occur. The trend observed for the peak potential with increasing pH is also indicated. The rate of switching depends on the electrolyte used³⁴ (with smaller ions the switching is faster) and the solvent employed.³⁵

It has been established that, when polyelectrolytes are incorporated as dopants in polyaniline, the switch from conducting to nonconducting material is shifted to very high pH solutions, enabling electrochemistry to be carried out on polyaniline in neutral solutions.³⁶ Poly(methoxyanilines) have been used as the basis of electromechanical actuators, where changes in dimensions in the thickness direction of more than 20% reported as the polymers are doped and dedoped.^{37,38} Similar effects are observed if some level of self-doping is introduced into the polyaniline backbone.³⁹

Chemical properties

Many of the properties of PPy mentioned in earlier chapters apply to polyaniline as well. The electron-rich nonpolar backbone of the polymer is accompanied by added functionality of the N heteroatoms that may participate in hydrogen bonding as well as introduce a polar group to the various forms. In the conducting state, polyaniline also has a positive charge delocalized over the backbone of the polymer and over a much larger range than in traditional ion exchange materials. The ion exchange properties of polyaniline can be derived from a similar source to PPy, although in the former, the positive charge is in the form of a radical cation rather than a dication. The effect of this difference on the chemical properties cannot be predicted with certainty. The dependence of this state of the polymer on the pH of its environment will also have a major contribution to the observed chemical properties.

Several studies^{40,41} have indicated that the strongest chemical interactions of polyaniline are anion exchange properties and that these properties differ in several ways from those of conventional ion exchange resins. The reason can be attributed to the charge delocalization. Charge configurational-related phenomena have also been observed in studies with amino acid interactions on polyaniline.⁴² For example, it has been shown that, for two amino acids with similar charge densities but different molecular configurations, the ability to interact with polyaniline was markedly different. Studies involving inverse chromatography⁴³ have shown that polyanilines are more hydrophilic than PPy, as might be expected from the increased charge density. It has also been observed that polyaniline stationary phases are capable of discriminating between polyaromatic hydrocarbons on the basis of planarity or length–breadth ratio.^{43a}

A smaller range of counterions has been incorporated into polyaniline than into PPy; therefore, the range of chemical interactions imparted by the counterions has not been as significant. A number of different functional groups are also available on substituted aniline monomers, although these have been investigated predominantly for their influence on the conductivity or polymerization of polyaniline, as mentioned previously. However, these could also be used to introduce various chemical interactions to polyaniline, in a manner similar to that described for PPy.

Incorporation of bioactive molecules into polyaniline is not so readily achieved because electropolymerization must normally be carried out at low pH. However, thin polymeric coatings containing enzymes have been produced by polymerization from buffer solutions (pH = 7).⁴⁴ Tatsuma and co-workers⁴⁵ have immobilized horse radish peroxidase into films composed of a sulfonated polyaniline and poly(L-lysine) or polyethyleneimine.

In other work, enzyme-catalyzed polymerization was used to produce PAN with DNA as dopant. Interestingly, the polyaniline adopts the chiral nature of the DNA strands.⁴⁶ A number of dopants have also been incorporated into polyaniline to enhance the inherent electrocatalyst properties of the polymer. For example, Ogura and co-workers added tungsten trioxide

to polyaniline-polyvinylsulfate electrodes, and used these to facilitate the electro reduction of CO_2 to lactic acid, formic acid, ethanol and methanol.⁴⁷ In another report from the same laboratory,^{47a} a range of different Fe complex structures were added to polyaniline Prussian Blue films to enable the electrocatalytic reduction of CO_2 .

Films of optically active polyaniline salts such as PANi(+)-HCSA, or the optically active EB derived from them, have recently been shown^{48,49} to exhibit discrimination toward chiral compounds such as the enantiomers of CSA^- and amino acids. The studies suggest that these novel chiral materials may indeed have potential for the separation of enantiomeric chemicals, such as chiral drugs.

Mechanical properties of polyaniline

The mechanical properties of PAN differ considerably between the electrochemically prepared polymer and that produced from solvent casting. As described above the electropolymerized ES is highly porous and, consequently, has low mechanical strength. Freestanding films may be prepared electrochemically, but their poor mechanical properties limit their usefulness. In contrast, the polymer made from solution is much less porous and is widely used as freestanding films and fibers. The effect of polymer structures and morphology on PAN mechanical properties are described below.

Electrochemically Prepared Films

A limited number of studies have considered the effects of electropolymerization conditions on the mechanical properties of PAN. Kitani et al.,⁵⁰ for example, have shown that it is possible to prepared freestanding films from PAN in the reduced (leucoemeraldine) state. When oxidized to the emeraldine state, the films became brittle. Similar behavior was described in Chapter 3 for polypyrrole and the change in mechanical properties in that case was related to the increased interchain bonding between charged chains that result in a decrease in toughness. Presumably, a similar explanation applies to polyaniline.

The polymerization potential has also been found to influence the mechanical properties of PAN films.⁵⁰ The most extensible films were formed at a polymerization potential of 0.65 V (vs. Ag/Ag⁺), which displayed an extension to break of around 40%. Preparation of the PAN films at 0.8 V and 1.0 V resulted in more-brittle films. It was suggested that degradation of the PAN at polymerization potentials in excess of 0.8V might explain the poor properties of the 1.0 V film. The difference in behavior of the films prepared at 0.65 V and 0.8 V was attributed to differences in their crosslink density. Unfortunately, structural characterizations of the PAN films prepared under these conditions were not conducted, making it impossible to explore the structure–property relationships in more detail.

Our studies have shown that the electropolymerization method produces a powdery deposit (Figure 5.5) and that the adhesion of the deposit to the working electrode depends on the reaction conditions. For example, a finer powder structure produced by using the NO_3^- counterion gave stronger adhesion than the coarser structures produced when the Cl^- counterion was used. Also, cyclic application of the electropolymerization potential gave the most strongly adherent deposits, while galvanostatic growth gave a polymer that was less adherent. Finally, the potentiostatic method produced the lowest adhesion. To date, the effect of these parameters on other mechanical properties of the coatings and films have not been reported.

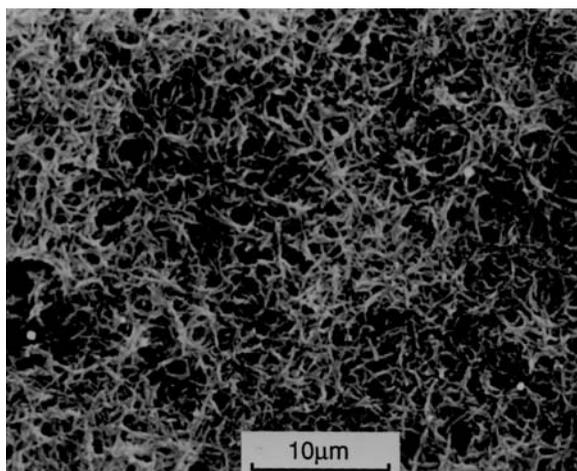


Figure 5.5 Scanning electron micrograph of polyaniline/HCl.

Solution Cast Films and Fibers

A number of workers have shown that it is necessary to synthesize PAN to high molecular weights to successfully prepare fibers and films with adequate mechanical properties. Laughlin and Monkman⁵¹ have shown that a molecular weight of 130,000 g/mol is sufficient, whereas Mattes et al.⁵² have investigated the effect of molecular weight in the range 100,000 to 300,000 g/mol. The higher the molecular weight, the more the films could be drawn and the higher was the tensile strength.

As expected, the stretching of PAN films and fibers has a dramatic effect on the mechanical properties. EB films can be stretched by more than five times their original length (at 140° C) and this process has been shown to produce a 10-fold increase in tensile strength (to 226 MPa⁵³). Similarly, thermal stretch orientation of EB fibers produces a tensile strength of 318 MPa, which reduces to 150 MPa when HCl doped. Similar increases in elastic modulus would be expected to result from the mechanical drawing, since the process causes considerable alignment of the polymer chains in the draw

direction. Such mechanical orientation also increases the crystallinity and conductivity of the PAN films and fibers.

Polyaniline can be successfully plasticized to improve the ductility and toughness. Residual solvent (e.g., NMP) in solution-cast films and fibers undoubtedly affects the mechanical properties: increasing elongation at break and reducing the elastic modulus. Fedorko et al.⁵⁴ have recently shown dramatic improvements in the ductility of PAN ES films using plasticizing dopants. Thus, the di(2-ethylhexyl)ester of 4-sulfophthalic acid (DEHEPSA) was used to prepare PAN-ES that were soluble (in the ES form) in dichloroacetic acid. Cast films had similar conductivities to ES-CSA of ~ 100 S/cm. Tensile testing gave an elongation at break of 28% for the ES-DEHEPSA films compared with only 2% for the ES-CSA. The tensile strength for both films were similar: 14 and 16 MPa, respectively. This tensile strength is comparable with that obtained for unoriented EB films.

Most fibers and films of PAN have been prepared from a solution of emeraldine base and converted to the emeraldine salt by acid doping. The choice of dopant acid has a profound effect on mechanical properties. In fact, MacDiarmid et al.⁵⁵ have shown that the mechanical properties depend in a complex way on dopant, casting solvent and polymer molecular weight. Full details of the effects of polymer structure (as influenced by dopant and solvent) on the mechanical properties are yet to be elucidated.

Thermal analysis has been used to study thermal transitions in polyaniline, specifically the glass transition. This polymer has been shown to display a distinct T_g with the transition being sensitive to the degree of plasticization. DMA studies on PAN EB films cast from NMP have shown the T_g to shift from 158°C to 99°C as the NMP content decreases from 18% to 10% (w/w). Gregory⁵⁶ has evaluated the thermal properties of the LB form of PAN using Differential Scanning Calorimetry (DSC) and DMA. A broad endotherm was observed at $\sim 385^\circ\text{C}$ substantially higher in temperature than the T_g at $\sim 200^\circ\text{C}$. The endotherm was attributed to melting of a crystalline phase as supported by XRD and microscopy data. DMA data also confirmed significant softening of the polymer at $\sim 375^\circ\text{C}$. The fibers and films used by Gregory were prepared from DMPU, a solvent that inhibits gelation of the EB in solution.

Optical properties of polyanilines

Emeraldine salt form of polyaniline. Semiempirical molecular orbital calculations⁵⁷ and, more recently, *ab initio* calculations⁵⁸ on the conducting emeraldine salt form of polyaniline predict, in contrast to PPy and polythiophene, the presence of a single broad polaron band deep in the band gap. This band is half filled, giving rise to an ESR signal.⁵⁹

These band structure calculations are in agreement with the observed UV-visible-NIR spectra of emeraldine salts, PAN. HA. In their “compact coil” conformation, emeraldine salts typically exhibit three peaks: a π - π^* (band

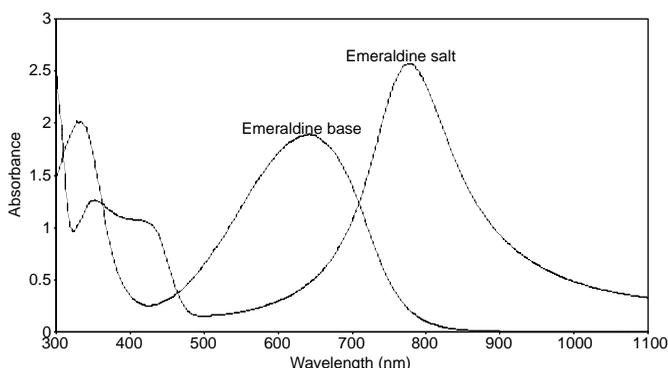


Figure 5.6 UV-visible spectrum of the emeraldine salt PAn.(±)-HCSA and its corresponding EV in NMP solvent. (Courtesy of C. Boonchu, Ph.D. thesis, University of Wollongong, 2002.)

gap) band at ca. 330 nm and two visible region bands at ca. 430 and 800 nm that may be assigned as $\pi \rightarrow$ polaron band and polaron $\rightarrow \pi^*$ band transitions, respectively⁶⁰ (see Figure 5.6).

Base forms of polyaniline. Electronic band structures have also been calculated for each of the base forms of polyaniline, namely, the fully reduced leucoemeraldine base (LEB), the half-oxidized EB and the fully oxidized pernigraniline base (PB).⁶¹ The observed UV-visible spectra of LEB, EB and PB are in good agreement with these calculated band structures. The lowest energy absorption band for LEB occurs at ca. 320 nm and may be assigned to the $\pi-\pi^*$ electronic transition, i.e., between the valence and conduction bands. For EB, as well as a similar low wavelength $\pi-\pi^*$ band, there is a strong band at ca. 600 nm that has been attributed to a local charge transfer between a quinoid ring and the adjacent imine-phenyl-amine units giving rise to an intramolecular charge transfer exciton.⁶² Pernigraniline base also exhibits two absorption peaks: a $\pi-\pi^*$ band at ca. 320 nm and a band at ca. 530 nm assigned to a Peierls gap transition.

Protonation of PB causes a violet-to-blue color change due to the formation of pernigraniline salt (PS). This change is associated with the loss of the PB band at 530 nm and the appearance of a strong PS peak at ca. 700 nm.

Dependence of UV-visible-NIR spectra on chain conformation. In general, conjugated polymers such as polyaniline show a strong coupling between their electronic structure and geometric features such as the polymer chain conformation. A number of theoretical studies have examined the influence of polyaniline chain conformation, and, in particular, the role of phenyl and phenyl/quinoid torsional angles along the chain, on the electronic structure of PAn (and consequently their electronic absorption spectra). These include semi-empirical calculations by Brédas et al.^{61,63,64} and by de Oliveira et al.⁶⁵

on oligomeric models of the polyaniline base forms LB, EB and PB, as well as some *ab initio* calculations.⁶⁶

The position and intensity of the absorption bands for polyaniline species is therefore sensitive to the conformation adopted by the polymer chains, as well as the conjugation length. With emeraldine salts, the λ_{max} for the longest wavelength absorption band is red shifted for polymers with longer conjugation length. Most interest in this particular polaron band has centered, however, on its use as a diagnostic test for the conformation of the polyaniline chains. As seen above in Figure 5.6, this band typically appears as a strong peak in the region 750–850 nm when the PAN chains adopt a “compact coil” conformation. However, when an “extended coil” conformation is adopted, this localized polaron band is replaced by a broad, strong free carrier tail in the NIR, with λ_{max} red shifted to 1500–2500 nm. The delocalization of the polaron along the PAN chains in this “extended coil” conformation results in a much enhanced electrical conductivity.

As a consequence, extensive recent interest has appeared in exploring means of modifying PAN chain conformations, using UV-visible-NIR spectra (and associated circular dichroism spectra for chiral PAN) to monitor such changes.

Circular dichroism spectra

The first reported optically active polyanilines were the emeraldine salts PAN.(+)-HCSA (+)-HCSA and PAN.(-)-HCSA (HCSA = 10-camphorsulfonic acid), prepared in our laboratories by the electropolymerization of aniline in the presence of either (+)- or (-)-HCSA.^{67,68}

An alternative facile approach to optically active PAN is the doping of EB with optically active dopant anions such as (+)- or (-)-10-camphorsulfonate (CSA⁻) in a variety of organic solvents.^{69–72} The PAN.(+)-HCSA and PAN.(-)-HCSA salts exhibit mirror imaged circular dichroism (CD) spectra, indicating enantioselectivity in the doping of the EB chains with (+)- and (-)- HCSA. Figure 5.7 shows the CD spectrum of PAN.(+)-HCSA in NMP solvent. It exhibits bisignate CD bands at ca. 720 and 795 nm associated with the high wavelength polaron band observed (Figure 5.6) at ca. 775 nm. Overlapping bisignate CD bands are also observed at lower wavelengths (including a characteristic band at ca. 450 nm), associated with the low wavelength polaron band and π - π^* absorption band observed in this region.

We have rationalized the optical activity of these PAN.HCSA (and related PAN.tartrate) salts in terms of the preferential adoption of a one-handed helical conformation by the PAN chains, depending on which enantiomer of the CSA⁻ anion is employed in the doping.^{67,68,71,72} Alternatively, as suggested by Meijer et al.⁷⁰ (and has been established for chiral poly(alkylthiophenes) — see Chapter 6), the observed optical activity may arise from the formation of chiral supramolecular aggregates. However, in contrast to chiral poly(alkylthiophenes), PAN(+)- HCSA exhibits strong CD spectra in “good”

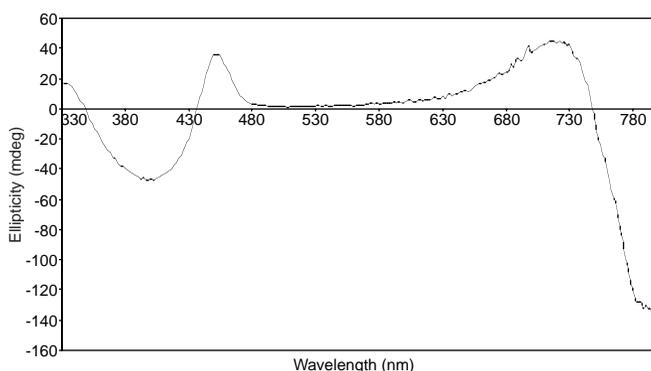


Figure 5.7 CD spectrum of PAN.(+)-HCSA in NMP. (Courtesy of C. Boonchu, Ph.D. thesis, University of Wollongong, 2002.)

solvents such as NMP and DMPU (where interchain aggregation is believed to be minimized) as well as in “poor” solvents, supporting one-handed helical chains as a major contribution to the observed CD spectra of PAN.HCSA salts in organic solvents.

Optically active poly(2-methoxyaniline).HCSA {(POMA.(+)-HCSA and POMA (-)-HCSA)} salts can also be made either electrochemically or by the above doping method, again exhibiting bisignate CD bands associated with the visible region absorption bands.^{73,74} More recently, optically active POMA. HCSA and poly(2-ethoxyaniline).HCSA salts have also been generated by oxidation of the corresponding substituted aniline monomers with the electron acceptor 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in organic solvents such as chloroform/THF mixture.^{75,76}

Optically active films of PAN.(+)-HCSA and POMA.(+)-HCSA can be de-doped in 1 M NH₄OH to give the corresponding optically active emeraldine bases,^{68,73} and the oxidation (with S₂O₈²⁻) and reduction (with N₂H₄) of such films has also been shown to yield optically active pernigraniline and leucoemeraldine base films, respectively, whose chiroptical properties have been exhibited by CD spectra.⁷⁷

Circular dichroism (CD) is a very sensitive spectroscopic tool for probing chain conformations in optically active polymers. For example, with peptides, CD spectroscopy has been widely employed to estimate the proportion of the chain present as the alternative α -helix, β -sheet and random coil conformations.⁷⁸ Following our recent discovery of both electrochemical^{66,67} and chemical^{69,71} routes to chiral PAN.HCSA and related ring-substituted emeraldine salts, we have employed CD spectroscopy extensively to: (a) distinguish between “extended coil” and “compact coil” PAN conformations, (b) probe redox and pH switching in PAN, (c) characterize conformational changes in solvatochromism and thermochromism for PAN, and (d) distinguish unequivocally between the conformations/structures of electrochemically and chemically prepared PAN. Similar valuable information on poly-

aniline structures and chiral recognition properties has been increasingly reported by other research groups over the last few years.

Solvatochromism and thermochromism

Marked changes in the UV-visible and CD spectra of PAn.HCSA emeraldine salts have been widely reported by changing the nature of the organic solvent, the solvatochromism being associated with changes in the PAn backbone conformation/structure. However, few studies of thermochromism exist. We have recently shown from CD studies of PAn.(+)-HCSA that the conformation of electrochemically deposited films is changed upon heating to 140° C from a largely "extended coil" conformation to a "compact coil" conformation.⁷⁹ This study also unequivocally established that electrochemically and chemically prepared PAn.(+)-HCSA salts have different conformations/structures. Su and Kuramoto^{74,75} have similarly pointed out that PAn(+)-HCSA and POMA.(+)-HCSA salts prepared from water and organic solvents possess different conformations, while Kaner et al. have recently reported that the presence of water in NMP solutions of PAn.(+)-HCSA can cause inversion of the configuration.⁸⁰

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chapter six

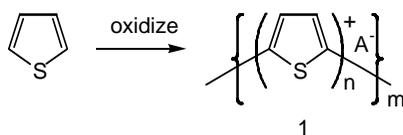
Synthesis and properties of polythiophenes

Polythiophenes (Structure 1, shown below) have much in common with polypyrroles (PPys). Thiophene is oxidized to form a conducting electroactive polymer with the greatest conductivity obtained from α - α linkages. Some important differences between the polythiophenes and the PPys are discussed below.

Synthesis of polythiophene

Electropolymerization

Polythiophene can be synthesized either electrochemically or chemically using a simple oxidation process according to:



As with PPy, n is usually between 2 and 4; A^- is a counterion incorporated into the polymer during growth to balance the charge on the polymer backbone and m is a parameter proportional to the molecular weight. As with PPys, the mechanism of polymerization involves formation of radical cations that react with each other or the starting monomer to develop the polymeric structure (Figure 6.1). The reaction of the radical cation with the thiophene monomer has been elegantly demonstrated in recent studies where small amounts of bi- or ter-thiophene are added to reduce the polymerization potential.¹ Even after the additive was consumed, polymerization continued at lower potentials.

This is particularly important because the development of systems utilizing thiophene have been thwarted by the “polythiophene paradox”.² It

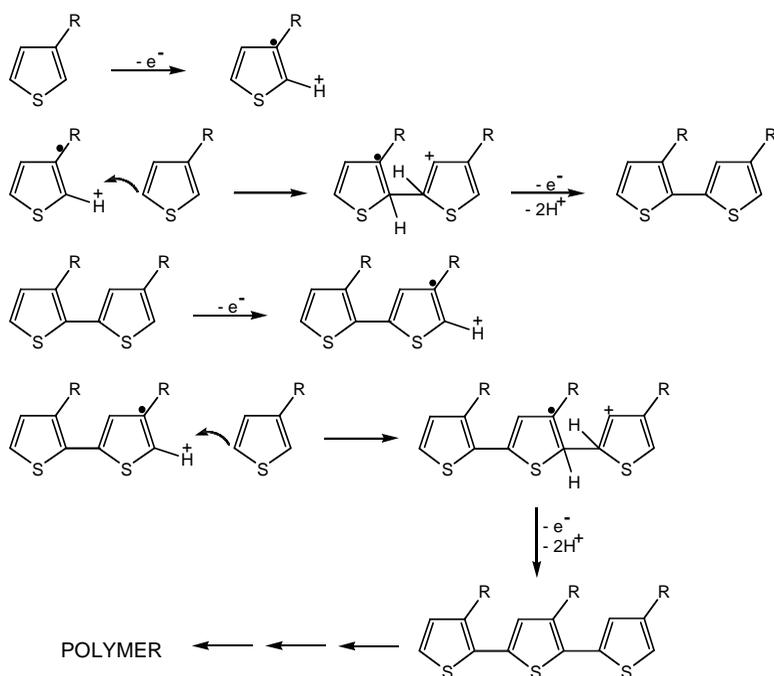
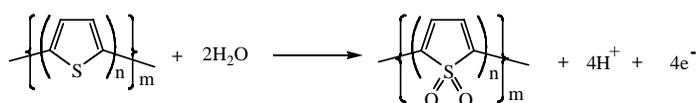


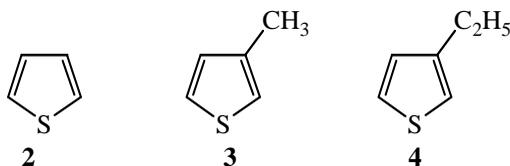
Figure 6.1 Polymerization of thiophene.

has been clearly shown that at potentials required to oxidize the thiophene monomer, the polymer itself becomes overoxidized. This overoxidation process proceeds according to:³



and results in deterioration in chemical and physical properties of the polymer. Using constant current or constant potential polymerization, the product obtained is a mixture of polythiophene and overoxidized polythiophene.

Various substituted thiophenes have also been oxidized to the corresponding polythiophenes, the most commonly studied being 3-alkyl thiophenes. Sato and co-workers⁴ did a comprehensive study using thiophene (Th 2, below), 3-methylthiophene (MTh - 3, below) and 3-ethylthiophene (ETH - 4, below).



They found that all monomers could be oxidized to form conducting polymers but that the oxidation potentials increased according to: MTh < ETh < Th. The fact that ETh was harder to oxidize than MTh was attributed to steric effects. This lowering of the oxidation potential by addition of alkyl groups at a β carbon position avoids the “polythiophene paradox” during polymerization.

Other workers^{5,6} have minimized overoxidation during polymerization by using bithiophenes or terthiophenes as starting materials for the polymerization process. The polymerization potential has been shown to decrease according to: terthiophene < bithiophene < thiophene. But, as reviewed by Roncali, polythiophenes produced from these starting materials generally have lower conductivity.⁷

However, addition of small amounts of bithiophene⁸ influences the polymerization process and results in polymers with increased conjugation length and, therefore, fewer structural defects. This translates to improved electronic properties.

We^{9,10} have recently shown that the attachment of a range of electron donating or withdrawing groups to the thiophene moiety (through a conjugated linker) (Figure 6.2) has a dramatic effect on the polymerization potential and subsequent photovoltaic performance.

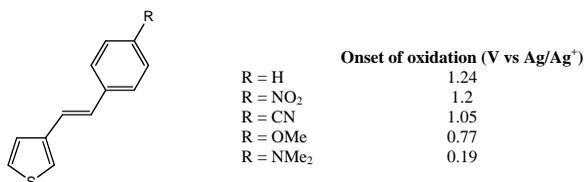
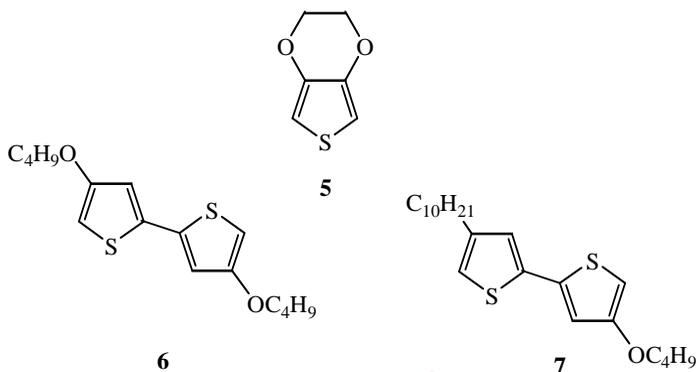


Figure 6.2 Effect of substituents on oxidation potential of substituted thiophenes.

A range of alkoxy and alkyl groups¹¹ (5, 6, 7) has also been added to the bithiophene starting material in order to reduce the oxidation potential even further. Attachment of the alkyl group (in 7) also facilitates the solubility of the polymer in nonpolar organic solvents.

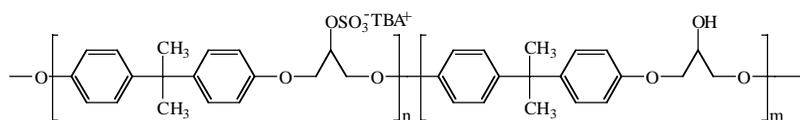


A range of copolymers involving functional thiophene have also been formed electrochemically. For example Sato and co-workers¹² formed a copolymer containing 3-dodecylthiophene and 3-methylthiophene. The material had a solubility of 75 (w/w)% in chloroform and a conductivity of 220, S cm⁻¹.

Polythiophenes are normally produced from nonaqueous media since the monomer is more soluble in these. Also, a wider electrochemical potential window is available and this is required since polythiophene is more difficult to oxidize than pyrrole. The influence of water on the polymerization process for thiophene and on the redox switching properties has been studied.^{13,14} The presence of water as low as 1% causes mislinkages and a subsequent deterioration in polymer properties.¹³ Other authors¹⁵ have claimed that optimal polymers are produced from propylene carbonate solvent.¹⁶ These same workers also point out that the minimum thiophene concentration required to enable polymerization is solvent dependent. The required minimal monomer concentration decreases for solvents with a large dielectric constant. They claim that solvents with a high dielectric constant (having an electron-withdrawing substituent) influence the reactivity of the cation radical intermediate and, therefore, play an important role in the polymerization process.

The counterion employed can also affect the rate of polymerization at a fixed potential. The effect of the counterion's chemical nature on the oxidation of 3-methylthiophene was found to be potential dependent.¹⁵ At low anodic potentials (+1.25 V to +1.34 V), the initial rate of reaction was found to be quickest when the ClO₄⁻ anion was used as dopant. The next fastest rate was with the BF₄⁻ ion, closely followed by PF₆⁻. This trend was similar to the oxidation potentials measured by cyclic voltammetry. A higher anodic potentials (+1.40 V to +1.5 V), the ClO₄⁻ ion showed the slowest reaction rate. At even higher potentials (> +1.50 V), the reaction involving ClO₄⁻ was severely inhibited with currents dropping to low values. The perchlorate ion is known to undergo oxidation at these potentials to form ClO₄. This species may well have reacted with the intermediate monomer radicals to inhibit the polymerization process.

Recently, novel polyelectrolytes **8** have been incorporated into polythiophene structures and found to generate a mechanically strong electroactive deposit.¹⁷



8

TBA = Tetrabutylammonium

Polythiophenes have been polymerized on a range of substrates¹⁵ including Pt, Au, Cr or Ni. However, as with PPy, they do not grow on more easily oxidized substrates such as Cu, Ag, Pb or Zn.

Other workers have shown that polymerization of functional thiophenes from aqueous media is possible if surfactants^{18–21} are used to help solubilize the monomer. In the case of sodium dodecylsulfonate (SDS) being used as a solubilizing agent for bithiophene,¹⁸ it was also found to lower the oxidation potential and inhibit the dissolution of the iron enabling electropolymerization on this active substrate. SDS was also found to lower the oxidation potential of 3,4-ethylenedioxythiophene (EDOT) structure,^{5¹⁹} and other copolymers containing alkoxythiophene and bithiophene groups.²⁰

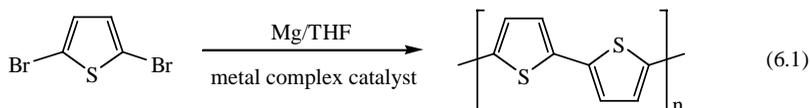
The effect of temperature on the polymerization process for thiophene²² has been investigated. Results show that when polymerization is carried out at 15 to 20°C, polymers with optimal properties are obtained. Ultrasonication has been used to improve the efficiency (improved yield, lowering of polymerization potentials) of the electropolymerization process for polythiophene.²³

Chemical polymerization

As with PPy, polythiophene can be produced using a chemical oxidant. However, due to the limited solubility of thiophene, this reaction must be carried out in nonaqueous media. Copper (II) perchlorate has been used as an oxidizing agent in acetonitrile to yield a simultaneous polymerization/doping process.²⁴ This results in polymer materials with conductivities of approximately 8 S cm⁻¹. Alternatively,²⁵ a Grignard reaction can be used (Figure 6.3) to produce polythiophene which is the first time conventional synthesis techniques have been used.

Others²⁶ have used a chemical polymerization process that ensures the production of well-defined head-to-tail coupled poly (3-alkylthiophenes) (*vide infra*).

The first controlled chemical syntheses of polythiophene were reported in 1980 by two different groups, using metal-catalyzed coupling of 2,5-dibromothiophene (Equation 6.1).^{27,28} In both cases, the dibromothiophene substrate was first reacted with Mg in THF, replacing either the 2- or the 5-bromo substituent with MgBr. Self coupling was then achieved with either Ni(bipy)Cl₂²⁷ or M(acac)₂ (M = Co, Ni, Pd) or Fe(acac)₃²⁸ as catalyst, the condensation reactions eventually leading to polythiophenes of low molecular weight.



Such polycondensation dehalogenation reactions remain a commonly employed route to polythiophene and a range of solvents, halogenothiophene substrates, and other metal-based catalysts have been examined, as recently reviewed.²⁹ For example, the reaction of 2,5-dibromothiophene with Ni(cyclo-

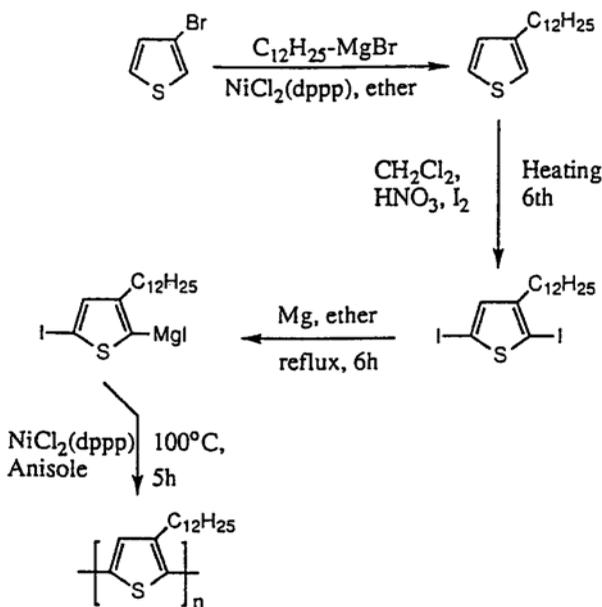


Figure 6.3 Chemical synthesis of alkylated polythiophenes.

octadiene)₂ and triphenylphosphine in DMF leads to an almost quantitative yield of polythiophene.³⁰ Solid state ¹³C NMR studies confirm exclusive 2,5-coupling of the thiophene repeat units in the polymeric product. The 2,5-dichlorothiophene monomer is less active as a substrate in such reactions; however, the corresponding 2,5-diiodothiophene is reported to be a good substrate.³¹

Direct oxidative polymerization of thiophene monomer has also been successfully employed to prepare polythiophene, for example using FeCl₃ in chloroform solvent.³² MoCl₅ may be similarly employed as both the oxidant and dopant.³³ Subsequent reduction with ammonia of the doped polythiophene products from these FeCl₃ and MoCl₅ oxidations provides the neutral polymer.

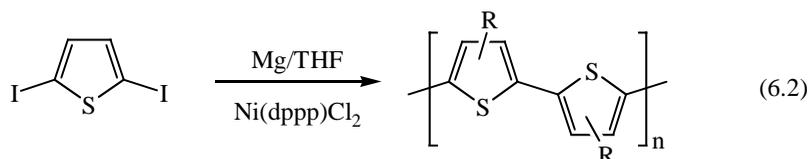
Despite their low molecular weights, these unsubstituted polythiophenes are insoluble in THF and other common organic solvents and are also infusible. Their poor processibility has therefore led to extensive studies of alkyl- and alkoxy- substituted polythiophenes in the hope of enhancing solubility in organic solvents and allowing melt-processing. Synthetic approaches to these substituted polythiophenes are described below.

Substituted polythiophenes

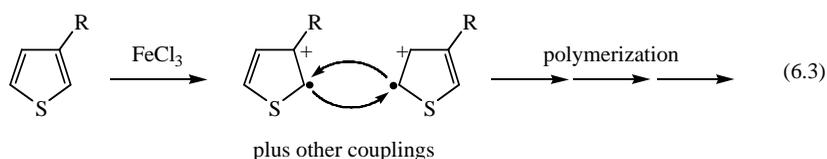
Poly(3-alkylthiophenes) and poly(3-alkoxythiophenes)

Elsenbaumer et al.^{34,35} reported the first synthesis of soluble poly(3-alkylthiophenes) in 1985, using the metal-catalyzed cross-coupling polymeriza-

tion reaction shown in Equation 6.2, with 2,5-diiodo-3-alkylthiophenes as substrates. Poly(3-alkylthiophene) products with butyl or longer alkyl substituents were found to be soluble in a wide range of common organic solvents such as chloroform, dichloromethane, THF, toluene and nitrobenzene, permitting the casting of thin films of the polymers. Melt processing into films was also possible, while ^1H NMR studies confirmed that only 2,5' -couplings had occurred. Undesirable 2,3' - and 2,4' -couplings (leading to branching structural defects) were absent, presumably due to steric hindrance by the 3-alkyl group.

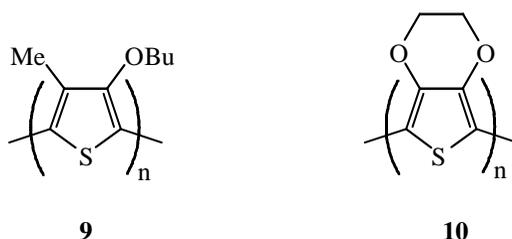


The direct oxidative polymerization of 3-alkylthiophenes with FeCl_3 in an organic solvent such as chloroform has also been widely used to prepare poly(3-alkylthiophenes), with molecular weights between 30,000 and 300,000.^{29,33,36-38} This route, like the above Grignard-type coupling methods, proceeds by 2,5' -couplings of the alkylthiophene repeat units, with little or no undesirable 2,4' -couplings. This is consistent with a mechanism proposed for the FeCl_3 -based polymerizations, involving initial oxidation of the 3-alkylthiophenes to radical cations with the radical centers predominantly located on the thiophene ring 2- and 5-positions, followed by chain propagation (Equation 6.3).³⁹



The FeCl_3 oxidative polymerization route has also been employed for the synthesis of poly(3-alkoxythiophenes).^{29,40,41} Increasing the alkoxy substituent chain length leads to improved solubility in organic solvents. The smaller steric demands of alkoxy groups compared to corresponding alkyl substituents results in less twisting of the polythiophene backbone. An extreme illustration of this is in the polymerization of 3,4-disubstituted thiophene monomers. Whereas the presence of two alkyl substituents causes marked twisting of the polymer chain from planarity and a consequent large decrease in electrical conductivity,⁴⁰ a film of poly(3-butoxy-4-methylthiophene) **9** exhibits a UV-visible spectrum ($\lambda_{\text{max}} = 545 \text{ nm}$) typical of a highly conjugated (planar) polymer and has a high conductivity after doping with

FeCl_3 ($\delta = 2 \text{ S cm}^{-1}$).⁴¹ Another interesting and useful di-substituted polymer is poly(3,4-ethylenedioxythiophene) (PEDOT) **10**. This can be readily prepared by the FeCl_3 oxidation of the corresponding monomer **5** and has an exceptionally high conductivity ($\delta = 13\text{-}30 \text{ S cm}^{-1}$, depending on the organic solvent employed in the synthesis).⁴²



Alkoxy-substituted bithiophenes have also been successfully polymerized, using $\text{Cu}(\text{ClO}_4)_2$ as oxidant.⁴³ As with related FeCl_3 oxidations of alkyl-substituted bithiophenes,⁴⁴ these dimeric substrates are easier to oxidize than the corresponding substituted thiophene monomers, due to their lower oxidation potentials.

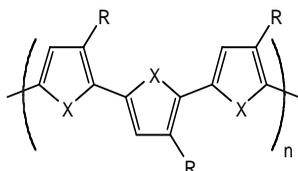
Despite the predominant 2,5' - coupling with both the 3-alkyl and 3-alkoxy thiophene monomer substrates **3**, the presence of the ring substituents introduces a further structural complication. Coupling of the substituted thiophene units can now lead to four possible triad regioisomers for the resultant polymers, depending on whether the coupling occurs in a 2,5' -head-to-tail (HT), 2,2' -head-to-head (HH), or 5,5' -tail-to-tail (TT) manner. These structures **11**–**14** for the polythiophene products are depicted in Figure 6.4 (X = S).

When a mixture of these regioisomers is formed, the resultant substituted polythiophenes are described as *regiorandom* or irregular. This has major implications for the properties of the polymers. Strong steric interactions between alkyl (R) groups in cases of HH couplings, as in regioisomers **12** and **13** cause marked twisting of the polymer chain from planarity, hence decreasing the conjugation length and electrical conductivity of the polythiophene. In contrast, the less sterically crowded *regioregular* HT-HT structure **11** results in little twisting, and this species can adopt an almost planar arrangement for its polymer backbone. These predictions are supported by gas phase molecular mechanics and *ab initio* calculations.^{45,46}

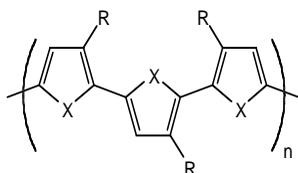
¹H NMR studies have shown that metal-catalyzed cross-coupling polymerizations of 3-alkylthiophenes such as reactions 6.4 above, generally lead to *regiorandom* polythiophenes. A similar situation holds for polymerizations performed by the oxidation of 3-alkylthiophenes with FeCl_3 .^{33,36,37,38} The poly(3-alkylthiophene) products from this latter route usually have only ca. 70-80% head-to-tail coupling, i.e., they are *regiorandom*. However, it has been reported that in the polymerization of 3-(4-octylphenyl)-thiophene **15**, the slow addition of the FeCl_3 oxidant can result in up to 94% head-to-tail (HT)



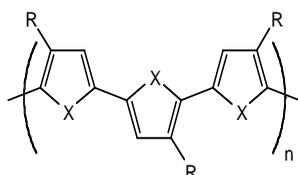
3 (R = alkyl, alkoxy, etc)



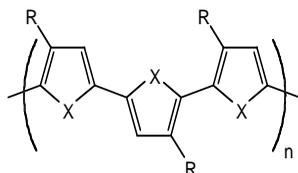
11 (HT-HT)



12 (HT-HH)



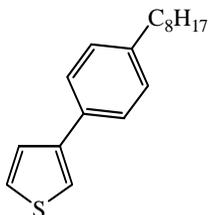
13 (TT-HT)



14 (TT-HH)

Figure 6.4 Structures of polythiophenes.

couplings.⁴⁷ Improved polymerization conditions have similarly led to an 84% HT polymer from the FeCl_3 oxidation of 3-octylthiophene.⁴⁸



15

Regioregular substituted polythiophenes

An important development has been the discovery of effective routes to highly regioregular (HT) poly(3-alkylthiophenes). The first such regiospecific polymerization was reported by McCullough and Lowe⁴⁹ in 1992. This one-pot synthesis involves the regioselective lithiation of 2-bromo-3-alkylthiophene **16** and subsequent *in situ* generation of the Grignard reagent **17**, followed by polymerization via the addition of NiCl₂(dppp) catalyst to give poly(3-alkylthiophenes) with 98 to 100% HT-HT couplings (Figure 6.5). These regioregular polymers (M_n = 20,000 to 40,000) possess markedly improved properties over the related regiorandom polymers, including enhanced electrical conductivity, nonlinear optical properties and crystallinity. For example, regioregular poly(3-dodecylthiophene) exhibits a conductivity of 1000 S/cm⁻¹ compared with 20 S/cm⁻¹ for its regiorandom analogue.⁵⁰

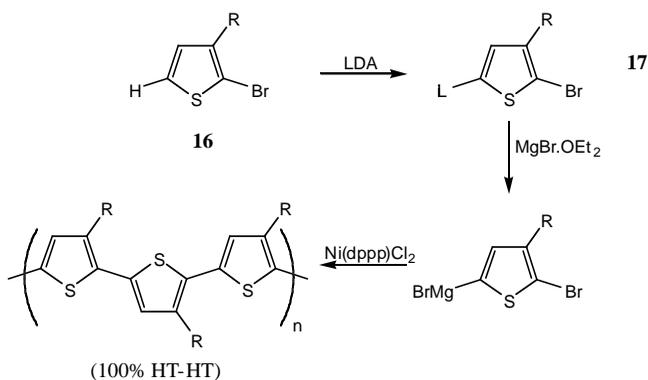
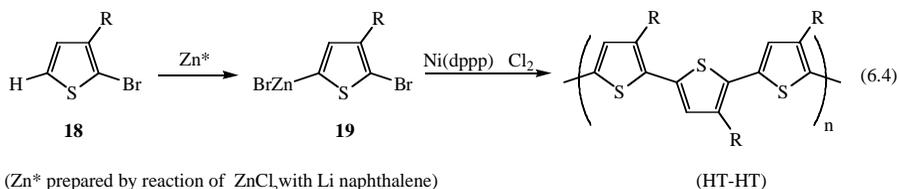


Figure 6.5 Regioregular synthesis of substituted polythiophene.

In a second useful approach to regioregular (HT) poly(3-alkylthiophenes), developed by Rieke et al.,⁵¹ highly reactive zinc (Zn*) is reacted with 2,5-dibromo-3-alkylthiophene substrates **18** to yield the metallated species **19** with high regiospecificity. Treatment of this intermediate with the cross-coupling catalyst NiCl₂(dppp) results in a regioregular (HT) poly(3-alkylthiophene) (Equation 6.4). The polythiophene products from the alternative McCullough and Rieke synthetic routes have similar properties.



An alternative, less sophisticated approach to regioregular substituted polythiophenes is the use of asymmetric 3,4-disubstituted thiophene monomers as substrates, resulting in the selective activation of either the 2- or 5 positions on

the thiophene ring. Using this method, poly(3-alkoxy-4-methylthiophenes) with > 95% HT couplings have been prepared via FeCl₃ oxidation.^{41,52}

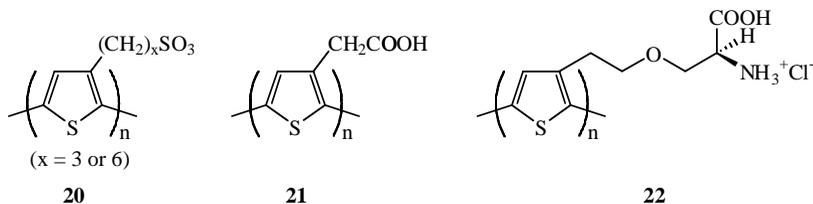
Using the above chemical synthetic approaches, a wide range of substituted polythiophenes have now been prepared, bearing functional groups that impart specific properties onto the polymers such as water solubility, sensor capabilities and chirality. Some specific examples are described below.

Polythiophenes with special functional groups

Water soluble polythiophenes

Several water-soluble sulfonated polythiophenes such as **20** ($x = 3$ or 6) have been prepared by the FeCl₃ oxidation of the corresponding monomers.^{53–55} ¹H and ¹³C NMR studies of these self-doped polymers in D₂O/DMSO-d₆ or D₂O/acetonitrile-d₃ showed a HT:HH ratio of 4:1 in both cases.⁵⁵

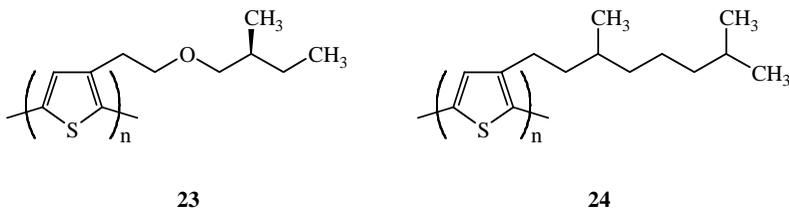
Related water-soluble polythiophenes with carboxylic acid substituents covalently bound at the thiophene ring 3-position have also been reported. For example, poly(3-thiophene acetic acid) **21** has been synthesized by Osada et al.⁵⁶ in 75% yield by the FeCl₃ oxidation of 3-thiophene methyl acetate, followed by alkaline hydrolysis and protonation. Its hydrogel has also been described.⁵⁷ The polymer has a molecular weight (M_w) of 16,000 and a polydispersity of 2.8. ¹H NMR studies show it to be *regiorandom*, with less than 40% HT-HT couplings.⁵⁶ Around pH 5-6 in aqueous solution, the polymer main chain of **21** undergoes an abrupt conformational change from the aggregated state to the extended state caused by electrostatic repulsions between the dissociated carboxylic acid substituents. McCullough et al.⁵⁸ have also prepared novel *regioregular* water-soluble polythiophenes with a propionic acid group at the ring 3-position, that self-assemble through carboxylic acid dimer pairs between adjacent chains. These undergo dramatic pH- and cation- induced color changes attributed to “unzipping” of the purple self-assembled state to a yellow, disassembled and twisted structure.



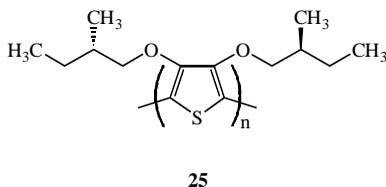
Another interesting water-soluble polythiophene is **22**, bearing a chiral amino acid side chain, which was prepared by Hjertberg, Inganäs and co-workers⁵⁹ by oxidative polymerization with FeCl₃. The chiroptical and solvatochromic properties of this optically active polymer are described in the later section entitled *Chiroptical properties of optically active polythiophenes*. The synthesis of other, organic solvent-soluble chiral polythiophenes is discussed directly below.

Chiral polythiophenes

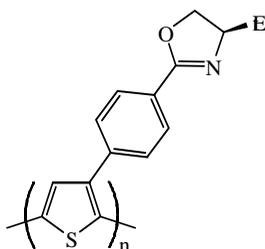
A large number of optically active polythiophenes have been prepared through the chemical polymerization of monomers bearing chiral substituents covalently bound at the 3-position of the thiophene ring. For example, Meijer et al.⁶⁰ prepared the regioregular (HT) chiral polythiophene **23** by polymerizing the (S)-(+)-2-phenylbutyl ether of 3-propylthiophene by the McCullough method. The strong optical activity observed for the polymer is induced by the chiral substituent, and is believed to be associated with aggregation of the polymer chains. Polymer **23** is soluble in a range of organic solvents, its chiroptical properties showing marked solvent and temperature dependence.



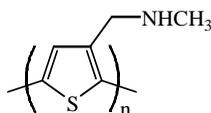
Similar thermochromic and solvatochromic effects have been observed by Bidan et al.⁶¹ for the optically active polymer **24** prepared in a regiospecific fashion (100% HT-HT coupling) by the McCullough method. In contrast, the analogous regiorandom polymer prepared by oxidation with FeCl₃ in chloroform is only weakly optically active. However, the disubstituted chiral polythiophene **25**, synthesized by Meijer et al.⁶² through the FeCl₃ route, is strongly optically active and also exhibits solvatochromism and thermochromism. This optical activity is again believed to be associated with a chiral π -stacked aggregated phase of the polymer, which is highly ordered due to the stereoregular structure of the substituent side chains.



Other optically active polythiophenes recently prepared using the regiospecific McCullough approach are **26** and **27**. The former polymer bears a chiral oxazoline group in its side chain and complexation of this group by metal ions induces solvent-dependent chirality in the polythiophene.^{63,64} Polythiophene formed using monomer **27** is water-soluble and becomes optically active upon binding to DNA.⁶⁵ To our knowledge, this represents the first example of induction of chirality into an achiral polythiophene through binding to a chiral moiety.



26



27

Post-polymerization modification — enhancing functionality

The synthesis of many substituted polythiophenes from their respective monomers is difficult because of the intolerance of the functional group to the synthetic conditions or due to electronic/steric retardation of the polymerization by the substituent. As described in earlier chapters for PPys and polyanilines, post-polymerization modification of preformed polythiophenes provides an alternative approach for preparation of functionalized polythiophenes. For example, nucleophilic substitution of overoxidized polythiophenes with methoxy and halogeno groups in the 4-ring position has been described.^{66,67} More recently, facile electrophilic substitutions of poly(3-hexylthiophene) to give 4-halogeno (Cl, Br) and 4-nitro derivatives have been shown to produce high yields (>90%) (Figure 6.6).⁶⁸ The halogenations were carried out using N-bromosuccinamide (NBS) and N-chlorosuccinamide (NCS) in chloroform at room temperature, while the nitration employed fuming nitric acid at 0°C. The halogenated polythiophenes may be useful precursors for further derivatization/functionalization.

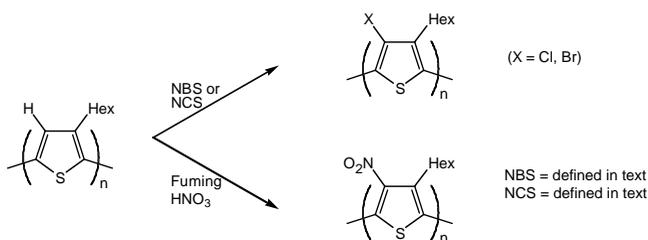


Figure 6.6 Electrophilic substitutions of polythiophenes.

Structure of Polythiophenes

In this section, the structural studies of polythiophenes are reviewed and the influence of structure on properties is considered in following sections. The description of polythiophene structures includes the alkyl-substituted thiophenes, such as poly(3-alkyl thiophenes) (P3ATHs).

Molecular Structure and Conformation

Chain Structure

The molecular structure of chemically polymerized 3-pentyl thiophene has been reported in one study.⁶⁹ Such polymers (poly(3-alkyl thiophenes) with alkyl groups longer than four carbons) are soluble in common solvents and, therefore, are conveniently studied using techniques including NMR, GPC and others. Proton NMR analysis of the chemically prepared P3PT showed that 81% of the polymer content was head-tail (HT) configuration, with the remainder HH or TT sequences. Infrared spectra taken of poly(3-pentyl thiophenes) P3PTh powder showed the absence of 2-4 coupled thiophenes. The conclusion was that all sequences were 2-5 coupled.

A comparison of doped and undoped PTh by ¹³C NMR has been reported by Hotta et al.⁷⁰ Their results show a remarkably simple spectra for both forms of the polymer consistent with all 2-5 ($\alpha\text{-}\alpha'$) coupling and in contrast to the more complex spectra obtained for polypyrrole.⁷¹ The doped PTh showed absorption shifted upfield compared with the undoped PTh, consistent with an increase in electron density of the former.

Molecular Weight

The study by Czerwinski et al,⁶⁹ described above, included an analysis of the molecular weight of soluble poly(3-pentylthiophene) by GPC. An estimate of the polymer molecular weight was made using polystyrene standards and the average molecular size was determined to be 118 repeat units. The polydispersity was 4.8, which is typical for such chemically oxidized polymers.

Bulk Structure

Crystallinity, molecular order, conformation in solid state

Electropolymerized Polythiophenes. As with PPys, the electrochemically prepared polythiophenes show small degrees of crystallinity (~ 5 %). The nature of the crystal structure has been investigated using x-ray diffraction. Ito and co-workers showed that electrochemically deposited PTh had a preferred molecular orientation parallel to the electrode surface.⁷² Again, this structural feature is the same as that observed in PPy (Chapter 2). Later work by these same researchers⁷³ investigated the reduced form of the electropolymerized PTh. The reduced PTh showed a crystallinity that was tentatively assigned an orthorhombic unit cell based on earlier work by Mo et al.⁷⁴ Reflections of the (110) and (200) planes were identified and corresponded to the unit cell dimensions: $a = 0.780$ nm, $b = 0.555$ nm, $c = 0.803$. Mechanical drawing of the reduced PTh (draw ratio 1.8) showed preferential orientation of the c axis parallel to the film surface. Sato et al. have also noted a preferred orientation parallel to the film surface upon mechanical drawing of reduced

PTh. However, the orientation effect was not as strong as that noted by Ito and the assigned crystal structure was somewhat different (orthorhombic $a = 0.108$ nm, $b = 0.474$ nm, $c = 0.756$ nm). The differences in the two studies may reflect the influence of different electrochemical preparation conditions. Surprisingly high crystallinity has been recently reported for electrochemically polymerized thiophene using a nickel electrode⁷⁵ with an ionic liquid (BF_3^- diethyl ether: $(\text{C}_2\text{H}_5)_3\text{O}^+.\text{BF}_4^-$) electrolyte. The estimated degree of crystallinity of PTh films made in this way was over 70% and the structure was assigned to a monoclinic unit cell with parameters $a = 0.624$ nm, $b = 0.593$ nm, $c = 596$ nm, and $\beta = 103.6^\circ$. The obtained films showed high tensile strengths (80 MPa) but relatively low conductivity (3.5×10^{-2} S cm).

Electrochemically prepared alkylated polythiophenes have been investigated by Garnier and co-workers.^{76,77} When comparing polythiophene and mono-substituted polyalkylthiophenes, these workers found an increase in crystallinity of the substituted thiophenes in comparison with the unsubstituted polythiophene. The degree of crystallinity was low (5%) but the crystal structure was assigned to a hexagonal cell ($a = 0.97$ nm, $c = 1.22$ nm). The structure could be described by a helical conformation with 11 thiophene units making one loop of the coil.

Solution Cast Polythiophenes. The crystal structure of solution cast thiophenes is qualitatively similar to that observed for the electrochemically prepared polymers. Given the complexity of the doped structure of these polymers, it is not surprising that there are discrepancies in the literature regarding the interpretation of the (relatively weak) x-ray diffractions. Similarly, the solution cast polymers give rather low-intensity scattering superimposed on a strong amorphous background. Comparison of various side chain lengths for P3ATs⁶⁹ shows an increase in the interchain spacing. The interchain spacing increases about 0.16 nm for each methylene group in the side chain.

Morphology and Density

The film morphology of electrochemically prepared polythiophene has been shown in numerous studies to be almost identical to that commonly observed for polypyrrole (and described in Chapter 2). A nodular surface is observed for both unsubstituted and 3-alkyl substituted thiophenes.⁷⁸ As with PPy, the electrochemical preparation of PTh at higher current densities produced rougher surface morphologies. The similarity in morphologies suggest a similar growth mechanism for electrochemically polymerized PPy and PTh.

A number of studies have investigated the effect of film thickness on PTh morphology. As with PPy, the films show a rougher surface texture with increasing polymerisation time.^{79,80} Tourillon and Garnier also compared unsubstituted (PTh) and 3-methyl substituted (P3MTh) and found different morphologies. In both cases, thin films gave flat and featureless surfaces. Thicker films (0.5 to 1.0 μm), however, showed wrinkled roughness of PTh

and nodular roughness for P3MTh when both were oxidized and doped with PF_6^- . A much flatter surface was produced when P3MTh was doped with CF_3SO_3^- . Different morphologies were observed in the reduced state, which also depended on the dopant present in the oxidized form of the polymer.

Masuda et al.⁸¹ have considered the morphology of PThs produced by an entirely different electrochemical procedure. In their work, the starting monomer was 2,5-bis(trimethylsilyl)thiophene (BTMSTh), which produces the unsubstituted PTh upon electropolymerization. Masuda et al. found that the PF_6^- doped PTh produced from thiophene monomer gave a nodular surface morphology, while BF_4^- gave a much flatter surface. However, for PTh produced from BTMSTh, the surface morphology was completely different: a fine nodular texture was produced with PF_6^- as dopant, but a quite rough nodular structure was produced with BF_4^- as dopant.

It is apparent that the determinants of PTh morphology are complex, as with other conducting polymers. However, the effects on mechanical and electrical properties, as well as switching properties, are likely to be significant and worthy of further investigation.

Properties of polythiophenes

Because polythiophene itself is prone to overoxidation during polymerization, most practical work has been carried out using alkylated thiophenes which have higher over-oxidation potentials. Synthesis of functionalized thiophenes (such as alkylated monomers) is much easier to achieve than with the pyrrole counterpart. The decreased activity of the sulfur group compared to that of the $-\text{NH}$ group means that the laborious steps involved in protecting the heteroatom during synthesis are not required for thiophene.

Conductivity

To achieve high conductivities, the polythiophene paradox must be overcome. The polymerization process and the conductivity of the resultant material are influenced by the concentration of monomer used during polymerization,⁸² because, if this is too low, the overoxidation reaction predominates, at least when galvanostatic polymerization is used. Synthesis at reduced temperatures will help avoid overoxidation and can be used to increase the conductivity of the resultant material.⁸³

As stated above, the presence of alkyl functional groups on the monomer⁸⁴ can be used to advantage in preventing overoxidation of the polythiophenes during synthesis. Conductivities as high as $7,500 \text{ S cm}^{-1}$ have been obtained for poly(methylthiophene).⁸⁵

As with PPys, the counterion used during electropolymerization influences the conductivity of polythiophenes.^{86,87} Electrochemically produced copolymers⁸⁸ of 3-dodecylthiophene (DTh) and 3-methylthiophene (MTh)

have been shown to exhibit conductivities intermediate to the two homopolymers. The actual value depends on the ratio of MTh/DTh in the polymer.

Other workers have reported that thinner, more compact polymers are more conductive than polymers grown to be thicker.⁸⁹ It has been shown that the conductivity of poly(2-octylthiophenes) decreases when exposed to atmospheres of higher humidity. This is presumably due to dedoping⁹⁰ of the polymer, although swelling at higher humidity would also decrease conductivity. The same group of researchers⁹¹ have shown that the conductive properties of polythiophenes could be stabilized by heat treatment. This thermal annealing process increased the crystallinity of the polymer.

The conductive properties of alkylated polythiophenes are known to be unstable, particularly at elevated temperatures. The mechanism of thermal undoping has been associated with thermal mobility. Consequently, various workers⁹² have considered synthesis of random copolymers (e.g., thiophene and 3-octylthiophene), with well-distributed octyl side groups leaving space around the main chains to accommodate dopants.

In general, the conductivity of materials produced using the chemical oxidation process is lower than for those made electrochemically. Higher conductivities can be obtained by chemical production of copolymers, for example, using polymethylthiophene and polyurethane,⁹³ conductivities as high as 26 S cm^{-1} have been reported.

Mechanical Properties of Polythiophenes

As with the polyanilines, polythiophenes can either be prepared directly by electropolymerization or by casting from solutions (for the alkyl-substituted thiophenes). Most interest has focused on the latter due to their improved mechanical properties compared with the electrochemically prepared films. The factors influencing the mechanical properties of PThs are reviewed in this section.

The relationship between the mechanical properties and the morphology of electrochemically prepared PTh has been examined by Ito et al.⁹⁴ Their results showed that the Young's modulus (E) and breaking strength (σ_b) decreased by approximately 50% when the current density during polymerization increased from 0.7 to 5.0 mA/cm². The oxidized PTh films were powdery, which presumably reduced the strength and gave a lower elongation at break. A higher current density for growth produced excessively high cell potentials that were thought to cause degradation of the polymer. The higher current density also increased the roughness of the surface nodules and the same relationship between nodular boundaries and tensile strength observed for polypyrroles (see Chapter 3) is also likely to hold for the PTh films. Thus, the higher current densities produce a rougher morphology and weaker boundaries between the nodules that results in mechanical failure at lower stress and strain.

The effect of doping on mechanical properties has been reported by a number of workers. Yoshino et al.⁹⁵ observed that undoped PTh had a higher

stiffness ($E = 1300 \text{ MPa}$) and tensile strength ($\sigma = 55 \text{ MPa}$) than the BF_4^- -doped PTh ($E = 360 \text{ MPa}$; $\sigma = 15 \text{ MPa}$). Similarly, Ito and co-workers observed that the mechanical properties (E , α_b and strain at break, ϵ_b) of the electrochemically reduced PTh films were all increased compared with the as-prepared oxidized films.⁹⁴ Again, the reduced films showed lower strength, modulus and elongation at break when prepared at a higher current density. In the best case (current density 0.7 mA/cm^2), the reduced PTh had a $E \sim 3.3 \text{ GPa}$, yield stress $\sim 70 \text{ MPa}$, $\alpha_b \sim 265 \text{ MPa}$ and $\epsilon_b \sim 95\%$. The general observation of increased stiffness and strength for the reduced polythiophene is the opposite of that observed for polypyrroles (see Chapter 3). In the case of PPy, the oxidized state was observed to be stiffer and stronger, but less ductile than the reduced state due to the ionic crosslinking that is induced by ionic nature of the polymer. In the case of PTh, it is possible that the increased solvent content that accompanies oxidation causes a plasticization effect that is greater than the ionic crosslinking so that the oxidized films are more ductile and flexible.

Moulten and Smith^{96,97} have reported on their studies of the effects of doping and alkyl-substituent length on the mechanical properties of P3ATHs cast from 3% solutions in chloroform. In contrast to the studies reported above for electrochemically prepared PTh, it was shown that the alkylthiophenes became stiffer (by an order of magnitude) and stronger (doubled) when doped with FeCl_3 . These workers also noted that anhydrous FeCl_3 doping produces brittle polymers, whereas the use of $1 \text{ M FeCl}_3 \cdot 6\text{H}_2\text{O}$ avoided this problem, presumably due to the plasticization by water molecules. The increase in stiffness and strength of the PTh upon doping was attributed to more effective interchain bonding through $\pi\text{-}\pi$ overlaps of neighbouring thiophene rings.

Mechanical drawing of PTh films and fibers has also been observed to increase the stiffness and strength.^{94,97} Ito and co-workers showed that drawing the reduced PTh increased E to 8.5 GPa and α_b to 265 MPa (draw ratio of 1.8).⁹⁴ Commonly observed in many polymers (including other ICPs), the increased stiffness and strength is attributed to the alignment of the macromolecules in the draw direction. Moulten and Smith⁹⁷ observed similar behavior with 3-substituted polythiophenes, however, the increase in stiffness and strength were not as significant as reported by Ito et al. In fact, for a given draw ratio, the increase in stiffness and strength decreased as the length of the alkyl chain increased. Similar results have been obtained by Van de Leur et al.⁹⁸ using dynamic mechanical analysis of hexyl-, octyl- and dodecyl-substituted PThs.

The mechanical properties of PThs have been modeled by Moulten and Smith⁹⁷ in terms of the macromolecular structure and intermolecular bonding. On the basis of their model, these authors have found good agreement between the measured and predicted Young's modulus. Thus, the effect of the alkyl side chain can be explained by a dilution effect, whereby longer side chains result in greater separation of the macromolecules. This means

that there are fewer load-bearing covalent bonds per unit cross-sectional area, so that the stiffness is lower. In addition, these workers found that coupling defects (i.e., head–head and tail–tail couplings in P3AThs) reduce the effective π - π overlaps between macromolecules and also reduce stiffness. A slight variation in the number of such defects was observed in the 3 P3AThs studied — slightly higher in the octyl- and dodecyl-substituted PThs compared with the hexyl-substituted PTh.

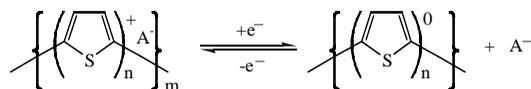
Chemical properties

Studies of the chemical properties of polythiophenes have been limited. As with PPys, a hydrophobic backbone is formed and the polymer has ion exchange properties. Modification of chemical properties by incorporation of appropriate counterions is not so readily addressable since polymerization must be carried out from nonaqueous solution and occurs at more anodic potentials compared with pyrrole.

However, some workers have incorporated a selection of counterions,^{87–89} Others⁹⁹ have incorporated heteropolyanions with a view to their use as electrocatalytic electrodes. The fact that thiophenes are easier to derivatize than pyrroles is also attractive in that chemical functionality can be introduced by derivatization. A range of functional groups have been introduced^{100–105} to modify the chemical properties of polythiophenes. The ability to attach active groups such as amino acids provides an attractive route for modifying the molecular recognition properties of the resultant properties. The decreased activity of the sulfur groups compared to the NH group also means that derivatization after polymerization is more easily accomplished.¹⁰⁶

Switching properties

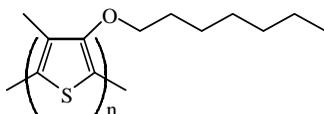
As with PPys, the properties of the polythiophenes can be modulated by application of electrical stimuli, according to:



This picture is undoubtedly oversimplified. Different sites are switched at different potentials, and when A^- is A relatively immobile (e.g., a polyelectrolyte anion) cation movement accommodates the oxidation/reduction process.

The switching properties are determined by the electrochemical conditions employed during growth, by the counterion incorporated and by the substituents attached to the thiophene ring.¹⁰⁷ For example, poly(3-heptoxyl-4-methyl-thiophene) **28**, switches at 0.76 V, while, under the same conditions, poly(3-octylthiophene) switches at 1.01 V. The electrolyte used for switching

also has a marked effect on the potential, rate and reversibility of the switching process.¹⁰⁸



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Polythiophenes are in general more hydrophobic materials than PPys. Electrochemical switching is not so efficient in aqueous media. As a result, some workers have used the ability to attach functional groups such as polyethers¹⁰⁹ to increase the hydrophilicity and to improve electrochemical behavior in aqueous solutions.

Optical properties of polythiophenes

Electronic band structure and UV-visible spectra

Theoretical studies indicate that neutral polythiophene (like PPy) has a non-degenerate ground state, with mesomeric aromatic and quinoidal structures of nonequivalent energy.¹¹⁰ Oxidative doping leads to the formation of two bands in the band gap corresponding to a polaron (radical cation). However, both calculations^{110,111} and measurements of UV-visible spectra during increasing doping¹¹² suggest that the polarons are unstable compared with spinless bipolarons (dications). The two subgap absorption bands that appear at ca. 0.5 and 1.5 eV with increasing doping of polythiophene have therefore generally been assigned to electronic transitions involving bipolarons. However, other studies of lightly doped poly(3-methylthiophene) suggest that polarons may instead be involved.¹¹³

The majority of UV-visible spectral studies have been carried out on neutral polythiophenes whose spectra are dominated by the band gap $\pi-\pi^*$ transition. The position of this peak has been widely used as a measure of the conjugation length of the polymer backbone, undergoing a red shift with increasing conjugation length. Extensive comparisons have been made between regioregular and regioirregular poly(3-alkylthiophenes), where the much lower energy $\pi-\pi^*$ transitions of regioregular polymers indicates a longer conjugation length compared to corresponding regioirregular polythiophenes.¹¹⁴ Another feature of the regioregular poly(alkylthiophenes) is the appearance of vibronic structure on the $\pi-\pi^*$ absorption bands.

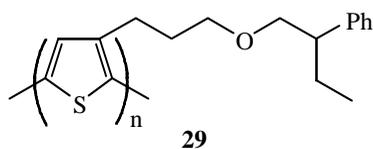
Thermochromism and solvatochromism in poly(3-alkylthiophenes)

A striking feature of neutral poly(3-alkylthiophenes) is their thermochromism, observed both in the solid state and in solution.^{115,116} Upon heat-

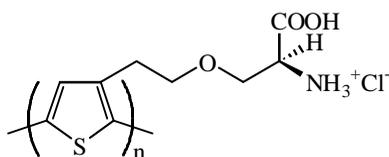
ing, a marked blue shift occurs for the highest wavelength π - π^* absorption band. Similar marked changes in color are observed upon transferring from a "poor" solvent to a "good" solvent.^{115,117} In both cases, these color changes have been attributed to a twisting of the polythiophene backbone from an essentially planar to a less ordered nonplanar conformation. This is supported by theoretical calculations.¹¹⁸ Further evidence for the conformational changes occurring in these systems comes from circular dichroism spectral studies of optically active poly(3-alkylthiophenes), described below.

Chiroptical properties of optically active polythiophenes

A wide range of optically active polythiophenes have been reported, prepared in general through the electrochemical or chemical oxidation of monomers in which a chiral substituent is covalently attached to the 3-position of the thiophene ring. The first example was the electrochemically prepared polymer **29**, which exhibited a very large optical rotation ($[\alpha]_D = + 3000^\circ$) compared with the corresponding monomer ($[\alpha]_D = + 21^\circ$).¹¹⁹ This high optical activity for the polymer was interpreted in terms of the adoption of a one-handed helical conformation by the polythiophene main chain induced by the presence of the chiral propyl-2-phenylbutyl ether substituent. Unfortunately, no circular dichroism spectrum was recorded. However, cyclic voltammograms of (*S*)-**29** recorded in acetonitrile solvent in the presence alternatively of (+)- and (-)-camphorsulfonic acid (HCSA) revealed significant chiral discrimination by the polymer in its doping by the enantiomeric CSA⁻ anions (50% higher with (+)-CSA⁻ compared with (-)-CSA⁻. The opposite enantioselectivity was observed with (*R*)-**29**.



Hjertberg et al.¹²⁰ have reported the circular dichroism (CD) spectrum of the related chiral polythiophene **30**, which contains a chiral amino acid group attached to the thiophene units by an ether linkage. In water solvent, a pair of exciton-coupled CD bands are observed in the visible region associated with the π - π^* transition band in the UV-visible spectrum at ca. 430 nm. These chiroptical features are attributed to a helical conformation adopted by the polymer backbone under the influence of the chiral side chain. However, in methanol solvent no CD bands are observed and the π - π^* absorption band is blue shifted. This suggests a change in polymer chain conformation in methanol solvent to a more planar arrangement.

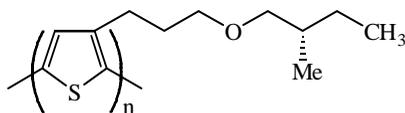


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In a series of elegant papers, Meijer et al.^{121–124} have observed remarkable solvent- and temperature-dependent CD spectra for a range of regio-regular (head-to-tail) chiral polythiophenes. For example, while the regio-regular polythiophene **23** is optically inactive in the “good” solvent chloroform, successive addition of the “poor” solvent methanol results in the progressive appearance of three (overlapping) exciton-coupled CD bands corresponding to each of the three vibronic bands of the π - π^* transition seen at 512, 540 and 592 nm in the visible spectrum.¹²¹ An extremely high chiral anisotropy factor ($g = \Delta\epsilon/\epsilon$) of ca. 2.2 % was determined for a solution of **23** in 40% CHCl_3 /60% CH_3OH . The authors attributed the observed optical activity to the helical packing of the polymer chains into a chiral supramolecular aggregate induced by the optical active side chains, rather than the adoption of a helical conformation by individual polythiophene chains. Films of polymer **23** spun cast from solution also show optical activity associated with the π - π^* absorption band, but lose this upon heating above the polymer melting point of 160°C.¹²² Surprisingly, while the original polymer optical activity is recovered upon slow cooling, rapid cooling generates a film with the inverse CD spectrum, indicating the formation of a chiral superstructure of opposite handedness.

This sensitivity of the handedness of chiral substituted polythiophenes to the conditions under which micro-aggregation occurs has been further confirmed in detailed thermochromic and solvatochromic studies by Meijer et al.^{123–125} on **23** and the related chiral polythiophenes **32** and **25**. Polymers **23** and **32** are optically inactive in dichloromethane solvent at room temperature, but develop strong CD spectra upon cooling to -73°C .¹²³ In contrast, in 1-decanol solvent **23** and **32** are optically active at room temperature, presumably due to the ability to form a chiral aggregated phase at room temperature in this “poor” solvent. Significantly, the CD spectra in 1-decanol are inverted compared to those recorded in dichloromethane, indicating the adoption of the opposite handedness by the chiral superstructures. The sensitivity of the hand of the chiral organization of the polymer chains to the ordering conditions suggests only a small difference in the energy between the two diastereomeric forms.¹²³ The disubstituted chiral polythiophene **32** similarly only exhibits optical activity at room temperature in the presence of “poor” solvents such as methanol.¹²⁴ In this aggregated form the photoluminescence spectrum of **32** is also circularly polarized. Heating

the solution to 120° C causes a conformational change to an optically inactive disordered form.¹²⁴



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Similar remarkable inversions of CD spectra have been reported by Bidan et al.¹²⁶ for the stereoregular form of polythiophene **25**. This polymer is optically inactive in the “good” solvent chloroform. No change in the UV-visible and CD spectra upon addition of up to 30% of the “poor” solvent methanol. However, from 35 to 37.5% methanol, strong CD bands appear in the visible region between 430 and 630 nm, presumably associated with the formation of a chiral aggregate. Interestingly, the addition of further methanol (42 to 50%) results in the progressive appearance of an inverted CD spectrum, consistent with the adoption of a chiral superstructure of the opposite hand. Other researchers¹²⁷ have recently reported similar inversions of chirality for the optically active polymer **18**, bearing a chiral oxazoline residue in its side chain.

Polymer **24** has also been reported to exhibit an unique, induced CD spectrum (associated with the polymer π - π^* absorption band) caused by the complexation of metal ions such as Cu(II) and Fe(III) to the oxazoline group in the “good” solvent chloroform.¹²⁸ The authors suggested that this induced optical activity arises from the formation of colloidal particles in which the polymer adopts a one-handed helical conformation. Another recent paper¹²⁹ reports what appears to be the first example of an optically active substituted polythiophene in a “good” solvent, i.e., where the polymer is believed to be in an unaggregated form. This disubstituted polymer exhibits bisignate CD bands at ca. 300 and 337 nm, associated with the π - π^* absorption band at 318 nm. The large blue shift of this π - π^* absorption band compared to other poly(3-alkylthiophene)s indicates a short conjugation length for this polymer, arising from twisting of the polythiophene backbone from planarity. It was suggested that the observed bisignate CD bands of unequal rotational strength arise from diastereomeric helical sections, with the majority adopting a (+)-Cotton screw-sense and the minority a (-)-screw-sense.

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chapter seven

Processing and device fabrication

All the practical uses of conductive electroactive polymers (CEPs), including intelligent material systems, require the ability to integrate them into other structures and/or to implement innovative device fabrication protocols using CEPs. As pointed out in previous chapters, the optimization of chemical properties results in some compromise in electrical and mechanical properties and vice versa. There is a further requirement for the use of integrated material systems in the development of intelligent structures and from that arises the need to spatially resolve function. The discrete physical location of sensing and actuating loci throughout a “mechanically stable” structure is required for many applications. Practically useful, intelligent structures based on these materials can therefore only be realized if the properties of CEPs can be retained and a structural integrity obtained by weaving the active components throughout other synthetic or naturally occurring systems. This can be achieved either by combining the conducting polymers within other structures or devices after polymerization or by assembling the conducting polymer within a host matrix.

Integration/fabrication after polymerization

For most conventional polymer structures, blending is used to achieve the desired properties of the composite structure. Conventional polymers are amenable to this approach because they are either soluble in common organic solvents or fusible (melt before decomposing). This has generally *not* been the case with CEPs, although significant advances have been made through modifications to the polymer structure. Outlined below are recent advances in the integration of CEPs into other polymer structures by either solution or melt processes.

Solution processable CEPs

Polyaniline is most amenable to solution processing. The emeraldine base (EB) form of polyaniline is soluble in selected solvents such as methyl

pyrrolidinone¹ or strong acids.^{2,3} More recently, it has been discovered that solubility of the doped form can be induced by the use of appropriate “surfactant-like” molecules as dopants.⁴ Camphor sulfonic acid or dodecyl benzene sulfonic acid have proven particularly useful in this regard. Once solubilized, these polyanilines can be cast into sheets or blended with other conventional polymer structures. For example, the presence of the surfactant counterion molecule facilitates the blending process⁵ with polymers such as:

- polyethylene
- nylons
- polycarbonate
- polystyrene
- polyvinyl acetate
- polyvinyl chloride

When PAn/CSA is dissolved in *m*-cresol with poly(methylmethacrylated) (PMMA), this can be spun cast to form optically transparent films.⁵

Pron and co-workers⁶ have blended polyaniline with cellulose acetate and cast from *m*-cresol to produce highly transparent and conductive ($\approx 1 \text{ S cm}^{-1}$) polyaniline. Addition of plasticizers (in particular phenylphosphonic acid) not only resulted in more flexible films but lowered the percolation threshold for polyaniline to an amazing 0.05% (w/w).

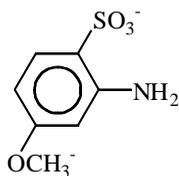
De Paoli⁷ has used the more soluble poly(*o*-methoxyaniline) doped with *p*-toluene-sulfonic acid to prepare a composite blend with poly(epichlorohydrin-co-ethylene oxide) but conductivities were relatively low ($10^{-3} \text{ S cm}^{-1}$) even with high 50% (w/w) conducting polymer loading.

Others⁸ have blended polyaniline doped with dodecylbenzenesulfonic acid with polyvinyl alcohol in water or with polyacrylate in organic solvents to obtain transparent conductive composites.

Solution processing of polypyrroles (PPys) and polythiophenes has been limited by these materials' lack of solubility. To overcome this, some work⁹⁻¹¹ has been concerned with attaching alkyl groups to PPys or polythiophenes to increase solubility. This has had the desired effect of increasing solubility in common solvents such as CH_2Cl_2 or CHCl_3 , in some cases in excess of 300 g/L polymer could be dissolved.

The solubility of polythiophenes has also been increased by attaching alkoxy groups to bithiophene monomers.¹² The presence of the alkyl group does, however, result in the production of polymers with lower conductivity. Other workers¹³⁻¹⁵ have been concerned with producing pyrroles and thiophenes with alkyl-sulfonated chains attached to increase the water solubility of the polymer.

Sulfonate groups have also been attached to polyaniline either after¹⁶ or before¹⁷ polymerization in order to induce water solubility. The latter approach requires addition of a methoxy (electron donating group) to the aniline ring to counterbalance the effects of the electron withdrawing sulfonate group during polymerization (see structure 1).



1

Again, solubility and hence processability are improved at the expense of the electrical (decreased conductivity) properties of the polymer.

Given the lack of solubility of conducting polymers that have the desired electrochemical and/or chemical properties, colloidal processing provides an attractive alternative. Colloids are readily dispersed throughout other solutions for subsequent processing into other structures. Conductive electroactive colloids of PPys or polyanilines are readily prepared by carrying out the oxidative polymerization in the presence of a steric stabilizer.¹⁸ Stabilizers such as polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP) and polyethylene oxide (PEO) have been used the range 10 to 100 nm can be prepared. While conductivity of the colloids is less than that of electrodeposited films, it is respectable (up to 10 S cm⁻¹).

Once formed, these colloids may be used for further processing. For example, they can be mixed with paints.¹⁹ The products formed are as conductive as those obtained when carbon black is added to paints. However, they are also electroactive and presumably (at least the colloidal component) retain the unique chemical properties of the conducting polymer.

In some cases, larger conducting polymer particles have been mixed with other polymers. For example, Bose and co-workers²⁰ incorporated chemically synthesized PPy into polyvinylchloride (PVC) or nafion. After casting, the materials were shown to be electroactive and demonstrate electrocatalytic properties.

Melt-processable CEPs

As with solution processing, there have been significant recent advances in melt processing of CEPs.²¹⁻²³ Again, most interest has been with polyaniline. The most successful approach has been to use specific dopants to induce melt processability. Thus, various dopants have been used that combine an acid group (eg. sulfonic or phosphoric acid) with hydrophobic segments (Figure 7.1). The latter causes a plasticization of the host polyaniline and reduces the strong interchain bonding caused by its aromaticity, H-bonding and charge delocalization. Once suitably plasticized, the doped polyaniline is able to be fused to form free-standing films by hot pressing.

In one series of studies, Paul and Pillai²² used various phosphate ester dopants to induce melt processability in polyaniline. Conductivities as high as 1.8 S cm⁻¹ were reported for melt pressed pellets of PANi-PDPPA.²³ The

These demonstrations of melt processability for PANi provide an avenue for the convenient preparation of films and fibres of CEPS. The absence of solvent makes the melt processing route more attractive and environmentally friendly than alternative solvent processing. In addition, the melt processable CEPS are then easily incorporated into polymer blends using the well-developed processing techniques (extrusion and so on) widely used for thermoplastic polymers.

Assembly of conducting polymers in host matrices

Conducting polymers can be integrated into other structures at the point of assembly using either the chemical or the electrochemical oxidative route.

Chemical polymerization

The simplest approach is to imbibe the oxidant or monomer into a suitable host structure. This material is then exposed to the monomer or oxidant, respectively, and the polymer material is grown throughout. For example Bjorklund and Lundstrom²⁴ described a procedure whereby cellulose paper was first exposed to a metal salt (FeCl_3) that would act as the polymerization agent. The metal salt-soaked paper was then exposed to the pyrrole monomer in liquid or vapor form. Materials with conductivities of approximately 2 S cm^{-1} could be produced using this approach.

We have found similar results in our laboratories making impregnated papers with PPy and PAN for inverse thin layer chromatography.²⁵ The method we used to prepare polyaniline-modified paper was to load filter paper strips with aniline, which was allowed to diffuse throughout the paper for about ten minutes. The strips were then immersed in FeCl_3 that had been acidified with HCl. Chemical polymerization was allowed to proceed for about forty hours. The chemical structure of polyaniline prepared in this manner was presumed to be the same as the electrochemically polymerized polymer. However, the morphology of the polymer surface was that of the filter paper substrate. The polyaniline adheres well to the filter paper when it is dried, and no problems with chemical instability were observed.

Other workers^{26,27} have invented processes whereby a range of textiles can be coated with CEPs (PPy and PAN) using a simple *in-situ* polymerization process. A uniform adherent, conducting and electroactive coating is produced using this simple approach. The mechanical properties of the base textile are not significantly affected. Hydrophilic textiles such as rayon or cotton could be coated, as well as hydrophobic fibers such as polypropylene or polyester. Quartz fibers and Kevlar have also been coated. The authors suggest that the adherent coating arises from the fact that it is not the monomer or oxidant that is adsorbed on to the textile, but rather the radical or oligomers.

Nylon, glass fabric and glass wool²⁸ have been coated with polyaniline using similar procedures. In this case, the material to be coated is soaked in a solution containing aniline and a doping agent such as benzene sulfonic acid, *p*-toluene-sulfonic acid, 5-sulfosalicylic acid, or sulfuric acid is added with the oxidant (ammonium peroxydisulfate). The fibers appear to be uniformly coated with the CEP, and the coatings obtained were electroactive.

PAn has been integrated into other structures (polyethylene, terephthalate, polyester and polystyrene) by soaking in monomer solutions and then exposing to acidic oxidant (FeCl_3) solutions.²⁹ Results suggest that the polymers were swollen by the aniline monomer and that polymerization occurred within these swollen media to produce dispersed polyaniline granules. Conductivities of the order of $10^{-1} \text{ S cm}^{-1}$ were obtained.

PPy has been coated on polymethylmethacrylate (PMMA) or polyethylene spheres³⁰ using a chemical polymerization process. The spheres were dispersed in methanol and then added to water containing FeCl_3 oxidant. Pyrrole dissolved in water was subsequently added. The coated spheres could be mixed with noncoated spheres of PMMA and hot-pressed to obtain films with conductivities of 3.5 S cm^{-1} .

Other workers have coated nylon by imbibing pyrrole into the film followed by exposure to oxidant.³¹ Polymerization only occurred in the surface layer ($5 \mu\text{m}$), resulting in formation of a heterogeneous structure. Nylon 6,6 (N66) with incorporated PPy had a much higher initial modulus of 2.6 GPa, compared with 1.7 GPa for N66 alone. However, the elongation to break was also markedly reduced, from 350% for N66 to 60% for N66/PPy.

Kelkar and Bhat³² described a modified method for making nylon PPy composites. In the modified method, the nylon is first doped with copper chloride. Since CuCl_2 acted as an initiation site for polymerization, the authors argue that this resulted in more continuous conducting polymer chains throughout the nylon and a higher bulk conductivity.

Chemical polymerization onto sulfonated (dopant-containing) synthetic polymers has also been described.³³ Sulfonated polyethylene-polystyrene was exposed to monomer and then the oxidant. A mixture of $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ led to more accurate control of the E° value of solution. These same workers also described a novel chemical/electrochemical method, whereby pyrrole was initially polymerized using a low concentration of Fe^{III} . The reduced Fe^{III} can then be reoxidized electrochemically to regenerate the oxidant. Using this chemical/ electrochemical process, composite polymers with conductivities as high as 35 S cm^{-1} were obtained.

PPys have been integrated into other structures by polymerizing in the presence of a dissolved polymer. For example,³⁴ polymerization of pyrrole has been achieved in a solution of polycarbonate dissolved in CHCl_3 with FeCl_3 as oxidant. The composite was then precipitated using a nonsolvent such as methanol, ethanol or acetone. The resultant structure was polycarbonate with conducting PPy dispersed throughout the matrix.

A similar procedure was used to produce PPy-poly(ethylene-*co*-vinyl acetate) [PEVA] composites.³⁵ The host polymer can be dissolved in a toluene solution with pyrrole. A concentrated dispersion is then formed by adding it to an aqueous solution containing a surfactant. An aqueous solution of the oxidant (FeCl_3) is then introduced to form the polymer. The conductivity of the resultant materials was approximately 5 S cm^{-1} . The PEVA-based composites can be processed into films and other shaped articles by hot-pressing at approximately $100\text{--}150^\circ \text{C}$ and $15\text{--}20 \text{ MPa}$ pressure for 1 hour. The mechanical properties are determined by the PEVA content. For example, for composites of PPy-PEVA containing 20% (w/w) PPy, soft flexible films that can be extended up to 600% were produced. For pure PPy films, elongations of less than 5% are achievable.

From the same laboratory, another report³⁶ describes the use of this approach to prepare PPy/poly(alkyl methacrylate). In this case a chloroform solution of poly(alkyl methacrylate) and pyrrole is dispersed in an aqueous surfactant solution whereupon the oxidant is added. The PPy deposits on the host polymer and again a nonsolvent is used to precipitate the composite. The composites can then be hot-pressed to obtain films or other objects. Compared with cold-pressing, hot-pressing improves the mechanical properties but decreases the conductivities. In the hot-pressed materials, a distinct PPy phase could not be observed.

A similar approach³⁷ was used to prepare polyaniline/poly(alkyl-methacrylate) composites. Sodium persulfate was used as the oxidant in acidic (HCl) media and the composite was precipitated by addition of methanol. Again, hot-pressing was found to improve the mechanical properties and conductivities of 2 S cm^{-1} were obtained. While higher conductivities could be obtained with cold-pressing, the mechanical properties were inferior.

Polyaniline composites have been formed by polymerizing aniline in the presence of a latex.³⁸ The latexes were chlorinated co-polymers (Haloflex EP 252), which were film-forming latexes. Interestingly, the thermal stability of the resultant composite was better than either of the individual components. Polyaniline-polyacrylamide³⁹ composites have been prepared by carrying out a chemical oxidation of aniline in the presence of polyacrylamide. Films that could be cast were stable up to 250°C . However, conductivities were low (approximately $5 \times 10^{-2} \text{ S cm}^{-1}$).

An alternative approach⁴⁰ involves polymerization of conventional polymer in the presence of a soluble conducting polymer (alkylated thiophene) to form a semi-interpenetrating network. The polythiophene was dissolved in solutions of styrene and divinyl benzene; conductivities in the range $0.01\text{--}0.10 \text{ S cm}^{-1}$ were obtained.

Conducting polymers have been formed inside other porous structures such as crosslinked polystyrene.^{41,42} In the latter report, attachment of alkyl chain to the pyrrole improved the wetting characteristics and hence the mechanical properties of the composite.

An interesting approach to conducting polymer composite formation was reported by Mohammadi and co-workers,⁴³ who use Cu(II) complexed

to polyvinylpyrrolidone as the oxidant. They reported that composites with adequate mechanical and electrical properties can be obtained using this approach.

Interfacial polymerization

Where the support material to be employed is porous to the monomer and/or oxidant, a novel approach coined “interfacial” or “diaphragmatic chemical” polymerization may be used (Figure 7.3).

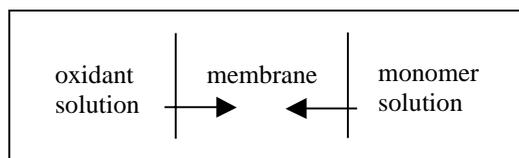


Figure 7.3 Interfacial polymerization to produce conducting polymer membrane.

Essentially, a membrane transport cell is used with oxidant on one side and monomer solution on the other. Where polymerization occurs depends on the relative mobility of the oxidant and the monomer.⁴⁴ In fact, this can be used to localize conducting polymer formation within the membranes. For example, with a nafion membrane and the use of $S_2O_8^{2-}$ as oxidant, polymerization is restricted to the oxidant side of the membrane due to anion exclusion (nafion is negatively charged). When Fe^{3+} is used as oxidant, polymerization occurs throughout the membrane. The use of different solvents can also affect the transport processes for oxidant and monomer. This was used to fix the point of polymerization by other co-workers who prepared PPy-poly(vinyl chloride) structures.⁴⁵ Similar procedures have been used to coat PPy onto cellulose acetate and PVC.⁴⁶

Others have used a vapor phase interfacial polymerization approach to produce thin conducting polymer coatings on conventional membranes.⁴⁷

Electrochemical integration

Provided electrodes can somehow be embedded into another polymeric material that has sufficient porosity to allow monomer and counterion species to ingress, electropolymerization can also be used to make composite materials.

Electropolymerization can be used to coat other substrates, not just planar electrodes, resulting in the production of conducting polymer “composites.” For example, electrochemical methods have been used to coat spherical graphite particles in a pulsed bed reactor.⁴⁸ In fact the substrate to be coated need not be conductive. Electropolymerization can be used to coat other structures by producing polymer in solution that is subsequently deposited onto other surfaces. This is possible because conducting polymers are formed

in solution even when electrochemical methods are used. Judicious cell design, therefore, enables conducting polymers to be produced at an electrode where it is not adhesive, and to coat other surfaces that adsorb it more readily. For example, nonconductive silica particles can be coated using this method.⁴⁹ This same principle has been used to coat fibers in a flow-through electrochemical cell (Figure 7.4).⁵⁰ For poly(3-methylthiophene) and PPy fiber, growth rates of approximately 30 cm hr^{-1} are achievable. Coated Kevlar or polyester string shows good adhesion of CEPs. Stand-alone conducting polymer fibers (with conductivities) of 6.2 S cm^{-1} have also been produced using this approach.

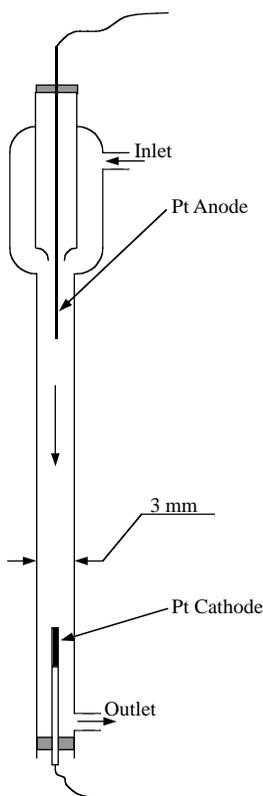


Figure 7.4 Schematic of the electrochemical flow cell used to grow conducting poly(3-MTh) on fibers. A centrifugal pump is used to pump the electrolyte solution through the gel (from Reference 50).

Electrochemical polymerization has also been used to coat natural fibres such as cotton, silk and wool⁵¹ or synthetic carbon fibers⁵² with PPy.

Polyanilines are particularly useful in that they can be dissolved at concentrations sufficient to allow solution spinning of homogeneous fibers.⁵³ This process has recently been commercialized by Santa Fe Science and

Technology (Figure 7.5). This does require the addition of gel inhibitors to allow the spinning process to be used.^{53,54}

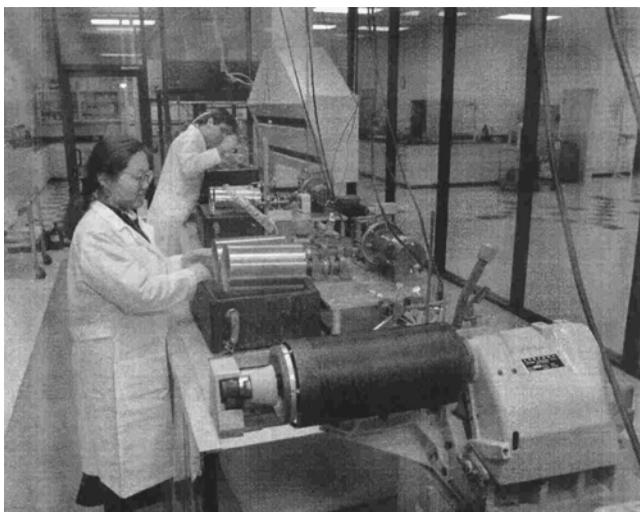


Figure 7.5 The polyaniline fiber-spinning facility at Santa Fe Science and Technology USA. (Photo courtesy Ben Mattes, Santa Fe Science and Technology.)

Monkman and co-workers⁵⁵ have reported conductivities as high as 1900 S cm^{-1} for homogeneous polyaniline fibres containing 2-acrylamido-2-methyl-1-propane sulfonic acid as dopant after drawing to 500%.

As early as 1984,^{56,57} it was reported that conductive polymer composites could be prepared electrochemically by polymerizing pyrrole on a working electrode coated with the support polymer (e.g., polyvinyl-chloride = PVC). According to Wang and co-workers,⁵⁸ the uniformity and conductivity of the polymer were improved if electrolyte was incorporated into the PVC prior to inducing electropolymerization.

Other workers have prepared poly(*N*-methyl-pyrrole)/poly(biphenol-A-carbonate) (PC) using this approach.⁵⁹ The electrodes were dip-coated with the PC and then electropolymerization was induced. Thermogravimetric analysis verified that a graft copolymer was produced. A similar procedure has been used to prepare polyaniline composites with the same host polymer.⁶⁰ The *in situ* electrochemical polymerization process has also been used to prepare polyacrylonitrile/PPy composite films.⁶¹

With these systems, conducting polymers start to grow from the electrode side. If polymerization times are short, only the electrode side is conductive, enabling a degree of spatial control that allows structures to be formed. As pointed out earlier, this may be important in producing intelligent material structures where localized polymerization is required to provide spatial distribution of function.

polymerization/gelation. Monomer and electrolyte can then be introduced to the gel and polymerization can be induced electrochemically. The electrochemical gel cell set-up is shown in Figure 7.4. Upon application of an appropriate potential, conducting polymer growth is initiated and eventually “fills” the gel (Figure 7.7).

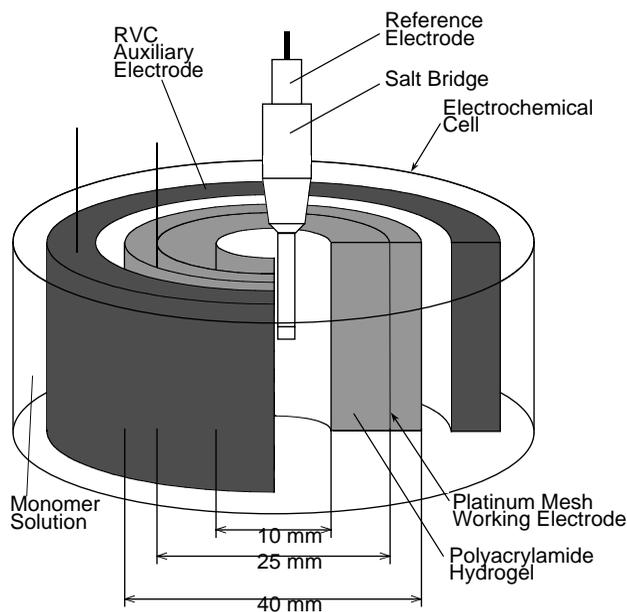


Figure 7.7 The gel cell.

Retaining the open porous structure of gels, these polymers contain approximately 90% water^{69,70} (Figure 7.8). They retain the redox switching characteristics of PPy films and the inherent ability of the hydrogel host to be dehydrated and rehydrated. Presumably, this is because the growth of the conducting polymer is regulated by the crosslinked hydrogel network. The resultant gel composites are electroactive and electrically conducting. The large open porous structure results in a high degree of electrochemical efficiency, which in turn improves the controlled release capabilities of the conducting polymer. This has been demonstrated by comparing the release profiles of a sulfonated dye from a simple PPy structure and from a conducting polymer gel composite. In the latter case, the rate of electrically stimulated release was increased by more than an order of magnitude.⁷⁰

The mechanical infrastructure provided by the gels enables polymers of large dimensions and various shapes to be produced. The conducting polymer will grow throughout the gel. By appropriate placement of electrodes, it is possible to grow composite structures with conducting polymers strategically placed within predetermined spatial resolution throughout the gel.

This ability to pattern in two or three dimensions is critical to the development of intelligent material structures containing inherently conducting polymers. Advances in patterning are described in the following section.

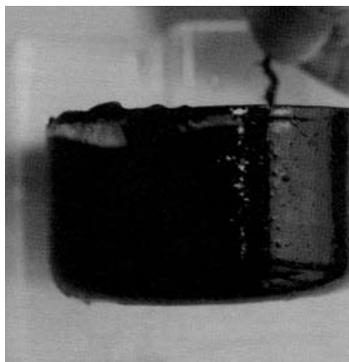


Figure 7.8 A slab of PPy gel composite.

Device fabrication

Processable conducting polymers, either by melt or solution means, are suitable for fabrication into the myriad of devices envisaged for these dynamic polymer systems. The nature of the fabrication process is necessarily determined by the performance required of the final product. However, the ultimate size and cost of the fabricated part are equally as important as the performance characteristics. In this section we review some recent developments in the area of printing and fiber spinning technologies that will impact on the fabrication of conducting polymer devices in the future.

Fiber spinning technologies

Fibers are useful building blocks for devices because of the well-developed spinning and weaving technologies that are available and because of the increasing use of high-performance fibers in advanced materials. Mass production of fibers and their weaving into textiles dates back to the early stages of the industrial revolution. The alignment of polymer chains (natural or synthetic) along the fiber axis produces enhanced performance: both conductivity and mechanical properties of conducting polymers have been shown to be improved by producing fibers (including a draw process). The assembly of fibers through weaving and other processes are the basis of the mass production of textiles, carpets and even paper products. Utilizing these well-developed technologies for the construction of conducting polymer-based devices is an extremely attractive prospect.

It is in the merging field of electronic textiles that the fiber spinning and conducting polymer technologies merge. An electronic textile contains electronic components seamlessly integrated into a conventional fabric structure.

Whilst some examples seem futuristic (computers or mobile phones built into a sports jacket) other appear more achievable. For example, the addition to conventional fabrics of fibers that can also provide energy storage (batteries, capacitors) or energy conversion (photovoltaic, thermal energy harvesting) will be extremely useful for persons living or traveling in remote areas. The energy fabrics can be manufactured into tents and blankets and the energy device can be used to power all manner of electrical devices from communications to cooking. Another application is in the area of biomedical monitoring. Here, a number of sensor fibers are built into garments and the sensor responses recorded and in some scenarios automatically transmitted to health service providers. The range of potential applications is immense and includes baby monitors and triage services for injured soldiers.

Already solution processable conducting polymers have been used to develop fiber products that may be used in the applications described above. In one commercial operation (Santa Fe Science and Technology, Inc.) continuous lengths of polyaniline fibers are made by a wet spinning operation. The continuous nature of the operations enables control of fiber diameter, draw ratio and properties and the company offers fibers of various denier. Conductivities of up to 1000 S cm^{-1} have been reported and the mechanical properties are described as being similar to Nylon-6. Figure 7.5 shows the SFST fiber-spinning operation.

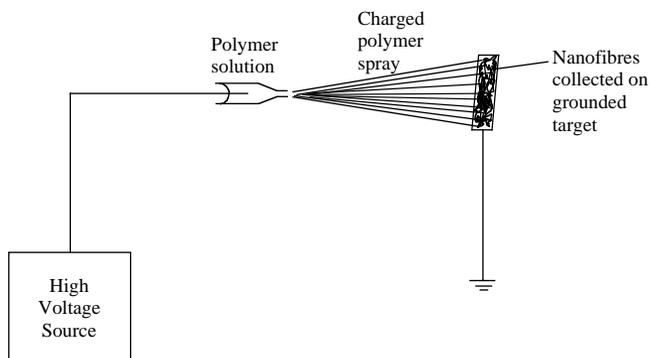


Figure 7.9 Schematic diagram of electrospinning. (Courtesy Dr. Chee Too, IPRI.)

Recently,⁷¹⁻⁷³ there has also been much interest in the formation of nanofibers principally using an electrospinning technique. The method (illustrated in Figure 7.9) is a straightforward way to make long polymer fibers with the diameter ranging from 100 nm to 2 μm . The method involves dissolving the polymer in a suitable solvent and then applying a large voltage difference between a metal capillary containing the solution (eg. a syringe) and a target. The target may be a metal foil upon which the nanofibers deposit. The high voltage induces the free charges in the polymer solution to move and the result is a jet of solution that flows from the capillary to the target to form an oriented network (Figure 7.9). Recently a

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method was also reported for fiber alignment using a modified electrospinning method.⁷³ Conducting polymer fibers have recently been formed by the electrospinning process as reported by MacDiarmid et al. while [Figure 7.10](#) shows fibers containing polythiophenes produced in this manner with one of our collaborators.

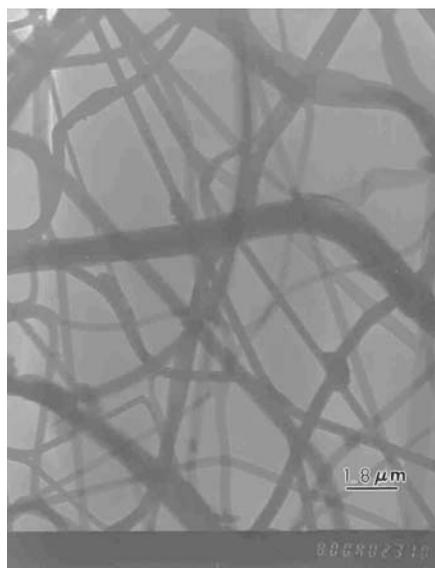


Figure 7.10 Electrospun fibers of polyvinyl alcohol containing sulfonated polyaniline. (Courtesy Dr. Chee Too (IPRI) and Dr. Lynne Samuelson (University of Massachusetts, Lowell).)

Printing technologies

Printing is also an old art that is now seen in a new light for fabrication of advanced products including electronic components. Solution processable CEPs are inherently suitable for fabrication using printing methods and their availability is already leading to low cost sensors and cheap, disposable electronics.

In our own laboratories⁷⁴ we have used conventional screen printing techniques for the manufacture of sensors ([Figure 7.11](#)). In one example, conducting tracks of 1 mm in width and 17 mm long were printed onto plastic substrates and conducting polymer was subsequently deposited over the tracks to make a four probe gas sensor. The great advantage of screen printing is its suitability for coating fabrics. Thus, the screen printing provides a new option for preparing electronic textiles in addition to the CEP fiber structures described above. The biggest disadvantage of screen printing is that only low resolution is typically available, making it unsuitable for microfabrication.

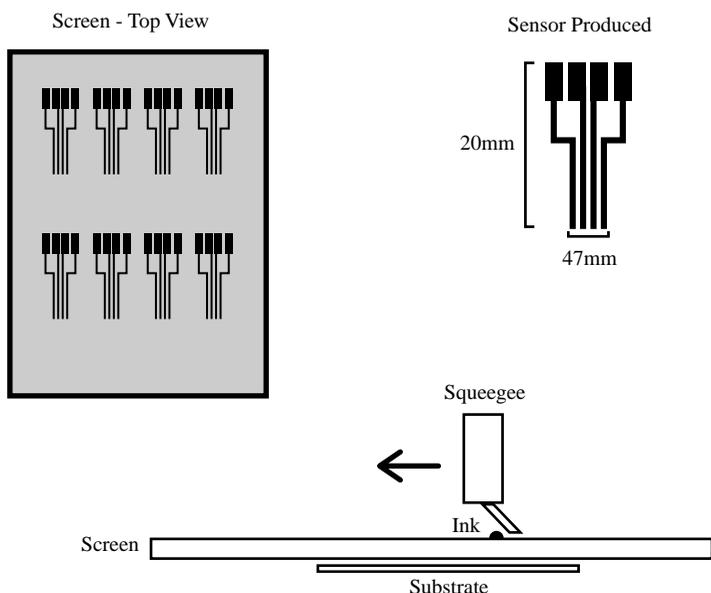


Figure 7.11 The screen-printing process involved in preparation of carbon track electrodes on polymer substrates. (Courtesy R. Shepherd. Ph.D. thesis, University of Wollongong, 2002.)

Recent developments show, however, that micro-scale electronics can be made even with readily available ink-jet printers. De Rossi and co-workers⁷⁵ have used ink-jet printing to make 3-dimensional structures from soluble conducting polymers. Several groups have reported the production of polymer light emitting diodes using ink-jet printing to deposit lines or pixels. The thickness of the deposited layers is approximately 200 nm and the minimum width is limited to ~200 nm. The resolution is ultimately limited by the ink-jet printing process that involves the deposition of droplets onto the substrate. The droplet size and spreading before evaporation determine the resolution. Richard Friend and co-workers⁷⁶ from the Cavendish Laboratory, University of Cambridge, have significantly improved the resolution of the ink-jet printing process by first patterning the surface with hydrophilic and hydrophobic regions. Using such methods, these researchers were able to prepare features to 5 μm in width and prepared all-polymer transistor circuits that showed performances similar to those made by photolithography methods.

Similar techniques have been used to generate finer resolution by micro-contact printing methods. These methods are suitable for preparing features as small as 100 nm.⁷⁷ The process involves forming a rubber stamp the surface of which is painted with a masking ink. The ink is transferred to the substrate and forms the pattern of the stamp on the substrate. The stamped areas can then be coated with soluble conducting polymers. In one example, poly-

thiophenes were deposited on hydrophilic areas formed in a prior micro-printing step. In another process, a polythiophene derivative was directly stamped onto a conductive ITO surface although the feature size was quite large (100 μm). A final variation of the microcontact printing technique has been widely explored by Alan MacDiarmid and colleagues.⁷⁸ In this method, the surface to be coated is stamped with a hydrophobic self assembled monolayer (eg. organothiol on a gold surface) and a conducting polymer is deposited by electropolymerization or chemically initiated polymerization. Conducting polymer lines and other shapes could then be deposited on virtually any substrate, including flexible plastics. In yet another variation, MacDiarmid⁷⁹ also showed that the mask could be made by a regular office laser printer. A printed substrate could be uniformly coated by *in situ* polymerization and the laser printed regions subsequently removed by ultrasonication.

These examples serve to illustrate the enormous interest in mass production techniques for preparing low-cost devices based on conducting polymers. No doubt the future development of such techniques will lead to commercial products allowing the integration of electronics into a number of conventional host structures, the most dramatic of which may include flexible plastic electronic components and electronic textiles and fabrics. These developments have been hastened by the recent advent of processable conducting polymers. Tremendous opportunities now arise in marrying these processable conducting polymers with the age-old arts of knitting, weaving and printing.

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