

## **PART VI**

---

# **POLYMERS FOR ADVANCED TECHNOLOGIES**

## CONDUCTING POLYMERS

MARÍA JUDITH PERCINO AND VÍCTOR MANUEL CHAPELA

### 29.1 INTRODUCTION

A polymer (material containing a long chain of similar molecular structures) is the first and foremost electrical and heat insulator. The idea that polymers or plastics could conduct electricity had been considered absurd. Their wide application as an insulating material is the reason they are studied and developed in the first place. In fact, these materials are commonly used for surrounding copper wires and manufacturing the outer structures of electrical appliances that prevent humans from coming in direct contact with electricity.

In 1958, polyacetylene was first synthesized by Natta et al. [1] as a black powder. The polyacetylene was found to be a semiconductor with conductivity between  $7 \times 10^{-11}$  to  $7 \times 10^{-3}$  S/m, depending upon how the polymer was processed and manipulated. The conventional method of polymerization in the laboratory requires a catalyst solution to be stirred thoroughly to carry out the reaction under homogeneous conditions. Acetylene polymerization was no exception. It had become customary for polymer chemists who synthesized polyacetylene to bubble acetylene gas into a catalyst solution with stirring. As a matter of fact, the product was obtained as an intractable black powder, from which it was very difficult to make specimens in a shape suitable for measurement of various spectra and properties because of its insolubility and infusibility. Soon after Shirakawa H. joined Ikeda's group [2], he succeeded in synthesizing polyacetylene directly in a form of thin film [3] by a fortuitous error in 1967. After a series of experiments to reproduce the error, they noted that a concentration of the Ziegler–Natta catalyst nearly a thousand times ( $10^3$ ) as large as usual had been used. It is worth noting that the

insolubility of polyacetylene contributes to the formation of film. One important factor that should be added is that the catalyst used at that time,  $\text{Ti}(\text{O}-n-\text{C}_4\text{H}_9)_4 - (\text{C}_2\text{H}_5)_3\text{Al}$ , is a quite unique one from the viewpoint of its good solubility in organic solvents such as hexane or toluene to give a homogeneous solution and its high activity to give exclusively high molecular weight and crystalline polymers. By contrast, most Ziegler–Natta catalysts form precipitates that give an inhomogeneous solution when a titanium compound is mixed with alkyl aluminum.

The polymer is called a *conjugated polymer* because of the alternating single and double bonds in the polymer chain. Because of the special conjugation in their chains, it enables the electrons to delocalize throughout the whole system and thus many atoms may share them. The delocalized electrons may move around the whole system and become the charge carriers to make them conductive. It has been recognized for many years that a very long linear conjugated polyene might have various interesting properties, especially optical, electrical, and magnetic properties. A polyene is an even number of methyne ( $=\text{CH}-$ ) groups, covalently bonded to form a linear carbon chain bearing one  $p$  electron on each carbon atom. Therefore, the chemical structure of the polyene is best represented by the formula  $\text{H}(\text{CH}=\text{CH})_n\text{H}$ , where  $n$  denotes the number of repeating units. Recently, the word *polyacetylene* has become more popular than polyene because polyacetylene has been a great object of study.

The polyene can be transformed into a conducting form when electrons are removed from the backbone resulting in cations or added to the backbone resulting in anions. Anions and cations act as charge carriers, hopping from one site to another under the influence of an electrical

field, thus increasing conductivity. However, the conjugated polymers are not conductive, since they are covalently bonded and do not contain valence band as pure metal does. It is universally agreed that the doping process is an effective method to produce conducting polymers. Doping allows electrons to flow due to the formation of conduction bands. As doping occurs, the electrons in the conjugated system, which are loosely bound, are able to jump around the polymer chain. Electric current will be produced when the electrons are moving along the polymer chains. Some examples [4] of conjugated conducting polymers are polyacetylene, polypyrrole, polyaniline, and polythiophene (Fig. 29.1). In future, conductive polymers or organic metals may replace inorganic metal in several critical areas. Certain aspects of the inorganic metals, such as not being environmentally friendly and having a high toxicity, are the reason why these organic metals have potential benefits as substitutes. The potential applications of these organic metals include corrosion protection, radars, batteries, sensors, as well as electrochromic cells. Much research will be needed before the applications may become a reality, since conjugated conducting polymers still have some drawbacks such as not being water soluble, having poor mechanical strength, and not being biodegradable [6, 7].

## 29.2 HISTORICAL BACKGROUND

Conducting-polymer research dates back to the 1960s, when Pohl, Katon, and their coworkers, first synthesized and characterized semiconducting polymers [8, 9]. The discovery of the high conductivity of polysulfur nitride (SN)<sub>x</sub>, a polymeric material containing interesting electrical properties, was a step forward for research in conducting polymers. The beginning of conducting-polymer research began nearly a quarter of a century ago, when films of polyacetylene were found to exhibit profound increases in electrical conductivity when exposed to halogen vapor [10–13]. Heeger, Shirakawa, and MacDiarmid produced conjugated conducting polyacetylene when monomer of acetylene was doped with bromine or iodine vapor; the resulting electrical conductivity was 10 times higher than that obtained with the undoped monomers. Further investigations, initially aimed to produce thin films of graphite, showed that exposure of this form of polyacetylene to halogens increased its conductivity a billion fold. When undoped, the polymer was silvery, insoluble, and intractable, with a conductivity similar to that of semiconductors. When it was weakly oxidized by compounds such as iodine, it turned a golden color and its conductivity increased to about 10<sup>4</sup> S/m. In the 1980s, polyheterocycles were first developed. Polyheterocycles were

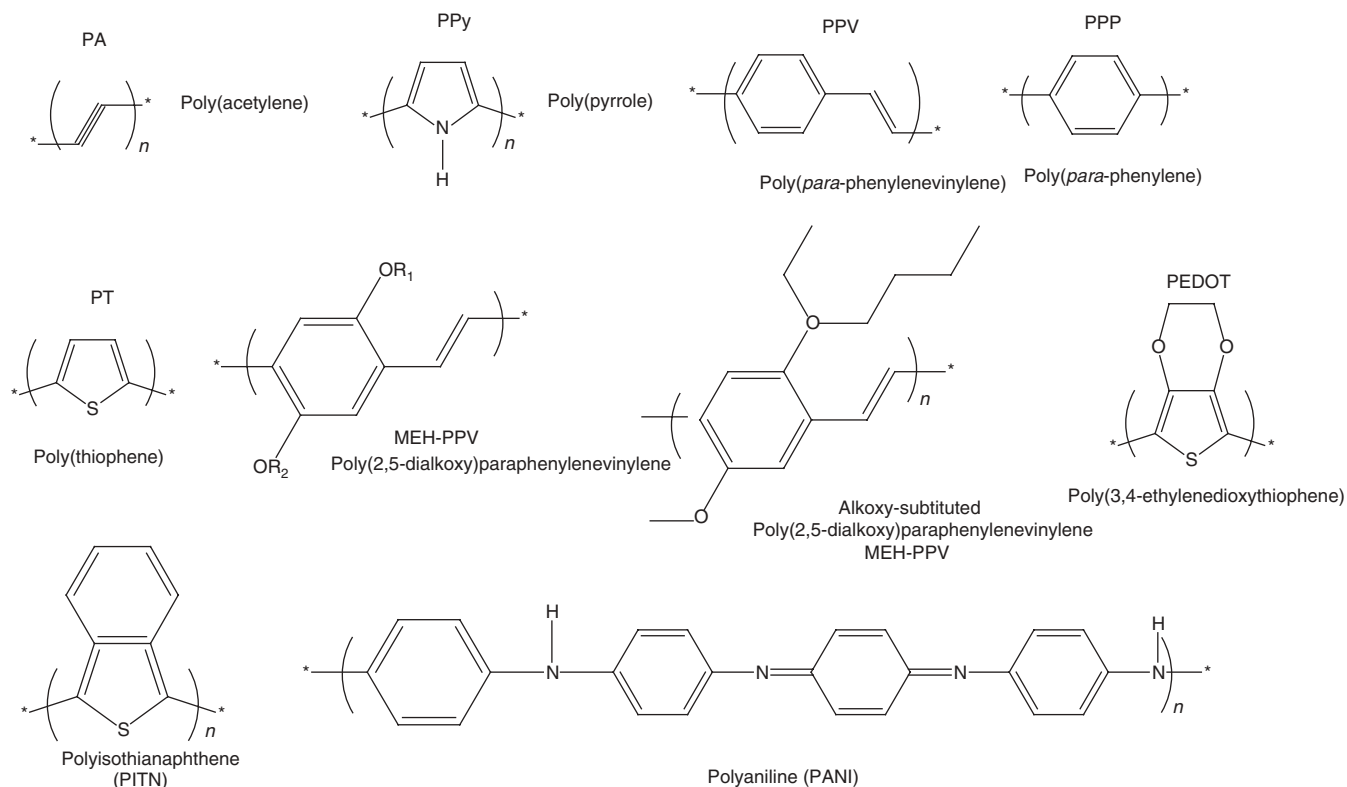


Figure 29.1 Examples of conjugated polymers [5].

found to be much more air stable than polyacetylene, although their conductivities were not so high, typically about  $10^3$  S/m. By adding various side groups to the polymer backbone, derivatives that were soluble in various solvents were prepared. Other side groups affected properties such as their color and their reactivity to oxidizing and reducing agents. A logarithmic conductivity ladder of some of these polymers is shown below. Since then it has been found that about a dozen different polymers and polymer derivatives undergo this transition when doped with a weak oxidation agent or reducing agent. They are all conjugated polymers. This early work has led to an understanding of the mechanisms of charge storage and charge transfer in these systems. All have a highly conjugated electronic state. This also causes the main problems with the use of these systems, those of processability and stability. The most recent research in this has been the development of highly conducting polymers with good stability and acceptable processing attributes. After their discovery, research papers dealing with polyconjugated systems were very extensive and systematic. The trend was to understand the chemical and physical aspects, either in neutral (undoped) state or charged (doped) states. According to SCIFINDER, more than 40,000 scientific papers have been published in this field of research since 1977 [14]. This previously underestimated family of macromolecular compounds turned out to be extremely interesting, from both the basic research and application points of view. In 2000, these three brilliant scientists, founders of the conjugated conducting-polymer science, were granted the Nobel Prize in chemistry.

### 29.3 THE STRUCTURES OF CONDUCTING POLYMERS

All materials can be divided into three main groups: conductors or metals, insulators, and semiconductors; they are differentiated by their ability to conduct or the ability to allow the flow of current. Generally, conducting polymers

are classified as semiconductors, although some highly conducting polymers, such as polyacetylene, fall into the metal category. Table 29.1 [6] compares some of the physical properties of insulators, semiconductors, and conductors.

Conjugated organic polymers that can have their conductivity increased by several orders of magnitude from the semiconductor regime are generally referred to as *electronic polymers* and have become of very great scientific and technological importance since 1990 because of their use in light-emitting diodes (LEDs) [7, 15]. The emeraldine base form of polyaniline and *trans*-(CH)<sub>x</sub> are shown in Table 29.2 to illustrate the increases in electrical conductivity of many orders of magnitude that can be obtained by doping. The conductivity attainable by an electronic polymer has very recently been increased an infinite number of times by the discovery of superconductivity in regioregular poly(3-hexylthiophene) [16]. Although this phenomenon was present only in a very thin layer of the polymer in a field effect (FET) configuration at a very low temperature (circa 2 K), it represents a historical quantum-leap superconductivity in an organic polymer.

### 29.4 CHARGE STORAGE

One early explanation of conducting polymers used band theory as a method of conduction. This proposed that a half-filled valence band would be formed from a continuous delocalized  $\pi$ -system. This would be an ideal condition for conduction of electricity. However, it turns out that the polymer can more efficiently lower its energy by bond alteration (alternating short and long bonds), which introduces a band width of 1.5 eV, making it a high energy gap semiconductor. The polymer is transformed into a conductor by doping it with either an electron donor or an electron acceptor. This is reminiscent of doping of silicon-based semiconductors where silicon is doped with either arsenic or boron. However, while the doping of silicon

TABLE 29.1 Comparison of Physical Properties of Metals, Insulators, and Conducting Polymers\*

Property	Conducting Polymers	Metals	Insulators
Electrical conductivity (S/cm)	$10^{-11} - 10^3$	$10^{-4} - 10^6$	$10^{-20} - 10^{-12}$
Carriers	Electrons of conjugated double bonds	Valence electrons of half-filled band	—
Concentrations of carriers per cm <sup>3</sup>	$10^{12} - 10^{19}$	$10^{22} - 10^{23}$	—
Effect of impurity	Impurities of 0.1–1% change conductivity by two to three orders of magnitude	Effect comparatively slight	Strong effect
Magnetic properties	Paramagnetic	Ferro and diamagnets	Diamagnets

\*Ref. 6.

TABLE 29.2 Conductivity between Conductive Polymers and Other Materials\*

	Conductivity, S/cm		
Doped <i>trans</i> -(CH) <sub>x</sub> -10 <sup>5</sup> S/cm	10 <sup>6</sup>	Ag, Cu	<i>Metals</i>
Doped polyaniline 10 <sup>3</sup> S/cm	10 <sup>5</sup>	Fe	
	10 <sup>4</sup>	Mg	
	10 <sup>3</sup>	In, Sn	<i>Semimetals</i>
	10 <sup>2</sup>	Ge	
	10 <sup>1</sup>		
	10 <sup>-2</sup>		
Undoped-(CH) <sub>x</sub> -10 <sup>-5</sup> S/cm	10 <sup>-4</sup>		
Undoped polyaniline 10 <sup>-10</sup> S/cm	10 <sup>-6</sup>		
	10 <sup>-8</sup>	Si	<i>Insulators</i>
	10 <sup>-10</sup>	AgBr	
	10 <sup>-12</sup>	Glass	
	10 <sup>-14</sup>	Diamond	
	10 <sup>-16</sup>	Nylon	
	10 <sup>-18</sup>	Quartz	
	10 <sup>-20</sup>		

\*Ref. 5.

produces a donor energy level close to the conduction band or an acceptor level close to the valence band, this is not the case with conducting polymers. The evidence for this is that the resulting polymers do not have a high enough concentration of free spins, as determined by electron spin spectroscopy. Initially the free spin concentration increases with the concentration of dopant. At larger concentrations, however, the concentration of free spins levels off at a maximum. To understand this, it is necessary to examine the way in which charge is stored along the polymer chain and its effect.

The polymer may store charge in two ways. In an oxidation process, it could either lose an electron from one of the bands or it could localize the charge over a small section of the chain. Localizing the charge causes a local distortion due to a change in geometry, which costs the polymer some energy. However, the generation of this local geometry decreases the ionization energy of the polymer chain and increases its electron affinity, making it able to accommodate the newly formed charges. This method increases the energy of the polymer less than it would if the charge was delocalized and, hence, takes place in preference of charge delocalization. This is consistent with an increase in disorder detected by Raman spectroscopy after doping. A similar scenario occurs for a reductive process. Typical oxidizing dopants used include iodine, arsenic pentachloride, iron(III) chloride, and (NOPF<sub>6</sub>) nitrosium hexafluorophosphate. A typical reductive dopant is sodium naphthalide. The main criterion is its ability to oxidize or reduce the polymer without lowering its stability or whether they are capable of initiating side reactions that inhibit the polymers ability to conduct electricity.

An example of the latter is the doping of a conjugated polymer with bromine. Bromine is too powerful an oxidant and adds across the double bonds to form sp<sup>3</sup> carbons. The same problem may also occur with NOPF<sub>6</sub> if left too long. The oxidative doping of polypyrrole proceeds in the following way. An electron is removed from the p-system of the backbone producing a free radical and a spinless positive charge. The radical and cation are coupled to each other via local resonance of the charge and the radical. In this case, a sequence of quinoid-like rings is used. The distortion produced by this is of higher energy than the remaining portion of the chain. The creation and separation of these defects costs a considerable amount of energy. This limits the number of quinoid-like rings that can link these two bound species together. In the case of polypyrrole, it is believed that the lattice distortion extends over four pyrrole rings. This combination of a charge site and a radical is called a *polaron*. This could be either a radical cation or radical anion. This creates a new localized electronic state in the gap, with the lower energy states being occupied by single unpaired electrons. The polaron states of polypyrrole are symmetrically located about 0.5 eV from the band edges.

Upon further oxidation, the free radical of the polaron is removed, creating a new spinless defect called a *bipolaron*. This mechanism is of lower energy than the creation of two distinct polarons. At higher doping levels, it becomes possible that two polarons combine to form a bipolaron. Thus, at higher doping levels, the polarons are replaced with bipolarons. The bipolarons are located symmetrically with a band gap of 0.75 eV for polypyrrole. This, eventually, with continued doping, forms into a continuous bipolaron bands. Their band gap also increases as newly formed bipolarons are made at the expense of the band edges. For a very

heavily doped polymer, it is conceivable that the upper and the lower bipolaron bands will merge with the conduction and the valence bands, respectively, to produce partially filled bands and metallic conductivity. This is shown in Figure 29.2.

Conjugated polymers with a degenerate ground state have a slightly different mechanism. As with polypyrrole, polarons and bipolarons are produced on oxidation. However, because the ground-state structure of such polymers are twofold degenerate, the charged cations are not bound to each other by a higher energy bonding configuration and can freely separate along the chain. The effect of this is that the charged defects are independent of one another and can form domain walls that separate two phases of opposite orientation and identical energy. These are called *solitons* and can sometimes be neutral. Solitons produced in polyacetylene are believed to be delocalized over about 15 CH units with the maximum charge density next to the dopant counterion. The bonds closer to the defect show less amount of bond alternation than the bonds away from the center. Soliton formation results in the creation of new localized electronic states that appear in the middle of the energy gap. At high doping levels, the charged solitons interact with each other to form a soliton band that can eventually merge with the band edges to create true metallic conductivity. This is shown in Figure 29.3.

## 29.5 DOPING

The concept of doping is the unique, central, underlying, and unifying theme, which distinguishes conducting polymers from all other types of polymers [17, 18]. During the doping process, an organic polymer, either an insulator or a semiconductor having a small conductivity, typically in the range  $10^{-10}$ – $10^{-5}$  S/cm, is converted into a polymer, which is in the “metallic” conducting regime (circa  $1$ – $10^4$  S/cm). The controlled addition of known, usually small ( $\leq 10\%$ ), nonstoichiometric quantities of chemical species results in significant changes in the electronic, electrical, magnetic, optical, and structural properties of the polymer. Doping is reversible to produce the original polymer with little or no degradation of the polymer backbone. Both doping and undoping processes, involving dopant counterions that stabilize the doped state, may be carried out chemically or electrochemically [19].

### 29.5.1 Redox Doping

All conducting polymers (and most of their derivatives), for example, poly(paraphenylene), poly(phenylene vinylene), polypyrrole, polythiophene (PT), polyfuran, poly(heteroaromatic vinylenes), and polyaniline (Fig. 29.1), undergo p- and/or n-redox doping.

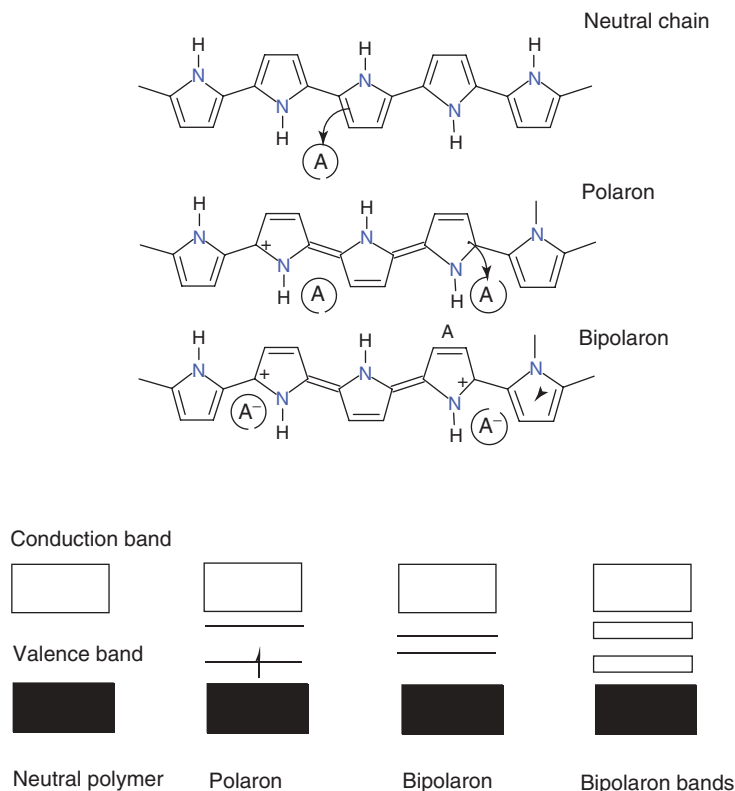
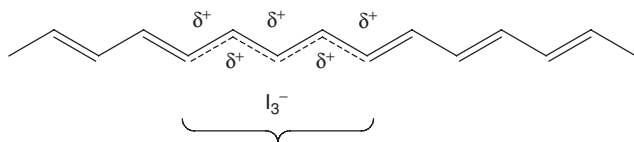


Figure 29.2 Mechanism of conduction on polymer doping.

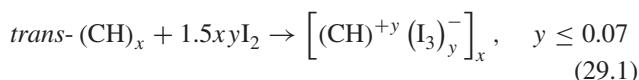




Scheme 29.1 Charge delocalization in a soliton.

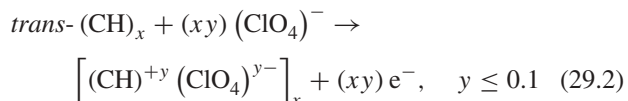
### 29.5.2 Chemical and Electrochemical p-Doping

p-Doping, that is, partial oxidation of the *p* backbone of an organic polymer, was first discovered by treating *trans*-(CH)<sub>x</sub> with an oxidizing agent such as iodine [17, 18]:



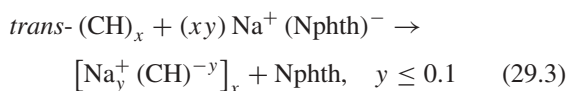
This process was accompanied by an increase in conductivity from circa  $10^{-5}$  to circa  $10^3$  S/cm. If the polymer is stretch-oriented five- to sixfold before doping, conductivities parallel to the direction of stretching up to about  $10^5$  S/cm can be obtained [15, 19]. Approximately 85% of the positive charge is delocalized over 15 CH units (depicted in Scheme 29.1 for simplicity over only five units) to give a positive soliton.

p-Doping can also be accomplished by electrochemical anodic oxidation by immersing a *trans*-(CH)<sub>x</sub> film in, for example, a solution of LiClO<sub>4</sub> dissolved in propylene carbonate and attaching it to the positive terminal of a DC (direct current) power source, the negative terminal being attached to an electrode also immersed in the solution [20]:



### 29.5.3 Chemical and Electrochemical n-Doping

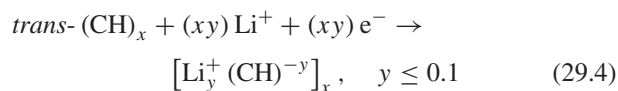
n-Doping, that is, partial reduction of the backbone *p*-system of an organic polymer, was also discovered using *trans*-(CH)<sub>x</sub> by treating it with a reducing agent such as liquid sodium amalgam or preferably sodium naphthalene [17, 18], (Nphth, ):



The antibonding  $\pi$ -system is partially populated by this process, which is accompanied by an increase in conductivity of about  $10^3$  S/cm.

n-Doping can also be carried out by electrochemical cathodic [21], by immersing a *trans*-(CH)<sub>x</sub> film in, for example, a solution of LiClO, dissolved in tetrahydrofuran and attaching it to the negative terminal of a DC power

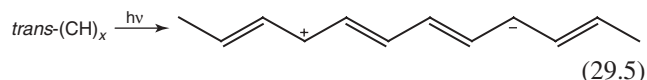
source, the positive terminal being attached to an electrode also immersed in the solution:



In all chemical and electrochemical p- and n-doping processes discovered for (CH)<sub>x</sub> and for the analogous processes in other conducting polymers, counter “dopant” ions are introduced, which stabilize the charge on the polymer backbone. However, other types of doping that can provide information not obtainable by chemical or electrochemical doping are the redox doping, which can be termed *photodoping* and the *charge-injection doping*.

### 29.5.4 Doping Involving No Dopant Ions

**29.5.4.1 Photodoping** When *trans*-(CH)<sub>x</sub>, for example, is exposed to radiation of energy greater than its band gap, electrons are promoted across the gap and the polymer undergoes “photodoping.” Under appropriate experimental conditions, spectroscopic signatures characteristic of, for example, solitons can be observed [22].



The positive and negative solitons are here illustrated diagrammatically for simplicity as residing only on one CH unit; they are actually delocalized over circa 15 CH units. They disappear rapidly because of the recombination of electrons and holes when irradiation is discontinued. If a potential is applied during irradiation, then the electrons and holes separate and photoconductivity is observed.

**29.5.4.2 Charge-Injection Doping** Charge-injection doping is most conveniently carried out using a metal/insulator/semiconductor (MIS) configuration involving a metal and a conducting polymer separated by a thin layer of a high dielectric strength insulator. It was this approach that resulted in the observance of superconductivity in a PT derivative, as described previously. Application of an appropriate potential across the structure can give rise, for example, to a surface charge layer, the “accumulation” layer that has been extensively investigated for conducting polymers [23–25]. The resulting charges in the polymer, for example, (CH)<sub>x</sub> or poly(3-hexylthiophene), are present without any associated dopant ion. The spectroscopic properties of the charged species so formed can, therefore, be examined in the absence of dopant ion. Using this approach, spectroscopic studies of (CH)<sub>x</sub> show the signatures characteristic of solitons and the mid-gap absorption band observed in the chemically and electrochemically doped polymer. However, Coulombic interaction between charge

on the chain and dopant ion is a very strong interaction and one that can totally alter the energetics of the system.

### 29.5.5 Nonredox Doping

This type of doping differs from redox doping described above in that the number of electrons associated with the polymer backbone does not change during the doping process. The energy levels are rearranged during doping. The emeraldine base form of polyaniline was the first example of the doping of an organic polymer to a highly conducting regime by a process of this type to produce an environmentally stable polysemiquinone radical cation. This was accomplished by treating emeraldine base with aqueous protonic acids (Scheme 29.2) and is accompanied by a nine to ten orders of magnitude increase in conductivity (up to around 3 S/cm) to produce the protonated emeraldine base [26–29]. Protonic acid doping has subsequently been extended to systems such as poly(heteroaromatic vinylenes) [30].

## 29.6 POLYANILINES

Polyanilines refer to an important class of electronic/conducting polymers. They can be considered as being derived from a polymer, the base form of which has the generalized composition given in Scheme 29.3a, which consists of alternating reduced and oxidized repeating units (Scheme 29.3a) [24–26]. The average oxidation state can be varied continuously from  $y = 1$  to give the completely reduced polymer, to  $y = 0.5$  to give the “half-oxidized” polymer, to  $y = 0$  to give the completely oxidized polymer (Scheme 29.3b–d). The terms *leucoemeraldine*, *emeraldine*, and *pernigraniline* refer to the different oxidation states of the polymer, where  $y$  is 1, 0.5, and 0, respectively, either in the base form, for example, emeraldine base, or in the protonated salt form, for example, emeraldine hydrochloride [26–28]. In principle, the imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts, the degree of protonation of the polymeric base depending

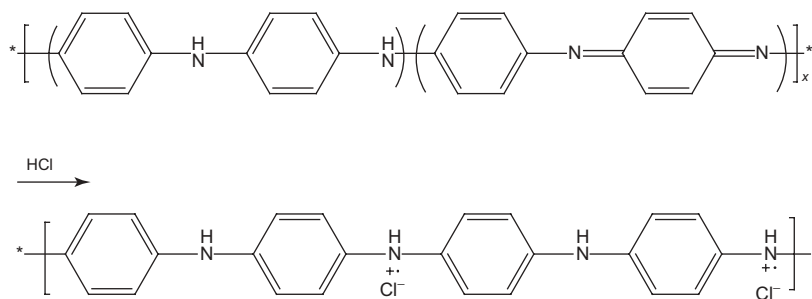
on its oxidation state and on the pH of the aqueous acid. Complete protonation of the imine nitrogen atoms in emeraldine base by aqueous HCl, for example, results in the formation of a delocalized polysemiquinone radical cation [26, 27] and is accompanied by an increase in conductivity of about  $10^{10}$ . The partly protonated emeraldine hydrochloride salt can be easily synthesized, either by the chemical or electrochemical oxidative polymerization of aniline [26–28]. It can be deprotonated by aqueous ammonium hydroxide to give emeraldine base powder (a semiconductor).

### 29.6.1 Allowed Oxidation States

As can be seen from the generalized formula of polyaniline base (Scheme 29.4a), the polymer could, in principle, exist in a continuum of oxidation states ranging from the completely reduced material in the leucoemeraldine oxidation state,  $y = 1$ , to the completely oxidized material in the pernigraniline oxidation state,  $y = 0$ . However, we have shown [28, 29] that at least in *N*-methyl-2-pyrrolidinone (NMP) solution in the range  $y = 1$  to  $y = 0.5$  (emeraldine oxidation state), only two chromophores are present, characteristic of  $y = 1$ , and  $y = 0.5$  species, and that all intermediate oxidation states consist, at the molecular level, only of mixtures of the chromophores characteristic of these two states. Since most of the properties of polyaniline of interest are concerned with the solid state, the authors have carried out a series of studies in the solid state that show that the same phenomenon is true in the oxidation-state ranges of  $y = 1$  to 0.5 and  $y = 0.5$  to 0. Within each of these ranges, all intermediate oxidation states consist, at the molecular level, only of mixtures of the chromophores characteristic of the two states defining the beginning and end of each range [30–32].

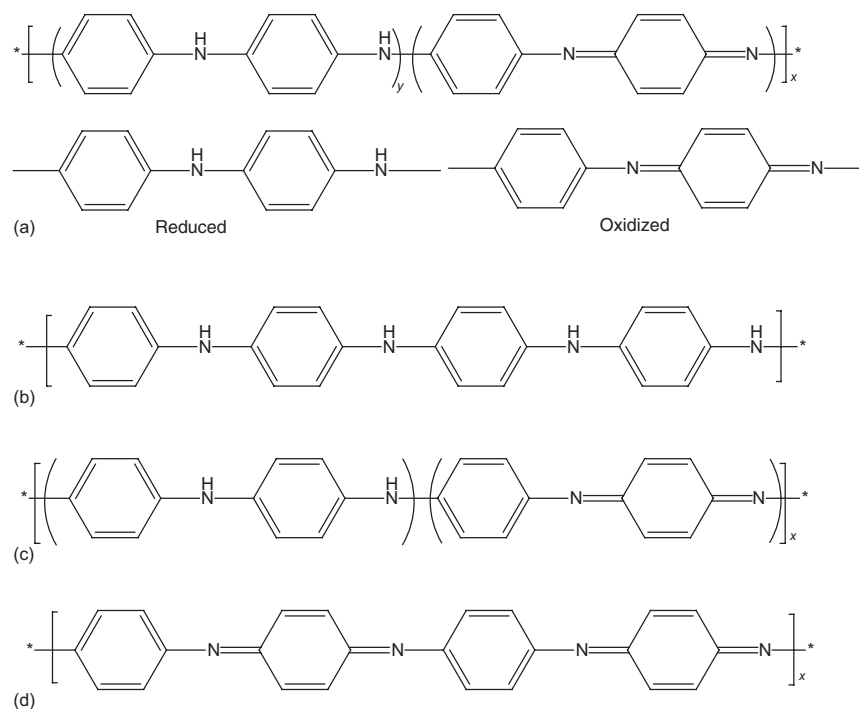
### 29.6.2 Doping

Polyaniline holds a special position among conducting polymers in that its most highly doped form can be reached by two completely different processes: protonic acid doping and oxidative doping. Protonic acid doping of emeraldine

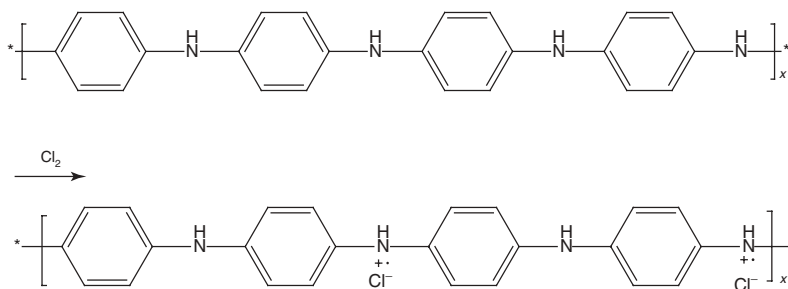


Scheme 29.2 Treatment of emeraldine base with acid.





**Scheme 29.3** Generalized composition of polyanilines indicating the (a) reduced and oxidized units, (b) completely reduced polymers, (c) half-oxidized polymer, and (d) fully oxidized polymer.



**Scheme 29.4** Oxidative doping of polyaniline.

base units with, for example, 1 M aqueous HCl, results in complete protonation of the imine nitrogen atoms to give the fully protonated hydrochloride salt [26, 27]. The same doped polymer can be obtained by chemical oxidation (p-doping) of leucoemeraldine base [28]. This actually involves the oxidation of the  $\alpha/\pi$ -system rather than just the p-system of the polymer as is usually the case in p-type doping. Its reaction with a solution of chlorine in carbon tetrachloride proceeds to give emeraldine hydrochloride (Scheme 29.4).

## 29.7 CHARGE TRANSPORT

Although solitons and bipolarons are known to be the main source of charge carriers, the precise mechanism is not

yet fully understood. The problem lies in attempting to trace the path of the charge carriers through the polymer. All of these polymers are highly disordered, containing a mixture of crystalline and amorphous regions. It is necessary to consider the transport along and between the polymer chains and also the complex boundaries established by the multiple numbers of phases. This has been studied by examining the effect of doping, temperature, magnetism, and the frequency of the current used. These tests show that a variety of conduction mechanisms are used. The main mechanism used is by movement of charge carriers between localized sites or among the soliton, polaron, or bipolaron states. Alternatively, where inhomogeneous doping produces metallic islands dispersed in an insulating matrix, conduction is by movement of

charge carriers between highly conducting domains. Charge transfer between these conducting domains also occurs by thermally activated hopping or tunneling. This is consistent with conductivity being proportional to temperature.

## 29.8 SYNTHESSES

Synthesized conjugated conducting polymers can be classified into two major categories: chemically polymerized and electrochemically polymerized materials. Via chemical polymerization, conjugated monomers react with an excess amount of an oxidant in a suitable solvent, such as acid. The polymerization takes place spontaneously and requires constant stirring. The second method is via electrochemical polymerization, which involves placing both counter and reference electrodes (such as platinum), into the solution containing diluted monomer and electrolyte (the dopant) in a solvent. After applying a suitable voltage, the polymer film immediately starts to form on the working electrolyte. A major advantage of chemical polymerization concerns the possibility of mass-production at a reasonable cost [33, 34]. This is often difficult with electrochemical methods. On the other hand, an important feature of the electropolymerization technique is the direct formation of conducting-polymer films that are highly conductive, simple, and suitable for use especially in electronic devices.

## 29.9 CONDUCTING POLYMERS

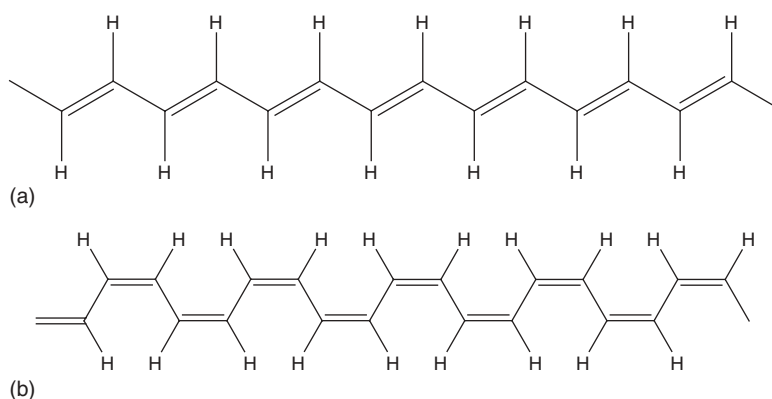
### 29.9.1 Polyacetylene *Trans* or *Cis*

S. Ikeda and his coworkers studied a mechanism of acetylene polymerization in connection with olefin polymerization by various Ziegler–Natta catalysts. They found that polymerization yields not only highly polymerized polyacetylene but also benzene, which is a cyclic trimer of acetylene, and that the ratio of these two products depends

upon the species of Ziegler–Natta catalyst employed. They also observed the formation of alkylbenzenes as a minor by-product of acetylene polymerization, with a catalyst system composed of titanium tetrachloride and trialkylaluminum. In a series of experiments using carbon-14 and deuterium, they noted that the ethyl group is introduced in the ethylbenzene when triethylaluminum labeled with carbon-14 or deuterium is used as the cocatalyst [35]. In other experiments, in which polyacetylene was oxidized by alkaline potassium permanganate, they observed the formation of propionic and acetic acids that are derived from the alkyl groups in trialkylaluminum used as the cocatalyst [35]. From these results, they concluded that polyacetylene and benzene could be formed from the same active site of the catalyst system. Thus, the reaction proceeds by *cis* opening of the triple bond in acetylene, followed by a *cis* insertion into the titaniumalkyl bond of the catalyst. This mechanism fits the orbital interaction model for the role of the catalyst by Fukui and Inagaki [36], according to which the initially formed configuration of the double bond is *cis* as a result of favored orbital interaction between the inserting acetylene and the active site of the catalyst. Whether cyclic trimerization occurs to give benzene or polymerization and proceeds to give polyacetylene is determined by the conformation of the growing chain, which takes either *cisoid* or *transoid* structure at the vicinity of the active site of the catalyst [36, 37]. As no *cis* form had been known until then, an important question remained, namely, why the mechanism is capable of yielding only *trans* configuration of the double bonds in polyacetylene [1, 38]. Scheme 29.5 shows the all-*cis* and all-*trans* forms of polyacetylene.

The configuration of the double bonds strongly depends on the temperature of polymerization. The *trans* content of polyacetylene prepared by the Ziegler–Natta catalysts decreases with decreasing polymerization temperature, as listed in Table 29.3, determined by infrared spectroscopy.

A thermal study by Ito et al. [39] indicated that irreversible isomerization of the *cis* form occurs at



**Scheme 29.5** All-*trans* (a) and all-*cis* (b) polyacetylene.

**TABLE 29.3** The Trans Contents of Polyacetylene Prepared at Different Temperatures\*

Temperature, °C	Trans Content, %
150	100.0
100	92.5
50	67.6
18	40.7
0	21.4
-18	4.6
-78	1.9

Catalyst:  $\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4 - (\text{C}_2\text{H}_5)_3\text{Al}$ ,  $\text{Ti}/\text{Al} = 4$ ,  $[\text{Ti}] = 10 \text{ mmol/l}$ .  
\*Ref. 39.

temperatures higher than  $145^\circ\text{C}$  to give a *trans* form (Fig. 29.4). Thus, the *cis* form is thermodynamically less stable than the *trans* one. The observed *cis*-rich polyacetylene synthesized at lower temperatures suggested the *cis* opening of the triple bond of an acetylene monomer. When the polymerization was carried out at higher temperatures, spontaneous isomerization of the growing *cis* double bonds occurred to give *trans* ones, consistent with the *cis* opening mechanism proposed by Ikeda [37].

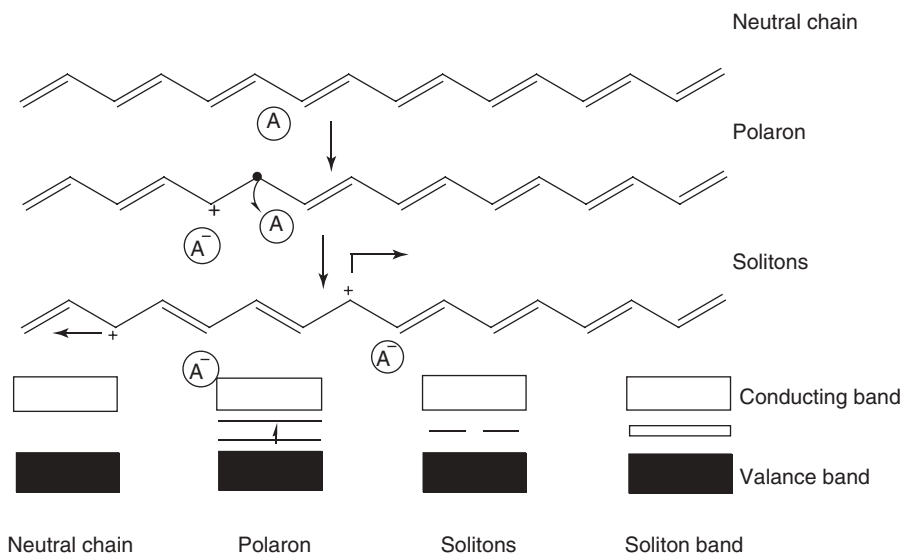
The electrical resistivity of films obtained with various *cis/trans* contents by the above preparation was measured by the conventional two-probe method under vacuum in a temperature range of  $-120$  to  $20^\circ\text{C}$  [40]. The resistivity and energy gap of *trans*-rich polyacetylene were  $1.03 \times 10^4 \Omega \text{ cm}$  and  $0.56 \text{ eV}$ , respectively, whereas the values of a *cis*-rich (80%) one were  $2.43 \times 10^8 \Omega \text{ cm}$  and  $0.93 \text{ eV}$ , respectively. Hatano et al. [41] reported that the resistivity and energy gap measured on compressed pellets of powder

polyacetylene synthesized by the same catalyst system were in the range of  $1.4 \times 10^4$  and  $4.2 \times 10^5 \Omega \text{ cm}$  and  $0.46 \text{ eV}$ , respectively, in good agreement with those for *trans*-rich polyacetylene film. In conclusion, it became apparent that the intrinsic electrical properties do not change much between powder and film.

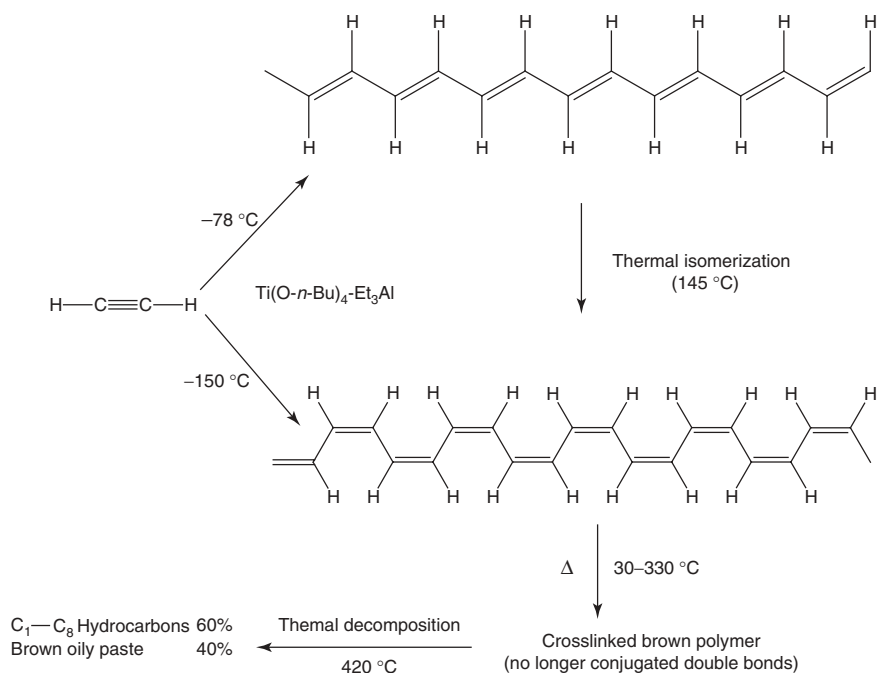
### 29.9.2 Polyaniline

Among the family of conjugated polymers, polyaniline is one of the most useful since it is air- and moisture-stable in both its doped, conducting form, and in its dedoped, insulating form [42–44]. Polyaniline is also unique among conducting polymers in that it has a very simple acid/base doping/dedoping chemistry (Fig. 29.4).

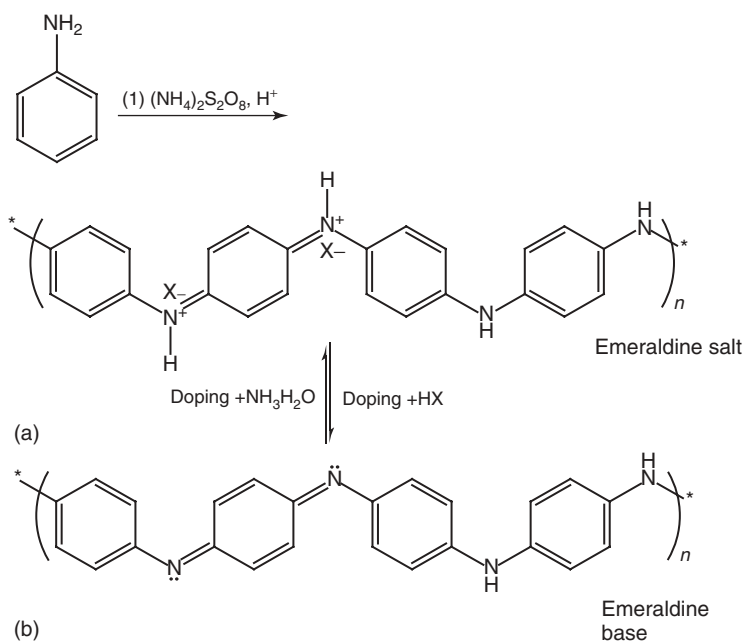
It has a great variety of potential applications, including anticorrosion coatings, batteries, sensors, separation membranes, and antistatic coatings [5, 46]. Conventional polyaniline synthesis (Fig. 29.5) is known to produce particulate products with irregular shapes. Therefore, many methods have been developed to make nanostructures of polyaniline (with diameters smaller than  $100 \text{ nm}$ ) by introducing “structural directing agents” during the chemical polymerizing reaction. A great variety of such agents have been reported in the literature, and these include surfactants [47–50], liquid crystals [51], polyelectrolytes [52], nanowire seeds [53], aniline oligomers [54], and, relatively complex, bulky organic dopants [55–59]. It is believed that such functional molecules can either directly act as templates (e.g., polyelectrolytes) or promote the self-assembly of ordered “soft templates” (e.g., micelles, emulsions) that guide the formation of polyaniline nanostructures.



**Figure 29.3** Mechanism of conduction upon polymer doping for conjugated polymers with a degenerate ground state.



**Figure 29.4** Thermal characterization of polyacetylene [39].



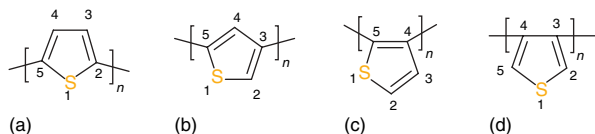
**Figure 29.5** The conventional synthesis of polyaniline and its morphology. (a, b) The oxidative polymerization reaction of aniline is typically carried out in an acidic solution (e.g., 1 M HCl) [45].

### 29.9.3 Polythiophene

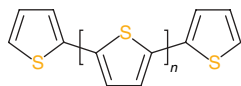
Another interesting family of conjugated polymers is the sulfur-containing polymers; above all, PT, its derivatives, and analogs attract the attention of researchers owing to a wide spectrum of valuable properties. PTs represent a special class of  $\pi$  processability and mechanical strength

[60]. Scheme 29.6 shows the possible arrangements of the repeating unit in PT.

The first PT synthesis was described in 1883. Washing of benzene with sulfuric acid afforded after further treatment with sulfuric acid a black insoluble material [61]. Oligomerization of thiophene induced by phosphoric



**Scheme 29.6** Possible arrangements of the repeating unit of polythiophene.

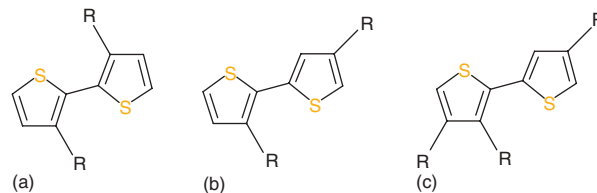


**Scheme 29.7** Polythiophene.

acid leads to the formation of the trimer [62]. It was not until the early 1980s, however, that any well-defined polymeric material was obtained. After the first syntheses by Yamamoto et al. [63] and using the Grignard-type coupling [64] of 2,5-dibromothiophene, a vast number of articles concerning the synthesis and properties of PTs have been published. PTs (Scheme 29.7) exhibit favorable properties such as stability in both the neutral and the oxidized state under ambient conditions, but the numerous studies are also a result of the synthetic know-how for the preparation of (poly)thiophene and its derivatives [65].

The early problems concerning structural defects and solubility have attained much attention in the course of PT research, and some elegant solutions have been found. Extended  $\pi$ -conjugation in PTs is only possible in polymers with perfect 2,5-linked repeating units. Unfortunately, 2,4- and 2,3-couplings can be found as well. These undesired couplings are found when the polymers are prepared by (electro)oxidative polymerization methods. This is due to the fact that, during the polymerization, both the absolute oxidation potential of the  $\alpha$ -position and the oxidation potential difference between the  $\alpha$ - and  $\beta$ -positions decrease as the number of rings increases. The occurrence of  $\alpha$ ,  $\beta$ -linked thiophene rings interrupts the conjugation and as a result will give rise to inferior materials. PTs are, as other polyaromatic compounds, insoluble in organic solvents due to their rigid backbone. This insolubility and related problems, such as characterization and processability, have been overcome by the introduction of flexible side chains at one of the  $P$ -positions. Appropriate solubility is achieved by using thiophenes with one alkyl side chain consisting of more than three carbon units at every repeating unit [66]. However, in 3-substituted PTs, there are several coupling patterns possible (Scheme 29.8): the head-to-head, head-to-tail, and tail-to-tail isomers [67, 68].

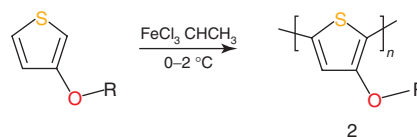
The head-to-head coupling is sterically unfavorable for coplanarity and causes considerable loss of conjugation, whereas the head-to-tail coupling displays only a limited effect on the conjugation. These significant differences



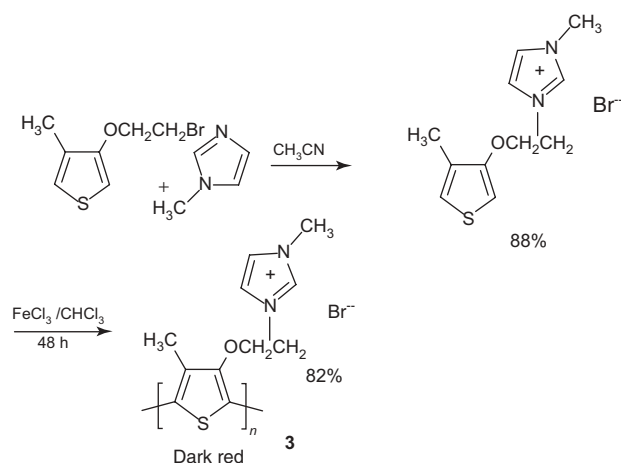
**Scheme 29.8** (a) Head-to-head, (b) head-to-tail, and (c) tail-to-tail coupling patterns in substituted polythiophenes.

in coplanarity between head-to-head and head-to-tail couplings show the subtleties in the trade-off between resonance energy and steric hindrance in polyheterocycles. Studies of regioregular PTs, recently made accessible via a number of elegant synthetic routes, have shown that the crystallinity is increased with regioregularity and that the possibility of side-chain crystallinity is essential for optimal properties. For the case of regio-random polymers, the optimal chain length of the alkyl side chains for properties such as conductivity and optical nonlinearities has been determined to be in the range of seven to nine carbon atoms [69]; the conductivity of doped regioregular PT with an  $n$ -dodecyl side chain surpasses that of the  $n$ -octyl-substituted polymer [70].

PTs are usually synthesized by the oxidative dehydrocondensation of thiophene and its derivatives that uses iron(III) chloride as an oxidizer and methylene chloride, chloroform, or nitromethane as solvents [71]. The principal direction of research in this area is the search for possible ways to improve engineering and service behavior of PTs through variation of the structure of parent monomers and resulting polymers. Thus, for example, the insertion of movable alkoxy groups into position 3 of the thiophene ring increases the solubility and processability of PTs and modifies their electric properties [72]. This phenomenon may be attributed to the electron-donor effect of alkoxy groups or to a more coplanar conformation of the corresponding PT as compared to products arising from the polymerization of common alkyl thiophenes [73]. The oxidative polycondensation of 3-alkoxythiophene at low temperatures and controlled addition of the monomer yields polymers with  $M = 2340\text{--}3140$  and small structural defects (Scheme 29.9) [74].



**Scheme 29.9** Oxidative polycondensation of 3-alkoxythiophene at low temperature.



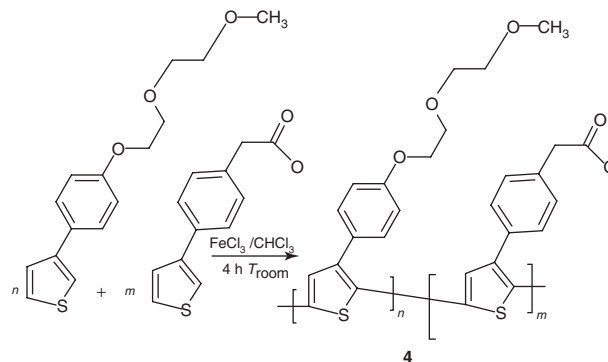
**Scheme 29.10** Preparation of an imidazolium-substituted PT-3.

Their thermal stability is slightly lower than that of the unsubstituted PT, and the value of  $T_g$  depends on the character of the alkoxy group ( $R = \text{Me}, \text{Bu}, \text{Hex}, \text{Octyl}$ ). The same strategy was employed for the synthesis of ionochromic PTs containing crown ether side groups [75]; these polymers show good solubility in chloroform, THF, acetone, and ethyl acetate. The incorporation of hydrocarbon substituents into side chains improves the solubility of PTs in polar solvents even more greatly and ensures their compatibility. PT derivatives have also found application in biochemistry. Thus, an imidazolium-substituted PT-3 (Scheme 29.10) that was prepared by the dehydropolycondensation of the corresponding monomer is used for the optical (colorimetric and fluorescent) determination of nucleic acids [76, 77].

This selective and universal method is based on conformational modifications of a cationic PT-5 [78] that occur via interaction with oligonucleotides or nucleic acids. As a result, the coloration of PT changes from dark red to blue or green. The synthesis of a soluble copolymer PT-4 ( $M = 2.4 \times 10^4$ ) containing carboxyl and ether bonds is depicted in Scheme 29.11 [79].

### 29.9.4 Polypyrrole

The first synthesis of polypyrrole, appreciating its conducting properties, was described in 1968 [80]. Electrochemical oxidation of a pyrrole solution in 0.1 N sulfuric acid afforded a black conducting film. Improvements through the use of organic solvents and different electrolytes have been made [81, 82] and the electrochemical method has been the most employed polymerization technique ever since. Oxidized polypyrrole is stable under ambient conditions and up to temperatures exceeding  $300^\circ\text{C}$  [82]. The neutral form of polypyrrole, on the other hand, has not been isolated



**Scheme 29.11** Synthesis of a soluble copolymer PT-4.

and characterized, due to its extreme susceptibility to oxidation. The electrochemical route to polypyrrole provides good quality films. Counterions have a considerable influence on the conductivity and mechanical properties [83]. Changing the counterion from oxalate to perchlorate increases the conductivity by a factor in the order of hundred thousand. Commercially available (BASF) polypyrrole with tosylate as counterion exhibits a conductivity of  $15 \text{ Scm}^{-1}$  and the stability of the material at ambient conditions is extremely good; a decrease of less than 15% per year is reported. Alkylsulfonates and phosphates have been used as electrolyte as well [84] and processable polymer blends are formed by using sulfonated polystyrene as counterions in the polymer.

The oxidation of a neutral polypyrrole film with chemical oxidizing agents increases the conductivity relative to that of the electrochemical oxidized materials [85]. 2,2'-Bipyrrrole has been used as monomer, but the properties of the polymer obtained are similar to those of the parent polymer obtained from pyrrole itself [86].

Pyrrole has been chemically polymerized with oxidants including sulfuric acid [87], bromine and iodine [88], copper(II) perchlorate [89], and iron(III) chloride [90]. Soluble polypyrrole can be prepared by the introduction of flexible side chains [91–93]. In contrast with the progress made in the synthesis of regioregular PTs, all 3-substituted polypyrroles reported so far have a regio-random structure.

Substitution on the nitrogen affords a regular soluble polymer; however, the conductivity is reduced drastically due to the strong steric interactions of the nitrogen substituent and the hydrogen atoms at the 3- and 4-positions of the adjacent pyrrole ring. Both rings are forced to go out of plane resulting in a loss of conjugation and hence a reduced conductivity [94]. Although the differences between a 3-substituted polypyrrole and an N-substituted polypyrrole at first glance are small with regard to steric hindrance, their conductivities differ significantly, again showing the subtleties in the structure–property relationship. The chemical oxidative method has also



been applied to 3-alkyl pyrroles and to 3,4-dimethoxy pyrrole [95].

The introduction of sulfonic acid groups in the alkyl side chains affords water-soluble self-doped polypyrrole. Using the sodium salt of the 3-alkylsulfonic acid pyrrole, the monomer acts as electrolyte for the electrochemical synthesis as well. A second long alkyl chain on the opposite side of the pyrrole ring affords a highly ordered lamellar polymer also soluble in chloroform [96].

Structural defects such as  $\alpha,\beta$ -couplings are inherent in oxidative polymerizations and to a minor extent can be present in the materials synthesized as described above. This failure to produce perfect 2,5-linked polypyrroles has been overcome by organometallic polymerization techniques. Thus, pyrroles with a Boc protecting group at nitrogen have been polymerized via the Stille coupling, affording a soluble nonplanar precursor polymer that has been deprotected by thermal treatment (Scheme 29.12). This polypyrrole, although of relatively low molecular weight ( $\sim 3400$ ), exhibits a perfect structure and is fully characterized. N-Boc-protected pyrrole has also been polymerized by the Ullmann coupling of the dibromo species, affording the same polymers as obtained by the Stille chemistry. A self-doped analog of polypyrrole has been obtained by means of the Ullmann coupling of *N*-butyl-2,5-dibromo-3,4-pyrrolidone [97].

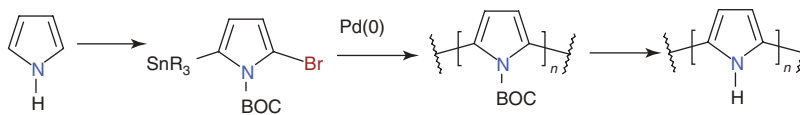
### 29.9.5 Poly(paraphenylene)

Poly(paraphenylene) can be reduced or oxidized to produce conducting materials with conductivities up to  $500 \text{ cm}^{-1}$ . Both conducting species are highly sensitive toward water and oxygen, whereas neutral poly(paraphenylene) is stable, both thermodynamically and chemically. For the synthesis of poly(paraphenylene), a number of different routes have been employed, namely, oxidative coupling, organometallic coupling, and dehydrogenation of polycyclohexylenes.

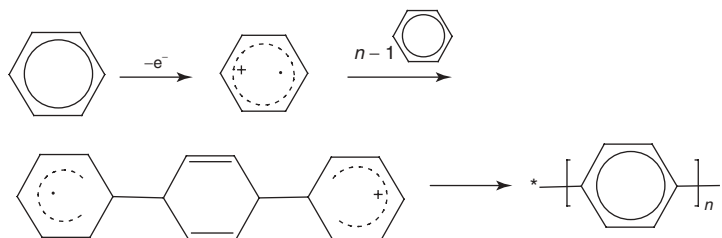
The first method reported for the synthesis of poly(paraphenylene) is the coupling of benzene by Lewis acid catalysis in the presence of an oxidant. In 1963, poly(paraphenylene) was synthesized by stirring benzene, aluminum chloride, and copper(II) chloride yielding an insoluble light brown powder [98]. The most favored mechanism is shown in Scheme 29.13. Benzene is oxidized to its radical cation that then propagates cationically. A second oxidation step produces the bis-cation, which loses two protons rearomatizing the terminal rings. Further oxidation of the dihydro structures finally affords the polymer [99].

Other Lewis acid/oxidant systems have been employed including  $\text{AsF}_3/\text{AsF}_5$  [100] and liquid  $\text{SO}_2$  or sulfuric acid and aluminum chloride [101]. Poly(paraphenylene) has been synthesized by the electrochemical oxidation of benzene in solvents such as liquid  $\text{SO}_2$  [102] and concentrated sulfuric acid [103], or with the addition of Lewis acids including aluminum chloride [104],  $\text{CuCl}_2/\text{LiAsF}_6$  [105], and  $\text{BF}_3\text{OEt}_2$  [106], affording polymeric films. To improve the solubility, poly(paraphenylene) has been sulfonated [107] and alkylated [108] with propyl halides to give materials with enhanced solubility.

A number of different organometallic coupling methods have been used for the synthesis of poly(paraphenylene) including the Grignard cross-coupling of dihalobenzenes with a nickel catalyst [109, 110], the cross-coupling of dihalobenzenes with zero-valent nickel complexes, and the electrochemical reduction of dihalobenzenes activated by zero-valent nickel complexes [111]. Soluble poly(paraphenylene)s have been synthesized by the introduction of flexible alkyl side chains using the nickel catalyzed cross-coupling reactions with magnesium or borium, although the improved solubility does not have a stimulating effect on the average degree of polymerization, which is of the order of 13. Higher molecular



Scheme 29.12 Polymerization and deprotection of N-Boc-protected pyrrole.



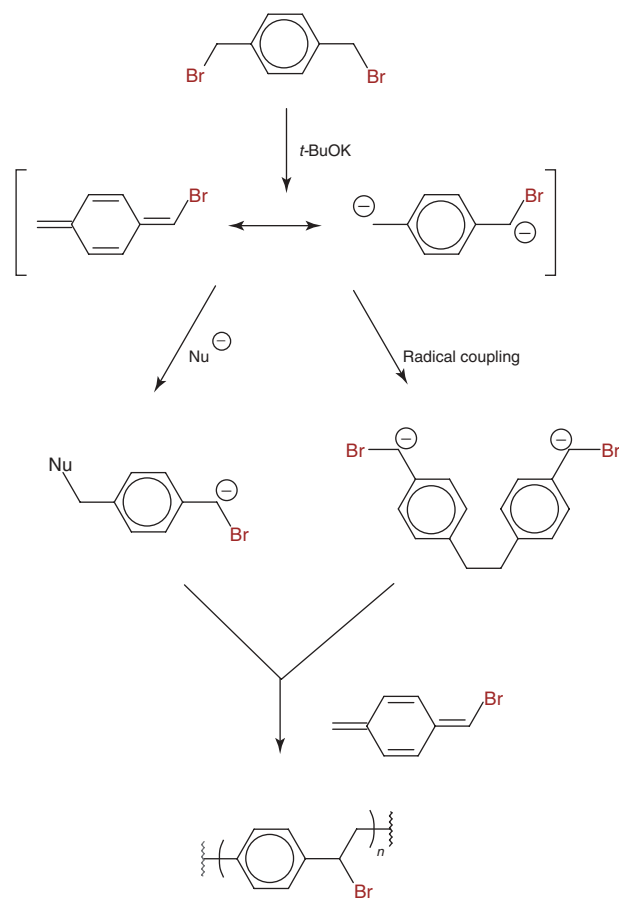
Scheme 29.13 Mechanism of the synthesis of poly(paraphenylene).

weight polymers, with an average degree of polymerization of approximately 100, have been obtained by the nickel (0)-induced polymerization of methyl 2,5-dichlorobenzoate, which on saponification and decarboxylation was transformed into poly(paraphenylene) [112]. A polymerization without a transition metal catalyst has been achieved by the hexamethylphosphoramide-induced polymerization of 1-bromo-4-lithiobenzene to provide soluble poly(paraphenylene)s with molecular weights up to 2000. These materials, however, consist of a considerable percentage (20–30%) meta linkages, which probably accounts for the remarkably high solubility [113].

### 29.9.6 Poly(*p*-phenylene Vinylene)

Poly(*p*-phenylene vinylene) (PPV) is a conjugated polymer, which becomes conductive by the addition of electron donors or acceptors [114, 115]. Several methods have been reported for the synthesis of PPV [3, 4, 6]. Direct chemical polymerization, which was used in the first attempt of synthesizing PPV, gave a product in the form of an insoluble powder that limited the use of the polymer in many applications [116]. The most popular method for the preparation of PPV is base-induced polymerization of sulfonium salt monomer in aqueous solution [114–118]. In this method, PPV films are obtained from the precursor polymer after thermal elimination of the sulfonium groups. PPV has also been prepared electrochemically by reducing *p*-xylylene-bis-(triphenylphosphonium). Two approaches are generally used for the synthesis of PPVs: the Wessling [119] route and the Gilch [120] route. The Wessling route involves treatment of *p*-xylylene sulfonium salts with an equal molar amount of base to form a soluble precursor polymer. The precursor polymer is then thermally treated to give the conjugated PPV. The Gilch route employs the treatment of  $\alpha,\alpha'$ -dihalo-*p*-xylenes with potassium *tert*-butoxide in organic solvents. Alkyl or alkoxy substituents on the aromatic ring are often used to impart solubility to the PPV. One of the most widely studied PPVs is poly(1-methoxy-4-(2-ethylhexyloxy)-*p*-phenylenevinylene) (MEHPPV) due to the enhanced solubility of this polymer [121]. The mechanism of this polymerization is not fully understood, and several processes have been suggested [8]. The polymerization is believed to proceed through a reactive quinodimethane intermediate that has been observed from UV spectra [122, 123]. However, the nature of the propagating species, radical or anionic, is not firmly established (Scheme 29.14).

Although many techniques to synthesize high molecular weight PPVs exist, they are largely limited to the synthesis of predominantly *trans*-PPVs [125]. Recent work by Katayama and Ozawa [126, 127] has, for the first time, provided access to all *cis*-PPVs by way of a stereospecific



**Scheme 29.14** Polymerization mechanism of  $\alpha,\alpha'$ -dibromoxylene by anionic and radical polymerization [124].

Suzuki–Miyaura cross-coupling polymerization of 1,4-bis((*Z*)-2-bromovinyl)benzenes with aryl-bis-boronic acids. The interest has been in an alternative approach, where rather than building a PPV with a pre-ordained stereochemistry, a postpolymerization *syn*-selective reduction on a poly(phenylene ethynylene) (PPE) is used [125]. This scheme has the advantage that high molecular weight PPEs can be synthesized using either Pd-catalysis or alkyne metathesis. This route could also potentially allow for the access to an additional array of PPVs that are uniquely accessible from PPEs. The transformation of the triple bonds in PPEs and other acetylene building blocks to alkenes has considerable potential.

## 29.10 CHARACTERIZATION TECHNIQUES

As most other polymers, conducting polymers can be characterized through a variety of analytical techniques. Many examples exist in the literature, some of which include the following:

1. cyclic voltammetry, for understanding redox processes in conducting polymers and evaluating potential battery and electrochromic window material candidates;
2. optical characterization of conducting polymers, for electrochromic window and nonlinear optical materials;
3. nuclear magnetic resonance, for structure confirmation, chain orientation, and molecular motion;
4. gel permeation chromatography, for molecular weight;
5. Raman analysis, for vibrational assignments;
6. differential scanning calorimetric and thermogravimetric analysis, for evidence of glass and melting transitions and decomposition temperatures;
7. dependence of conductivity on temperature, electric field, and magnetic susceptibility, to understand the conductivity mechanism;
8. electroluminescence to screen for potential use in LEDs;
9. X-ray analysis, including Rutherford backscattering, to understand the crystal structure and to obtain elemental depth profiles, to gain insight into the conductivity mechanism.

## 29.11 PRESENT AND FUTURE POTENTIAL

### 29.11.1 Applications

Potential applications for conducting polymers are numerous; some potential applications for conducting polymers are discussed below.

**29.11.1.1 Corrosion Protection** The recent methods of corrosion protection are not very lasting and are coming under increased scrutiny by the Environmental Protection Agency (EPA). As an example, the use of chromium and cadmium for anticorrosion will soon be banned. A mechanism for corrosion protection involves the use of a sacrificial electrode, such as zinc coating, which will corrode (oxidize) in safekeeping the substrate. Unfortunately, the coatings do not last very long. The oxidized zinc metal is dissolved by water or moisture. For this reason, there are extreme environmental concerns, since toxic metals are being released into the ecosystem. Barrier coatings, such as epoxy, are employed extensively but are not very durable once a pit or hole in the coating has been formed. The corrosive species then attacks the underlying metal and thereby increases the exposed surface, accelerating the corrosion process. MacDiarmid first suggested the corrosion inhibiting property of conducting polymers in 1985 [128]. Initial studies on the protection of metal surfaces against corrosion

by conducting polymers were reported in the literature that same year. A major type of corrosion occurs by oxidation of a metallic surface by a water medium to produce oxides and hydroxides. As these are formed, soluble species are produced, the surface pits increase their surface area, and the rate of decomposition accelerates. One way to provide corrosion protection is to coat the metal with a barrier to prevent the reactive species from reaching the surface. Galvanization with zinc (or other metals with low oxidation potential) prevents corrosion via the creation of an interfacial potential at the metal–zinc interface. The zinc will corrode preferentially. While the reactive species may encounter the metal, the increased oxidation causes the metal to be insensitive. Corrosion is therefore inhibited.

### 29.11.1.2 Sensors and Electromechanical Devices

Since conducting polymers change properties by incorporation of ions and solvents (the property change easiest to measure is conductivity), it is possible to develop and market ion-specific sensors based on conducting polymers. Conducting polymers could permit the incorporation of sensors into clothing. There are some challenges involved, such as background noise due to water absorption, lifetime, selectivity, and sensitivity. Conducting polymers also change volume depending on their oxidation state. It is, therefore, possible for conducting polymers to convert electrical energy into mechanical work. Conducting polymers actuators were proposed by Baughmann et al. [13]. An oxidation-induced strain of polyaniline and polypyrrole-based actuators has been reported, and the first “self-contained” actuators were reported by MacDiarmid [128]. There are many interesting possibilities for conducting-polymer actuators, but a great deal of work needs to be done.

The conducting polymers have useful applications in the development of chemical sensors. During the past two decades, conducting polymers have emerged as one of the most interesting materials for the fabrication of electrochemical sensors [129]. The great advantage of conducting polymer-based sensors over other available techniques is that the conducting polymers have the potential to exhibit improved response properties and are sensitive to small perturbations. Earlier inert polymers were being used only to provide mechanical strength to the membranes, but conductive polymers improve the sensitivity of the sensors due to their electrical conductivity or charge transport properties. Conducting polymers are also known for their ability to be compatible with biological molecules in neutral aqueous solutions [130]. Moreover, the polymer itself can be modified to bind biomolecules to a biosensor [131]. Another advantage of conducting polymers is that the electrochemical synthesis allows direct deposition of a polymer film on the electrode substrate, followed by biomolecule immobilization [132]. It is thus possible to control the spatial distribution of

the immobilized enzymes, film thickness, and modulation of enzyme activity. Conducting polymers can act as an electron promoter. Moreover, conducting polymers can be deposited over defined areas of electrodes. The unique properties of conducting polymers have been exploited for the fabrication of electrochemical sensors and biosensors [130–134]. Among many analytical techniques available, the development of chemical sensors has made significant strides in the last two decades. The rapidly growing applications of chemical sensors reflect the extent to which analytical chemists require these devices for cheap, accurate, convenient, and quick analysis of various samples. Chemical sensors are miniaturized analytical devices, which can deliver real-time and online information about the presence of specific compounds or ions in complex samples. Usually, an analyte recognition process takes place, followed by the conversion of chemical information into an electrical or optical signal.

**29.11.1.3 Batteries** This field is the first area where conducting polymers promise to have a big commercial impact. Batteries have several key components: the electrodes allow for collection of current and transmission of power; the cathode material becomes reduced when the anode material is oxidized and vice versa; and the electrolyte provides a physical separation between the cathode and the anode, and provides a source of cations and anions to balance the redox reactions. Aside from picking the best conducting polymer available, there are many other issues, not related to conducting polymers, that affect battery performance, such as electrolyte stability and stability of the counter half-cell reaction (which is at least as important as the conducting-polymer electrode), and compatibility between the electrolyte and the materials.

There was a great deal of initial excitement about conducting polymers as active materials in batteries. Owing to their low density, it was thought that battery with power densities much higher than those of the ordinary lead/acid battery could be readily obtained. Since the charge on a polymer backbone is distributed over three or four repeat units, the charge capacity per unit of mass for conducting polymers is marginally better than that of metals. Conducting-polymer batteries were investigated by BASF/VARTA and Allied Signal. Bridgestone has marketed a button-sized battery using polyaniline and lithium. Conducting polymer still has a potential use in lithium-based high power density batteries, which use the high potential difference between lithium and the polymer to achieve high power densities, although stability and shelf life are still issues. As more and more individuals use cellular phones, laptop computers, and cordless drills, the importance of batteries that will handle many deep cycles (at least 60% depth of discharge)

becomes increasingly apparent. Conducting polymer-based batteries shows promise, but much work needs to be done.

**29.11.1.4 Electrochromic Cell** These cells are used to go from opaque to transmissive states at selected regions of the electromagnetic spectrum. Batteries and electrochromic cells have many common critical issues for commercial viability. They require cathodic and anodic reactions to be almost perfectly balanced (cyclic voltammetry is a good comparison tool for materials). The electrochromic window is similar to that of a battery with some additional requirements: at least one of the electrodes must be transparent to the given electromagnetic spectrum; the cathode material (which colors upon being oxidized) must be electrochemically reversible; and the ion-conducting electrolyte must not only provide physical separation between the cathode and anode, a source of cations and anions to balance redox reactions, but must also be transparent to the given region of the spectrum; and the anode material (which colors upon being reduced) must also be electrochemically reversible.

The ion-conducting electrolyte in electrochromic cells is usually an inorganic salt dissolved in a solvent such as propylene carbonate with a polymer such as poly(methyl methacrylate) added as a stiffener. The ion-conducting electrolyte acts as a source and sink for the ions as the various redox processes take place and maintains ionic contact between the materials. Conducting polymers also have an application in electrochromic cells, attenuating various regions of the electromagnetic spectrum. Aside from the batteries issues mentioned in the previous section, electrochromic cells have some additional requirements. Although thinner layers (for optical window) are usually sufficient, retention of extinction coefficient and contrast ratios are critical. Many electrochromic cells need to last for more than 10,000 cycles and have switching times of a few minutes. In this case, spectroelectrochemistry is a good evaluation tool for conducting-polymer materials. Spectroelectrochemistry measures both the electrical and the optical response of the material in question. Again, it must be emphasized that this method is not suitable for devices; spectroelectrochemistry is usually performed in a great excess of electrolyte and, therefore, the counter half-cell reactions are often ill defined. There is a great deal of data that indicate that conducting polymers are good candidates for materials in electrochromic cells. In particular, polythiophene, polypyrrole, and polyaniline have been cycled more than 10,000 times. These data, although good for evaluating differences between polymers, may not accurately reflect the performance of conducting polymers in a sealed, self-contained device. This is because the counter half-cell reaction and those devices often require “deep cycle,” that is, near complete oxidation/reduction. The device usually starts to degrade at 10–100 times



fewer cycles than conducting polymers studied by cyclic voltammetry. This does not necessarily mean that polymer is degrading, as either the counter half-cell reaction or the limited amount of electrolyte may control the lifetime of the device. Furthermore, cyclic voltammetry measures the retention of charge capacity in a polymer film and not the electrochromic contrast ratio. Although a 20% drop in charge capacity might be acceptable in a battery, a 20% decrease in a contrast ratio for electrochromic cells may be unacceptable. In devices that are based on retention of surface conductivity, it appears that conductivity is lost long before a significant amount of charge capacity decreases. The evaluation of conducting polymer for battery and electrochromic application should be similar to the actual condition (depth of discharge, cycle time, and transmission of extinction ratio).

**29.11.1.5 Controlled-Released Applications** Another application for conducting polymers is controlled-released devices. Ions can be selectively released, as well as biologically active ions such as adenosine 5'-triphosphate (ATP) and heparin. A conducting polymer with a given oxidation potential is electrodeposited onto a substrate with a mobile counter ion. Another polymer layer (polymer B with a higher oxidation potential than polymer A) is electrodeposited (directly on top of polymer A) using an immobile counter ion (polyanion). During complete reduction (step 1), it is almost impossible for the polymeric anion ( $Y^-$ ) to move into the electrolyte solution and, therefore, cations ( $M^+$ ) from the solution must move into the outer polymer layer, but the mobile anions ( $X^-$ ) from the inner layer move into the electrolyte. During selective oxidation of polymer A (2), the mobile anions ( $X^-$ ) move from the solution to the inner layer. During oxidation of polymer B (3), the cations ( $M^+$ ) move back into solution. This potential-dependent ion transport is an interesting way to deliver ionic drugs to certain biological systems. Anions can be exclusively delivered by cycling back and forth through step (2), cations can be exclusively delivered by cycling back and forth through step (3), or anions can be delivered and cations can be received by cycling through step (1). It is very important for the inner polymer layer to have a lower oxidation potential than the outer layer. If this is not the case, the inner layer, which is the one connected to the electrode, will act as an electrical insulator and will prevent the oxidation of the outer layer. Once the oxidation potential of the inner layer is reached, a pulse charge will occur, making selective ion transport difficult (rectification). Furthermore, a biologically compatible counter-half cell is necessary for a practical device. This might not present too much of a problem if the drug delivery system is used only once. If repeated uses of the same device are necessary, then issues such as reversibility

(as those of batteries and electrochromics) will need to be resolved.

**29.11.1.6 Radar Application** Radio direction and ranging (RADAR) uses electromagnetic waves that bounce off a particular target and are collected by a receiver, which analyzes the signal and determines the range, direction, and speed of the object in question. Reflections occur whenever there is a sharp impedance difference between the medium (usually air) and the object. Impedance differences are most notable between metals and air. Metals tend to reradiate (reflect) the incoming signal. Conducting-polymer camouflage works a little differently, in that it reflects back in a way that it has more continuously variable impedance. A conducting-polymer textile used for camouflage has no sharp edges or wings and tends to appear indistinguishable from the surrounding hills and trees and absorbs more than 50% of incident microwave radiation. Microwave (100 MHz–12 GHz) properties of conducting polymers have been studied, as have the millimeter wave (24–40 GHz) properties of polypyrrole-coated fibers. Conducting polymers as radar absorbers in antennas, Salisbury screens, camouflage, and other types of shielding are of interest to the military.

**29.11.1.7 LEDs** A significant event occurred when Friend et al. [134, 135] published an electroluminescence study on the neutral (nonconducting) form of paraphenylene vinylene. This work has opened up a new avenue of research and, more importantly, a potential market for the material. The electroinjecting electrode is usually a low work function (easily oxidized) metal and the hole-injection electrode is a high work function metal, or indium tin oxide, or a conducting polymer with an oxidation potential higher than that of the active layer. Some general trends have been observed: as a lower work function metal (less stable because it is easily oxidized) is used, the efficiency increases but the lifetime decreases. Studies have been reported in which a layer of neutral conjugated polymer, with a reduction potential closer to zero than that of the active conducting-polymer layer, increases efficiency. A simplistic overview of the function of an LED is as follows: an electron is injected into the polymer from the cathode while a hole is injected from the anode; there is an oxidized polymer on one side of the polymer film and a reduced polymer on the other side. The hole and the electron then migrate toward the center of the film and, when they meet each other, they recombine and give off light. The frequency of the light emitted is roughly equal to the difference between the oxidation and the reduction potential of the polymer (the electrochemical band gap) and, therefore, is related to the electronic band gap. Polymers with a different band gap have distinct values for the difference between oxidation and reduction

potential, and emit different wavelength of light. Several articles on conducting polymer LEDs and the effect of various additives, electrode modifications, tuning emission, the effect of impurities, and discussions of hole tunneling, photoexcitation, and unusual symmetric bias, have been published. The efficiency of LEDs is constantly being improved along with novel developments such as flexible LEDs, polarized LEDs, and light-emitting electrochemical cells. The emission of red, green, blue, and white light have all been demonstrated, and so has brightness in the order of 400 cd/m, which is similar in brightness to fluorescent lights or computer displays.

A challenge in the operation of LEDs is the fact that it appears that the mobility of the hole is higher than the mobility of the electron. The barrier height (as a resistance) between the polymer and each of the electrodes must be low and roughly equal, so that the hole and the electron recombine near the center of the conducting-polymer layer, to ensure good operation. Another limiting factor is the competition between radiative and nonradiative decay that, for PPV-type systems, is about 25%, which does not limit device performance at this juncture. Yet another challenge is the fact that the polymers that initially perform well in LEDs contain electron-rich double bonds. These double bonds are fairly easy to oxidize and are most likely one of the major causes for device degradation. Thermal and photo-oxidation of the double bonds in LED polymers have been discussed in detail. The efficiency, lifetime, and brightness depend on a variety of factors. One major challenge is balancing the electron mobility to that of the hole mobility. This is done by adding electron transport layers and hole transport layers such as trisubstituted amines. These layers reduce the barrier height and encourage the holes and electrons to combine near the center of the film. Electron and hole transport layers could permit the use of more stable metals without compromising efficiency. Conducting polymers enable a wide variety of structures to be synthesized and therefore many different wavelengths of light are possible. Although conducting polymers will not replace fluorescent light bulbs (which have efficiencies of around 70%), because conducting-polymer LEDs are easily patterned, operate at low DC voltages, and have uniform areas of light, there is a potential market for low level backlighting and alphanumeric displays.

## REFERENCES

- Natta G, Mazzanti G, Corradini P. *Atti Accad Naz Lincei Cl Sci Fis Mat Rend* 1958;25(8):3. Natta G, Mazzanti G, Corradini P. *Atti Accad Naz Lincei Cl Sci Fis Mat Nat Rend* 1958;25:2.
- Shirakawa H. *Rev Mod Phys* 2001;73:713.
- Ito T, Shirakawa H, Ikeda S. *J Polym Sci Polym Chem Ed* 1974;12:11.
- Heeger AJ. *Rev Mod Phys* 2001;73:681.
- MacDiarmid AG. *Angew Chem Int Ed* 2001;40:2581.
- Harun MH, Saion E, Kassim A, Yahya N, Mahmud E. *J Acoust Soc Am* 2007;2:63.
- Skotheim TA, Elsenbaumer RL, Reynolds JR, editors. *Handbook of Conducting Polymers*. 2nd ed. New York: Marcel Dekker; 1998.
- Pohl HA, Bommann JA, Itoh W. *Am Chem Soc Div Polym Chem Preprints* 1961;2(1):211.
- Katon JE, Wild BS. *J Chem Phys* 1964;40(10):2977.
- Bredas JL, Chance RR, Silbey R. *Phys Rev B* 1982;26:5843.
- Clarke TC, Geiss RH, Kwak JF, Street GB. *J Chem Soc Chem Commun* 1978;(12):489.
- Pron A, Rannou P. *Prog Polym Sci* 2002;27:135.
- Shirakawa H, Louis EJ, MacDiarmid AG, Chiang CK, Heeger AJ. *J Chem Soc Chem Commun* 1977;(16):578.
- Stenger-Smith JD. *Prog Polym Sci* 1998;23:57.
- Nalwa HS. In: Nalwa HS, editor. *Handbook of Organic Conductive Molecules and Polymers*. New York: Wiley; 1997.
- Schon JH, Dodabalapur A, Bao Z, Kloc C, Schenker O, Batlogg B. *Nature* 2001;410:189.
- Chiang CK, Jr Fincher CR, Park YW, Heeger AJ, Shirakawa H, Louis EJ, MacDiarmid AG. *Phys Rev Lett* 1977;39:109.
- Chiang CK, Druy MA, Gau SC, Heeger AJ, Louis EJ, MacDiarmid AG. *J Am Chem Soc* 1978;100:1013.
- Kanatzidis MG. *Chem Eng News* 1990;68(49):36.
- Nigrey PJ, MacDiarmid AG, Heeger AJ. *J Chem Soc Chem Commun* 1979;(14):594.
- Jr MacInnes D, Druy MA, Nigrey PJ, Nairns DP, MacDiarmid AG, Heeger AJ. *J Chem Soc Chem Commun* 1981;7:317.
- Heeger AJ, Kivelson S, Schrieffer JR, Su W-P. *Rev Mod Phys* 1988;60:781.
- Ziemelis KE, Hussain AT, Bradley DDC, Friend RH, Rilhe J, Wegner G. *Phys Rev Lett* 1991;66:2231.
- Burroughes JH, Jones CA, Friend RH. *Nature* 1988;335:137.
- Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, Burns PL, Holmes AB. *Nature* 1990;347:539.
- Chiang J-C, MacDiarmid AG. *Synth Met* 1986;13:193.
- MacDiarmid AG, Chiang J-C, Richter AF, Epstein AJ. *Synth Met* 1987;18:285.
- MacDiarmid AG, Epstein AJ. *Faraday Discuss Chem Soc* 1989;(88):317.
- MacDiarmid AG, Epstein AJ. In: Salaneck WR, Clark DT, Samuelsen EJ, editors. *Science and Applications of conducting Polymers*. Bristol: Adam Hilger; 1990. p 117.
- Han CC, Elsenbaumer RL. *Synth Met* 1989;30:123.
- Lu FL, Wudl F, Nowak M, Heeger AJ. *J Am Chem Soc* 1986;108:8311.



32. Sun Y, MacDiarmid AG, Epstein AJ. *J Chem Soc Chem Commun* 1990;(7):529.
33. Toshima N, Hara S. *Prog Polym Sci* 1995;20:155.
34. Chao TH, March J. *J Polym Sci A Polym Chem* 1988;26:743.
35. Ikeda S, Tamaki A. *J Polym Sci Polym Phys Ed* 1966;4:605.
36. Fukui K, Inagaki S. *J Am Chem Soc* 1975;96:4445.
37. Ikeda S. *Kogyo Kagaku Zasshi* 1880;1967:70.
38. Berets DJ, Smith DS. *Trans Faraday Soc* 1968;64:823.
39. Ito T, Shirakawa H, Ikeda S. *J Polym Sci Polym Chem Ed* 1975;13:1943.
40. Shirakawa H, Ito T, Ikeda S. *Makromol Chem* 1978;179:1565.
41. Hatano M, Kambara S, Okamoto S. *J Polym Sci* 1961;51:S26.
42. Huang WS, Humphrey BD, MacDiarmid AG. *J Chem Soc Faraday Trans* 1986;82:2385.
43. MacDiarmid AG. *Synth Met* 1997;84:27.
44. MacDiarmid AG, Chiang JC, Halpern M, Huang WS, Mu SL, Somasiri NLD, Wu WQ, Yaniger SI. *Mol Cryst Liq Cryst* 1985;121:173.
45. Huang J. *Pure Appl Chem* 2006;78(1):15.
46. Chandrasekhar P. *Conducting Polymers, Fundamentals and Applications: A Practical Approach*. Boston: Kluwer Academic; 1999. p 760.
47. Zhang X, Manohar SK. *Chem Commun* 2004;20:2360.
48. Yu L, Lee JI, Shin KW, Park CE, Holze R. *J Appl Polym Sci* 2003;88:1550.
49. Michaelson JC, McEvoy AJ. *Chem Commun* 1994;79:18.
50. Li GC, Zhang ZK. *Macromolecules* 2004;37:2683.
51. Huang LM, Wang ZB, Wang HT, Cheng XL, Mitra A, Yan YX. *J Mater Chem* 2002;12:388.
52. Liu JM, Yang SC. *J Chem Soc Chem Commun* 1991;(21):1529.
53. Zhang X, Goux WJ, Manohar SK. *J Am Chem Soc* 2004;126:4502.
54. Li WG, Wang HL. *J Am Chem Soc* 2004;126:2278.
55. Qiu HJ, Wan MX, Matthews B, Dai LM. *Macromolecules* 2001;34:675.
56. Wei ZX, Wan MX. *J Appl Polym Sci* 2003;87:1297.
57. Wei ZX, Zhang ZM, Wan MX. *Langmuir* 2002;18:917.
58. Wan MX. *Conducting Polymer Nanotubes In: Nalwa HS, editor. Encyclopedia of Nanoscience and Nanotechnology*. Vol. 2. Los Angeles: American Scientific Publishers; 2004. p 153.
59. Qiu HJ, Wan MX. *J Polym Sci A Polym Chem* 2001;39:3485.
60. Chen S-A, Tsai C-C. *Macromolecules* 1993;26:2234.
61. Meyer V. *Chem Ber* 1883;16:1465.
62. Meisel SL, Johnson GC, Hartough HD. *J Am Chem Soc* 1950;72:1910.
63. Yamamoto T, Sanechika K, Yamamoto A. *J Polym Sci Polym Lett* 1980;18:9.
64. Lin Lin JW-P, Dudek LP. *J Polym Sci A Polym Chem* 1980;18:2869.
65. Gronowitz S, editor. *Thiophene and Its Derivatives, Part I*. The chemistry of heterocyclic compound. Vol. 44. New York: John Wiley & Sons; 1985.
66. Jen K-W, Miller GG, Elsenbaumer RL. *J Chem Soc Chem Commun* 1986;(17):1346.
67. Sato M, Morii H. *Macromolecules* 1991;24:1196.
68. Leclerc M, Diaz FM, Wegner G. *Makromol Chem* 1989;190:3105.
69. Roncali J, Garreau R, Yasser A, Marque P, Gamier F, Lemaire M. *J Phys Chem* 1987;91:6706.
70. McCullough RD, Tristram-Nagle S, Williams SP, Lowe RD, Jayaraman M. *J Am Chem Soc* 1993;115:4910.
71. [a]Fichou D, editor. *Handbook of Oligo- and Polythiophenes*. Vol. 3. Weinheim: Wiley-VCH; 1999.[b]McCullough RD. *Adv Mater* 1998;10:93.
72. Roncali J. *Chem Rev* 1997;97:173.
73. Leclerc M, Daoust G. *Synth Met* 1991;41:529.
74. Hu X, Xu L. *Polymer* 2000;41:9147.
75. Boldea A, Levesque L, Leclerc M. *J Mater Chem* 1999;9:2133.
76. Tyagi S, Kramer FR. *Nat Biotechnol* 1996;14:303.
77. Taton TA, Mirkin CA, Letsinger RL. *Science* 2000;289:1757.
78. Ho H-A, Boissinot M, Bergeron MG. *Polym Prepr (Am Chem Soc Div Polym Chem)* 2002;43:133.
79. Jonforsen M, Ahmad I, Johansson T. *Synth Met* 2001;119:529.
80. Dall'Olio A, Dascola G, Varacca V, Bocchi VC. *R Acad Sci* 1968;C 267:433.
81. Diaz AF, Kanazwa KK, Gardini GP. *J Chem Soc Chem Commun* 1979;(14):635.
82. Kanazawa KK, Diaz AF, Gill WD, Grant PM, Street GB, Gardini GP, Kwak JF. *Synth Met* 1979;180(1):329.
83. Qian R, Qiu J, Shen D. *Synth Met* 1987;18:13.
84. Wernet W, Monkenbusch M, Wegner G. *Mol Cryst Liq Cryst* 1985;118:193.
85. Street GB, Clarke TC, Krounbi M, Kanazawa K, Lee V, Pfluger P, Scott JC, Weiser G. *Mol Cryst Liq Cryst* 1982;83:253.
86. Lindenberger H, SchXfer-Siebert D, Roth S, Hanack M. *Synth Met* 1987;18:37.
87. Salmon M, Kanazawa KK, Diaz AF, Krounbi M. *J Polym Sci Polym Lett* 1982;20:187.
88. Chan HS, Munro HS, Davies C, Kang ET. *Synth Met* 1988;22:365.
89. Castillo-Ortega NM, Inoue MB, Inoue M. *Synth Met* 1989;28:C65.
90. Lei J, Cai Z, Martin CR. *Synth Met* 1992;46:53.
91. Rillhe J, Ezquerra TA, Wegner G. *Synth Met* 1989;28:C177.
92. Masuda H, Tanaka S, Kariyama K. *J Chem Soc Chem Commun* 1989;(11):725.

93. Zotti G, Schiavon G, Berlin A, Pagani G. *Synth Met* 1989;28:C183.
94. Kanazawa KK, Diaz AF, Geiss RH, Gill WD, Kwak JF, Logan JA, Rabolt JF, Street GB. *J Chem Soc Chem Commun* 1979;19:854.
95. Merz A, Schwarz R, Schropp R. *Adv Mater* 1992;4:409.
96. Collard DM, Fox MA. *J Am Chem Soc* 1991;113:9414.
97. Brockmann TW, Tour JM. *J Am Chem Soc* 1994;116:7435.
98. Kovacic P, Kyriakis A. *J Am Chem Soc* 1963;85:454.
99. Milosevich S, Saichek K, Hinchey L, England WB, Kovacic P. *J Am Chem Soc* 1983;105:1088.
100. Aldissi M, Lepins R. *J Chem Soc Chem Commun* 1984;4:255.
101. Aeiyaeh S, Soubiran S, Lacaze PC, Froyer J, Pelous Y. *Synth Met* 1989;32:103.
102. Delamare M, Lacaze P-C, Dumousseau J-Y, Dubois J-E. *Electrochim Acta* 1982;27:61.
103. Levi MD, Pisarevskaya EY, Molodkina EB, Danilov AI. *J Chem Soc Chem Commun* 1992;1:14.
104. Kacriyama K, Sato M, Someto K, Tanaka S. *J Chem Soc Chem Commun* 1984;18:1199.
105. Sato M, Tanaka M, Kaneto K, Yoshino K. *Polym Commun* 1985;26:356.
106. Oshawa T, Inoue T, Takeda S, Kaneto K, Yoshino K. *Polym Commun* 1986;27:61.
107. Kovacic P, Marchionna VJ, Koch FW, Oziomek J. *J Org Chem* 1966;31:2467.
108. Jones MB, Kovacic P, Lanska D. *J Polym Sci A Polym Chem* 1981;19:89.
109. Taylor SK, Bennett SG, Khoury I, Kovacic P. *J Polym Sci Polym Lett* 1981;19:85.
110. Toshima N, Asakura T. *Bull Chem Soc Jpn* 1993;66:948.
111. Aboukassim A, Chevrot C. *Polymer* 1993;34:401.
112. Chaturvedi V, Tanaka S, Kaeriyama K. *Macromolecules* 1993;26:2607.
113. Tour JM, Stephens EB. *J Am Chem Soc* 1991;113:2309.
114. Murase I, Ohnishi T, Naguchi T, Hirooka T. *Polym Commun* 1984;25:1327.
115. Gagnon DR, Capistran JD, Karasz FE, Lenz RW, Antoun S. *Polymer* 1987;28:567.
116. Gourley KD, Lillya CD, Reynolds JR, Chien JCW. *Macromolecules* 1984;17:1025.
117. Wessling RA. *J Polym Sci Polym Symp* 1986;72:55.
118. Lenz RW, Han CC, Karasz FE. *J Polym Sci A Polym Chem* 1988;26:3241.
119. Wessling RA, Zimmerman RG, inventors. US patent 3,401,152. 1968; Wessling RA, Zimmerman RG, inventors. US patent 3,532,643. 1970.
120. Gilch HG, Wheelwright WL. *J Polym Sci A Polym Chem* 1966;4:1337.
121. Pohl HA. *Chem Eng* 1961;68(22):105.
122. Lahti PM, Modarelli DA, Denton FR, Lenz RW, Karasz FE. *J Am Chem Soc* 1988;110:7258.
123. Denton FR, Sarker A, Lahti PM, Garay RO, Karasz FE. *J Polym Sci A Polym Chem* 1992;30:2233.
124. Neef CJ, Ferraris JP. *Macromolecules* 2000;33:2311.
125. Moslin RM, Espino CG, Swager TM. *Macromolecules* 2008;42(1):452.
126. Katayama H, Nagao M, Nishimura T, Matsui Y, Umeda K, Akamatsu K, Tsuruoka T, Nawafune H, Ozawa F. *J Am Chem Soc* 2005;127:4350.
127. Katayama H, Nagao M, Nishimura T, Matsui Y, Fukuse Y, Wakioka M, Ozawa F. *Macromolecules* 2006;39:2006:39.
128. MacDiarmid AG. *Short Course on Conducting Polymers*. New York: New Platz; 1985.
129. Guiseppi-Elie A, Wallace GG, Matsue T. *Chemical and Biological Sensors Based on Electrically Conducting Polymers* In: Skotheim TA, Elsenbaumer R, Reynolds JR, editors. *Handbook of Conducting Polymers*. 2nd ed. New York: Marcel Dekker; 1998. p 963.
130. Chaubey A, Malhotra BD. *Biosens Bioelectron* 2002;17:441.
131. Mulchandani AK, Wang CL. *Electroanalysis* 1996;8:414–419.
132. Bartlett PN, Whitaker RG. *Biosensors* 1988;3:359–379.
133. Arbizzani C, Mastragostino M, Scrosati B. *Conducting polymers for batteries, supercapacitors and optical devices* In: Nalwa HS, editor. *Handbook of Organic Conductive Molecules Sensors and Polymers*. Vol. 4. Chichester: Wiley; 1997. p 595–619 Chapter 11.
134. Friend RH, Gymer RW, Holmes AB, Burroughes JH, Marks RN, Taliani C, Bradley DDC, Dos Santos DA, Brédas JL, Lögdlund M, Salaneck WR. *Nature* 1999;397(14):121.
135. Friend RH. *Pure Appl Chem* 2001;73(3):425.