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Introduction

1.1 CONDUCTING POLYMERS

1.1.1 History of Conjugated Conducting Polymers

Polymers have emerged as one of the most important materials in the twentieth century. The twenty-first century will undoubtedly see the use of polymers move from primarily passive materials such as coatings and containers to active materials with useful optical, electronic, energy storage and mechanical properties. Indeed, this development has already begun with the discovery and study of conducting polymers. Electronically conducting polymers possess a variety of properties related to their electrochemical behavior and are therefore active materials whose properties can be altered as a function of their electrochemical potential. The importance and potential impact of this new class of material was recognized by the world scientific community when Hideki Shirakawa, Alan J. Heeger and Alan G. MacDiarmid were awarded the Nobel Prize in Chemistry in 2000 for their research in this field [1–5]. Although these materials are known as new materials in terms of their properties, the first work describing the synthesis of a conducting polymer was published in the nineteenth century [6]. At that time 'aniline black' was obtained as the product of oxidation of aniline, however, its electronic properties were not established.

It has been known for more than 40 years that the electronic conductivity of conjugated organic polymer chains, is orders of magnitude higher than that of other polymeric materials [7–9] although they are not metallic, however, the possibility of producing polymers

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Self-Doped Conducting Polymers M.S. Freund and B.A. Deore

with conductivities approaching those of metals was not recognized. A key discovery that changed the outlook for producing highly conducting polymers was the finding in 1973 that the inorganic polymer polysulfur nitride $(SN)_x$ is highly conducting [10]. The room-temperature conductivity of $(SN)_x$ is of the order of 10^3 S/cm, approaching the conductivity of copper, $\sim 10^5$ S/cm. Below a critical temperature of about 0.3 K, $(SN)_x$ becomes a superconductor [11]. These discoveries were of particular importance because they proved the possibility of generating highly conducting polymers, and stimulated the enormous amount of focus and activity necessary for the discovery of other polymeric conductors. In the period of 1976 and 1977, it was observed that the room-temperature conductivity of $(SN)_x$ could be enhanced by an order of magnitude following exposure to bromine or other similar oxidizing agents [12], suggesting that it was possible to increase the number of charge carriers in the material *via* doping.

In 1958, polyacetylene was first synthesized by Natta *et al.* as a black powder and found to be a semiconductor with conductivity in the range of 10^{-11} to 10^{-3} S/cm, depending upon how the polymer was processed and manipulated [13]. This polymer remained a scientific curiosity until 1967, when a coworker of Hideki Shirakawa at the Tokyo Institute of Technology was attempting to synthesize polyacetylene, and a silvery thin film was produced as a result of a mistake. It was found that the amount of Ziegler–Natta catalyst, $Ti(O\text{-}n\text{-}But)_4\text{-}Et_3Al$, was three orders of magnitude higher than required. When this film was investigated it was found to possess a higher conductivity than previously observed, approaching that of the best carbon black (graphite) powders. In the years between 1971 and 1975, Shirakawa and coworkers prepared crystalline polyacetylene films using refinements of the technique in the presence of Ziegler catalyst; however, the nature of conductivity was not pursued [14–16]. The real breakthrough in the development of conjugated organic conducting polymers was only reached after the discovery of metallic conductivity in crystalline polyacetylene films with p-type dopants such as halogens during collaborative research involving Shirakawa, MacDiarmid and Heeger in 1977 [1, 2]. A year later, it was discovered that analogous effects could be induced by electron donors (n-type dopant) [17]. Following this work there has been an explosion of activity around the characterization, synthesis and use of conducting polymers in a wide range of fields from electronics to medicine.

An organic polymer that possesses the electrical and optical properties of a metal while retaining its mechanical properties and processability, is termed an ‘intrinsically conducting polymer’ (ICP). These properties are intrinsic to the 'doped' form of the polymer. The conductivity of ICPs lies above that of insulators and extends well into the region of common metals; therefore, they are often referred to as 'synthetic metals.' The common feature of most ICPs is the presence of alternating single and double bonds along the polymer chain, which enable the delocalization or mobility of charge along the polymer backbone. The conductivity is thus assigned to the delocalization of π-bonded electrons over the polymeric backbone, exhibiting unusual electronic properties, such as low energy optical transitions, low ionization potentials and high electron affinities [18].

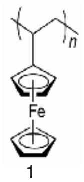
1.1.1.1 Conducting Polymer Composites

ICPs are 'doped conjugated polymers' and are fundamentally different from 'conducting polymer composites' [19], 'redox polymers' [20] and 'ionically conducting polymers' such as polymer/salt electrolytes [21]. Conducting polymer composites are typically a physical mixture of a nonconductive polymer and a conducting material such as a metal or carbon powder distributed throughout the material. Conductive carbon blacks, short graphite fibers, and metal coated glass fibers, as well as metal particles or flakes, were used in early experiments for the preparation of such composites. Their conductivity is governed by percolation theory, which describes the movement of electrons between metallic phases and exhibits a sudden drop in conductivity (percolation threshold) at the point where the dispersed conductive phase no longer provides a continuous path for the transport of electrons through the material. The conductivity above the percolation threshold of these materials can be as high as 10^{-1} S/cm, at 10–40 wt% fractions of the conductive filler [22, 23]. There are a number of drawbacks associated with such composite materials (fillers), namely: (i) their conductivity is highly dependent on processing conditions, (ii) there is often an insulating surface layer formed on the conductor and (iii) the composite may become mechanically unstable due to heavy loading of the conducting particles. More recently, composites as well as blends and grafting of ICP materials have been utilized in order to impart processability and improve the mechanical properties of these composites [24].

1.1.1.2 Redox Polymers

In 'conjugated conducting polymers', the redox sites are delocalized over a conjugated π system; however, 'redox polymers' have localized redox sites. The redox polymers are well known to transport electrons by hopping or self-exchange between donor and acceptor sites. The redox conductivity is comparatively lower than that of conjugated conducting polymers, likely due to slow electron transport to/from the redox centre. Apart from conjugated organic polymers such as polypyrrole, polythiophene and polyaniline, the first generation of redox polymers included the following main group materials:

(i) Saturated organic polymers with pendent transition metal complexes, such as polyvinylferrocene **1**[†] and metal complexes of polyvinylpyridine **2**[†][25].



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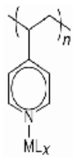

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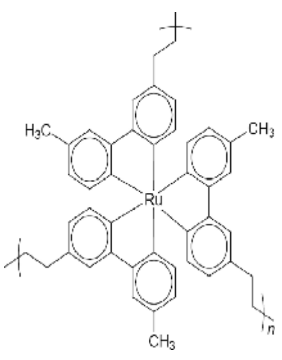
(ii) Electrochemically polymerized transition metal complexes with multiple polymerizable ligands, such as poly[ruthenium(4-vinyl-4′-methyl-2,2′-bipyridine)$_3^{2+}$] **3**[†] [26], poly[iron(4-(2-pyrrol-l-ylethyl)-4′-methyl-2,2′-bipyridine)$_3^{2+}$] **4**[†] [27], and poly[tetra(4-pyrrole-l-ylphenyl)porphyrin] (**poly-5**[†]) [28]. These differ from the polymers in group (i) in that they do not contain extended



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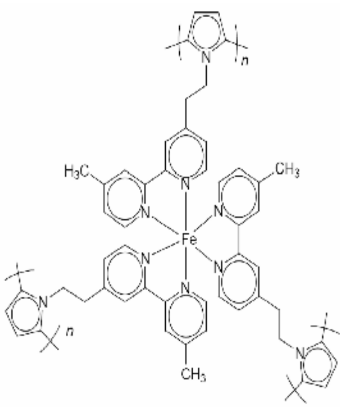

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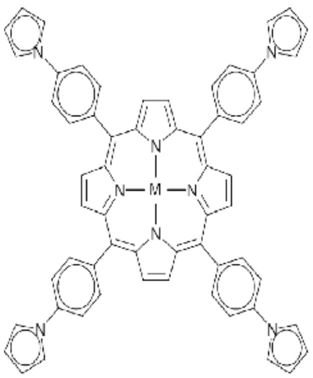

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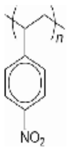
organic chains. The complexes are linked in a 3-D network primarily by intermolecular dimerization of the ligands.

(iii) Saturated organic polymers with pendent electroactive organic moieties [29], such as poly(4-nitrostyrene) **6**.[#]

(iv) Ion exchange polymers containing electrostatically bound electroactive ions, such as Nafion containing $Ru(bpy)_3{}^{2+}$ (bpy = 2,2′-bipyridine) and quaternized polyvinylpyridine containing $Fe(CN_6)^{3-/4-}$.

More recently, there has been growing interest in a new type of redox polymer that is a hybrid of materials from conjugated organic polymers and group (ii), referred to as conjugated metallopolymers [30, 31]. Examples include metal complexes of poly(2,2′-bipyridine) **7**[#] and the polyferrocenes **8**[#]. The key feature of this class of material is that the metal is coordinated directly to the conjugated backbone of the polymer, or forms a link in the backbone, such that there is an electronic interaction between the electroactive metal centers and the electroactive polymer backbone. This can enhance electron transport in the polymer, enhance its electrocatalytic activity, and lead to novel electronic and electrochemical properties.



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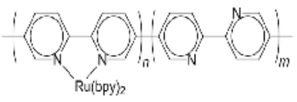

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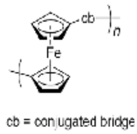

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1.1.1.3 Ionically Conducting Polymers

Ionically conducting polymers (polymer/salt electrolytes) are of great interest because they exhibit ionic conductivity in a flexible but solid membrane. Ionic conductivity is different than the electronic conductivity of metals and conjugated conducting polymers, since current is carried through the movements of ions. They have been critical to the development of devices such as all-solid-state lithium batteries. The research and development of solid polymer electrolytes began when Wright *et al.* found ion conductivity in a PEO-alkaline metal ion complex in 1973 [32]. The ionic conductivity at that time was 10^{-7} S/cm at room temperature. Since then many salts, including those containing di- and trivalent cations, have been combined with a variety of polymers in order to form polymer electrolytes [33–35]. The considerable potential of these materials as solid ionic conductors was first recognized by Armand in 1979 [36]. Since that time there has been intense interest in the synthesis and characterization of this class of material, as well as considerable focus on their potential use as solid electrolytes in electrochemical devices such as rechargeable lithium batteries, electrochromic displays and smart windows [37]. Polymer electrolytes also represent a fascinating class of coordination compounds such as the oxo-crown ethers [38]. Amorphous polymer electrolytes have been studied intensively for 30 years, and although the conductivities have increased substantially over that period, they remain too low ($<10^{-4}$ S/cm) for many applications. The recently discovered crystalline polymer electrolytes represent a new class of solid ionic conductors and offer a different approach to ionic conductivity in the solid state. It is only in recent years that substantial progress in understanding the structure of these materials has become possible through the methods of crystal structure determination from powders [39, 40]. In general, polymer electrolytes have lower conductivity than liquid electrolytes and cannot deliver high power at room temperature and, in particular, low temperature batteries. Still, polymer electrolytes have many excellent properties such as ease of battery fabrication in various shapes, and better safety than conventional organic liquid electrolytes.

1.1.1.4 Intrinsically Conducting Polymers

Intrinsically conducting polymers offer a unique combination of ion exchange characteristics and optical properties that make them distinctive. They are readily oxidized and reduced at relatively low potentials, and the redox process is reversible and accompanied by large changes in the composition, conductivity and color of the material. These polymers are made conducting, or 'doped', by the reaction of conjugated semiconducting polymer with an oxidizing agent, a reducing agent or a protonic acid, resulting in highly delocalized polycations or polyanions [41]. The conductivity of these materials can be tuned by chemical manipulation of the polymer backbone, by the nature of the dopant, by the degree of doping and by blending with other polymers. In addition, polymeric materials are lightweight, processible and flexible.

Since Shirakawa, Heeger and MacDiarmid [1, 2] discovered that polyacetylene can reach extremely high electronic conductivities, the field of conducting polymers has attracted the interest of thousands of scientists and engineers. Much of the combined research efforts of industrial, academic and government researchers have been directed toward developing materials that are stable (mechanically and electronically) for use in applications, easily processible and can be produced simply and at a low cost. These goals have been surprisingly difficult to reach and only recently have companies been able to bring products to market. Examples of commercial providers of bulk ICP include Zipperling Kessler & Co., who provide polyaniline powder suspensions sold under the name 'ORMECON', the Bayer Corporation who provide highly transparent and stable poly(3,4-ethylendioxythiophene) (PEDOT) water dispersion with variable conductivity under the name 'Baytron,' and Panipol who provide polyaniline powder dispersible in polyolefines.

Recent advances in the field of ICPs have led to a variety of materials with great potential for commercial applications such as rechargeable batteries, light emitting diodes (LEDs), photovoltaics, membranes, electronic noses and sensors, etc. The field of conducting polymers is broad, involving synthesis, characterization and implementation. Over the past three decades there has been explosive growth in conducting polymer research. Since 1977, thousands of articles on conducting polymers have been published in scientific journals every year. The most cited journals in this field include *Synthetic Metals*, *Applied Physics Letters*, *Journal of Applied Physics*, *Advanced Materials*, *Macromolecules* and *Chemistry of Materials*. There have been excellent reviews on conducting polymers that cover synthesis [42–46], applications [4, 5, 47–49] and the current understanding of electronic structure [50–52]. Also, approximately 58 books and 8 handbooks to date cover the field in detail.

Of the many interesting conducting polymers that have been developed over the past 30 years, those based on polyanilines, polypyrroles,

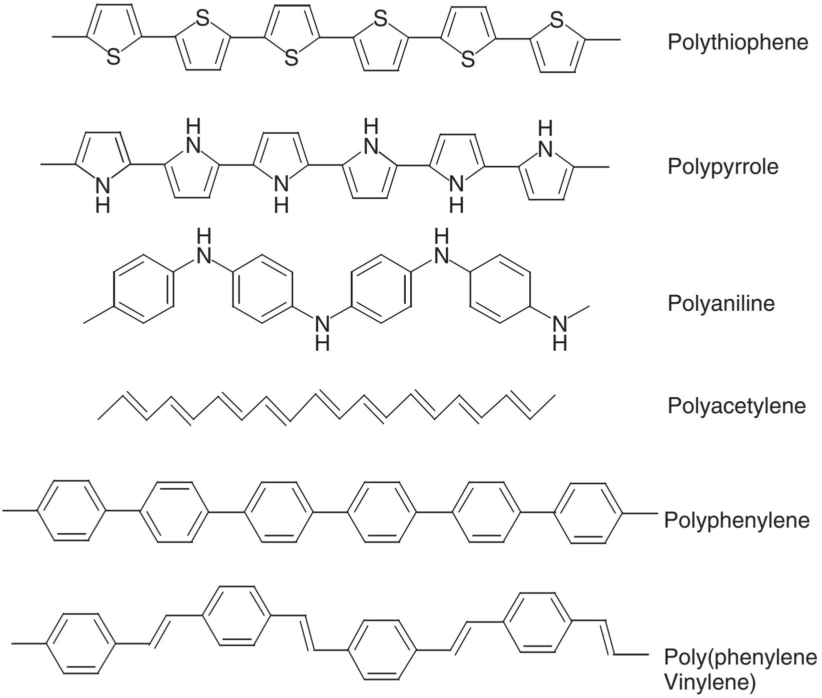

Figure 1.1 Chemical structure of some conjugated polymers.

polythiophenes, polyphenylenes and poly(*p*-phenylene vinylene)s have attracted the most attention. Figure 1.1 shows the structure of some conjugated polymers in their neutral insulating form. In order to make them electronically conductive, it is necessary to introduce mobile carriers into the conjugated system; this is achieved by oxidation or reduction reactions and the insertion of counterions (called 'doping'). Dedoped conjugated polymers are semiconductors with band gaps ranging from 1 to several eV, therefore their room temperature conductivities are very low, typically 10^{-8} S/cm or lower. However, by doping, conductivity can increase by many orders of magnitude. The concept of doping is unique and distinguishes conducting polymers from all other types of polymer [1, 53]. During the doping process, an organic polymer, either an insulator or semiconductor having small conductivity, typically in the range of 10^{-10} to 10^{-5} S/cm, is converted to a polymer which is in a 'metallic' conducting regime (1 to 10^4 S/cm). The highest value reported to date has been obtained in iodine-doped polyacetylene ($>10^5$ S/cm)

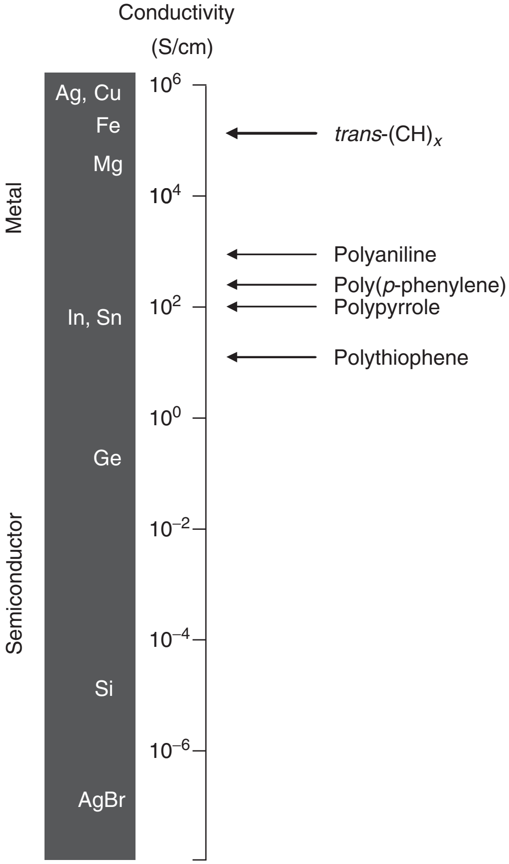

Figure 1.2 Conductivity of some metals and doped conjugated polymers.

and the predicted theoretical limit is about 2 × 10^7, more than an order of magnitude higher than that of copper [1]. Conductivity of other conjugated polymers reaches up to 10^3 S/cm [2, 3, 54, 55] as shown in Figure 1.2.

1.1.2 Concept of Doping in Intrinsically Conducting Polymers

Doping in a conventional semiconductor such as silicon is very different from that in a conjugated organic polymer. In conventional semiconductors, the dopant is a small amount of a donor or acceptor that is introduced into the atomic lattice resulting in a change in the occupancy of the electronic states in the solid as a result of thermal ionization of the dopant. The band structure and the density of states are essentially unchanged by the introduction of the dopant [56].

Doping of a conducting polymer, on the other hand, involves the introduction of a large amount of a donor or acceptor (in the range of a few up to 30 wt%). The presence of such a large amount of dopant and structural changes in the polymer result in a material that is significantly different from the nondoped material. The dopant perturbs the polymer extensively not only because of its significant physical size and the fact that it does not incorporate into the molecular structure, but also because of the extensive charge transfer that takes place between the polymer chain and the dopant, causing both to become ionic and leading to changes in the geometry of the chain. The doping level can also be reversibly controlled to obtain conductivities anywhere between the insulating nondoped form to the fully doped, highly conducting form of the polymer.

Doping involves either oxidation or reduction of the polymer backbone. Oxidation removes electrons and produces a positively charged polymer and is described as ‘p-doping.’ Similarly, reduction produces a negatively charged backbone and is known as ‘n-doping.’ The oxidation and reduction reactions can be induced either by chemical species (e.g., iodine, sodium amalgam or sodium naphthaline) or electrochemically by attaching the polymer to an electrode. The electrochemical doping process proceeds in much the same way as with chemical doping, with the exception that the driving force for the oxidation and reduction is provided by an external voltage source (i.e., by the electrochemical potential of the working electrode). Electrochemical p- and n-doping can be accomplished under anodic and cathodic conditions by immersing polymer film in contact with an electrode in an electrolyte solution. In these p- and n-doping processes, the positive and negative charges on polymers remain delocalized and are balanced by the incorporation of counterions (anions or cations) which are referred to as dopants. The chemical doping process of polyacetylene is shown in Figure 1.3. Upon p-doping, an ionic complex consisting of positively charged polymer chains and counteranions (I_3^-) is formed. In the case of n-type doping, an ionic complex consisting of negatively charged polymer chains and countercations (Li^+) is formed. The electronic conductivity can be controlled by the amount of dopant present.

1.1.3 Conduction Mechanism

The electronic properties of any material are determined by its electronic structure. The theory that most reasonably explains electronic structure

$$(CH)_n + 3/2\, ny(I_2) \longrightarrow [(CH)^{y+}(I_3^-)_y]_n$$

p-doping

$$(CH)_n + y(Li) \longrightarrow [(CH)^{y-}(Li^+)_y]_n$$

n-doping

Figure 1.3 Chemical and electrochemical doping of polyacetylene.

of materials is band theory. Quantum mechanics stipulates that the electrons of an atom can only have specific or quantized energy levels. However, in the lattice of a crystal, the electronic energy of individual atoms is altered. When the atoms are closely spaced, the energy levels are form bands. The highest occupied electronic levels constitute the valence band and the lowest unoccupied levels, the conduction band (Figure 1.4). The electrical properties of conventional materials depend on how the bands are filled. When bands are completely filled or empty no conduction is observed. If the band gap is narrow, at room temperature, thermal excitation of electrons from the valence band to the conduction band gives rise to conductivity. This is what happens in the case of classical semiconductors. When the band gap is wide, thermal energy at room temperature is insufficient to excite electrons across the gap and the solid is an insulator. In conductors, there is no band gap since the valence band overlaps the conduction band and hence their high conductivity.

Conducting polymers are unusual in that they do not conduct electrons *via* the same mechanisms used to describe classical semiconductors and hence their electronic properties cannot be explained well by standard band theory. The electronic conductivity of conducting polymers results from mobile charge carriers introduced into the conjugated π-system

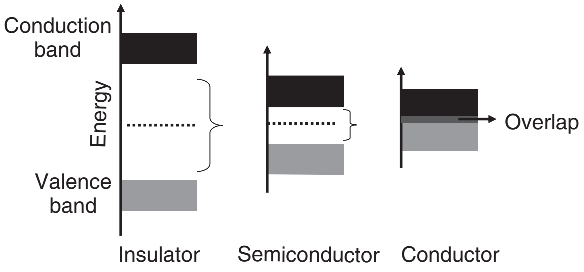

Figure 1.4 Energy band in solid.

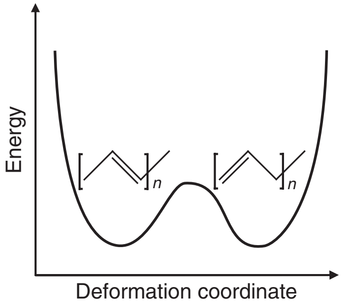

Figure 1.5 Energetically equivalent forms of degenerate polyacetylene. (Reproduced from *Polymer International*, 2004, 53, 1397, A. Moliton, R. C. Hiorns. Copyright Society of Chemical Industry. Permission is granted by John Wiley & Sons, Ltd on behalf of the SCI.)

through doping. To explain the electronic phenomena in these organic conducting polymers, new concepts including solitons, polarons and bipolarons [57–61] have been proposed by solid-state physicists. The electronic structures of π-conjugated polymers with degenerate and nondegenerate ground states are different. In π-conjugated polymers with degenerate ground states, solitons are the important and dominant charge storage species. Polyacetylene, $(CH)_x$, is the only known polymer with a degenerate ground state due to its access to two possible configurations as shown in Figure 1.5. The two structures differ from each other by the exchange of the carbon–carbon single and double bonds. While polyacetylene can exist in two isomeric forms: *cis*- and *trans*-polyacetylene, the *trans*-acetylene form is thermodynamically more stable and the *cis–trans* isomerization is irreversible [52].

Oxidative (p-type) doping of polyacetylene involves the chemical or anodic oxidation of the polymer to produce carbonium cations and radicals with simultaneous insertion of an appropriate number of anions between the polymer chains that neutralize the charge as shown in Figure 1.6 [62]. Two radicals can then recombine to give a spinless dication referred to as a positive soliton, which can act as the charge carrier [57]. Each soliton constitutes a boundary which separates domains that differ in the phase of their π-bonds. The ground state structure of polyacetylene is twofold degenerate and, therefore, 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

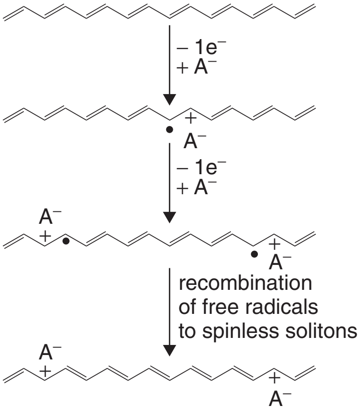

Figure 1.6 p-Type doping in polyacetylene. (Reprinted from *Progress in Polymer Science*, **27**, A. Pron, P. Rannou, 135. Copyright (2002), with permission from Elsevier.)

and identical energy. In solid-state physics a charge associated with a boundary or domain wall is called a soliton, because it has the properties of a solitary wave that can move without deformation and dissipation [63]. A soliton can also be viewed as an excitation of the system that leads from one potential well to another well of the same energy (see Figure 1.5 degenerate polyacetylene).

A neutral soliton occurs in pristine *trans*-polyacetylene when a chain contains an odd number of conjugated carbons, in which case there remains an unpaired π-electron, a radical, which corresponds to a soliton (Figure 1.7). In a long chain, the spin density in a neutral soliton (or charge density in a charged soliton) is not localized on one carbon but spread over several carbons [57, 64, 65], which gives the soliton a width. Starting from one side of the soliton, the double bonds become gradually longer and the single bonds shorter, so that arriving at the other side, the alternation has completely reversed. This implies that the bond lengths do equalize in the middle of a soliton. The presence of a soliton leads to the appearance of a localized electronic level at mid-gap, which is half occupied in the case of a neutral soliton and empty (doubly occupied) in the case of a positively (negatively) charged soliton (Figure 1.7). Similarly, in n-type doping, neutral chains are either chemically or electrochemically reduced to polycarbonium anions and simultaneously charge-compensating cations are inserted into the polymer matrix. In this case, negatively charged, spinless solitons are charge carriers.

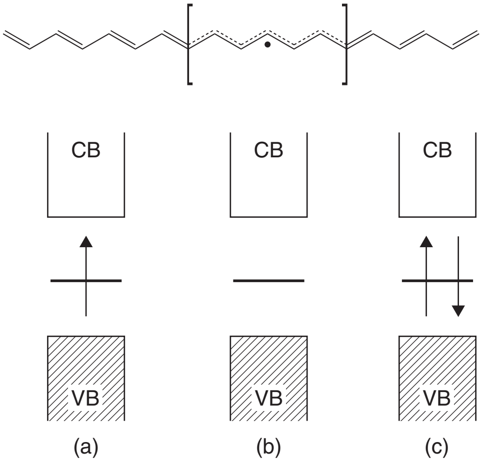

Figure 1.7 Top: schematic illustration of the geometric structure of a neutral soliton on a *trans*-polyacetylene chain. Bottom: band structure for a *trans*-polyacetylene chain containing (a) a neutral soliton, (b) a positively charged soliton and (c) a negatively charged soliton. (Reprinted with permission from *Accounts of Chemical Research*, **18**, 309. Copyright (1985) American Chemical Society.)

The π-conjugated systems based on aromatic rings, such as polythiophene, polypyrrole, polyaniline, polyparaphenylene and their derivatives have nondegenerate ground states. In these polymers, the ground-state degeneracy is weakly lifted (Figure 1.8) so that polarons and bipolarons (confined soliton pairs) are the important and dominant charge storage configurations. For example, the oxidative doping of polypyrrole is shown in Figure 1.9. The removal of one electron from the π-conjugated system of polypyrrole results in the formation of a radical cation. In solid-state physics, a radical cation that is partially delocalized over a segment of the polymer is called a polaron. It is stabilized through the polarization of the surrounding medium, hence the name. Since it is really a radical cation, a polaron has spin 1/2. The radical and cation are coupled to each other via local resonance of the charge and the radical. The presence of a polaron induces the creation of a domain of quinone-type bond sequence within the polypyrrole chain exhibiting an aromatic bond sequence. The lattice distortion produced by this is of higher energy than the remaining portion of the chain. The creation and separation of these defects cost energy, which limits the number of quinoid-like rings that can link these two species, i.e., radical and cation, together. In the case of polypyrrole it is believed that the distortion extends over four pyrrole rings.

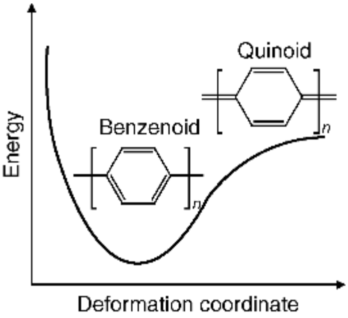

Figure 1.8 Non-degenerate ground state polyparaphenylene. Reproduced from *Polymer International*, 2004, **53**, 1397, A. Moliton, R. C. Hiorns. Copyright Society of Chemical Industry. (Reproduced with permission. Permission is granted by John Wiley & Sons Ltd on behalf of the SCI.)

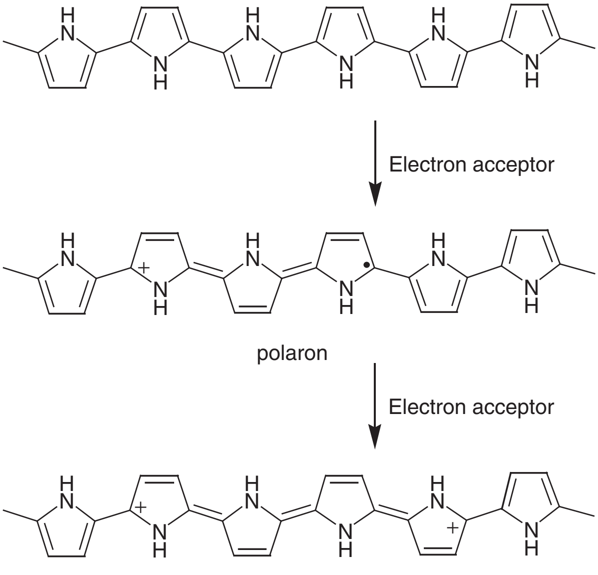

Figure 1.9 Polaron and bipolaron formation on π-conjugated backbone of polypyrrole.

Upon further oxidation, the subsequent loss of another electron can result in two possibilities: the electron can come from either a different segment of the polymer chain thus creating another independent polaron, or from a polaron level (removal of an unpaired electron) to create a dication separating the domain of quinone bonds from the sequence of aromatic-type bonds in the polymer chain, referred to as a bipolaron. This is of lower energy than the creation of two distinct polarons; therefore, at higher doping levels it becomes possible for two polarons to combine to form a bipolaron, thereby replacing polarons with bipolarons [52, 66]. Bipolarons also extend over four pyrrole rings.

Experimental and theoretical investigations of the evolution of the electronic and transport properties as a function of doping level have been conducted on polyacetylene [67–70], polypyrrole [71–74], polythiophene [74, 75] and polyparaphenylene [61, 74, 76]. Theoretical studies of the evolution of the polypyrrole electronic band structure as a function of doping level have been performed using methods ranging from highly sophisticated *ab initio* techniques to simple Hückel theory with σ compressibility. They all converge on the same picture [73, 74]. The polypyrrole band structure upon doping is shown in Figure 1.10 [52]. In the nondoped state, the band gap of polypyrrole is 3.2 eV. The presence of a polaron creates a new localized electronic state in the gap, with the lower energy states being occupied by a single unpaired electron. The polaron levels are approximately 0.5 eV away from the band edges. The polaron binding energy is 0.12 eV, constituting the difference between the 0.49 eV decrease in ionization energy and the 0.37 eV $\pi + \sigma$ energy needed for the change in geometry. The geometry relaxation in the bipolaron is stronger than in the polaron case (i.e., the geometry within the bipolaron is more quinoid-like than within the polaron), so that the empty bipolaron electronic levels in the gap are $\sim$0.75 eV away from the band edges. The bipolaron binding energy is 0.69 eV, meaning that a bipolaron is favoured over two polarons by 0.45 $(0.69 - 2 \times 0.12)$ eV. This evolution is supported by electron spin resonance measurements on oxygen-doped polypyrrole [77]. At low doping, the electron spin resonance signal grows, in accordance with the fact that polarons with spin 1/2 are formed. At intermediate doping, the electron spin resonance signal saturates and then decreases, consistent with polarons recombining to form spinless bipolarons. At high doping, in electrochemically cycled samples, no electron spin resonance signal is observed although the system is highly conducting, indicating that the charge carriers in that regime are spinless. Analysis of the Pauli contribution to the susceptibility indicates that the density of states at the Fermi level is extremely small, <0.03 states eV^{-1} per monomer.

The band structure for a doping level of 33 mol % (based on polymer repeat unit), which is usually achieved in the electrochemically grown

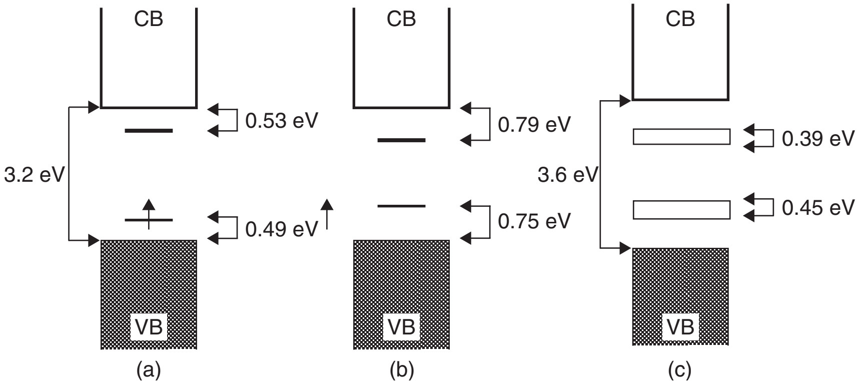

Figure 1.10 Evolution of the polypyrrole band structure upon doping: (a) low doping level, polaron formation; (b) moderate doping level, bipolaron formation; (c) high doping level (33 mol%), formation of bipolaron bands. (Reprinted with permission from *Accounts of Chemical Research*, **18**, 309. Copyright (1985) American Chemical Society.)

polypyrrole films is shown in Figure 1.10. With continued doping, the overlap between the bipolaron states forms two ~0.4 eV continuous bipolaron bands in the gap. The band gap increases from 3.2 eV in the neutral state to 3.6 eV in the highly doped state. This is due to the fact that the bipolaron states forming in the gap are at the expense of states in the valence and conduction 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 valence bands respectively to produce partially filled bands and metal-like conductivity.

Among conjugated polymers, polyaniline represents a special case where doping of the neutral, unoxidized form of the polymer involves electron and proton transfer. The individual steps are shown in Figure 1.11. Polyaniline exists in three well defined oxidation states: leucoemeraldine, emeraldine and pernigraniline. Leucoemeraldine and pernigraniline are the fully reduced (all amine nitrogens) and the fully oxidized (all imine nitrogens) forms, respectively, and the emeraldine form has an amine/imine ratio of ~0.5 [78, 79]. Starting from the electronically insulating leucoemeraldine, electronically conducting emeraldine can be obtained by standard chemical or electrochemical oxidation similar to other conjugated polymers. Upon further oxidation a fully oxidized pernigraniline can be obtained.

In addition, these various oxidation states are pH sensitive and (except leucoemeraldine) can also be readily switched between doped salt and

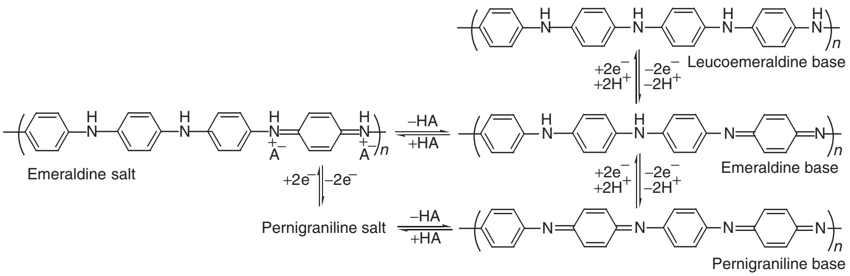

Figure 1.11 Oxidative and protonic acid (nonoxidative) doping of polyaniline.

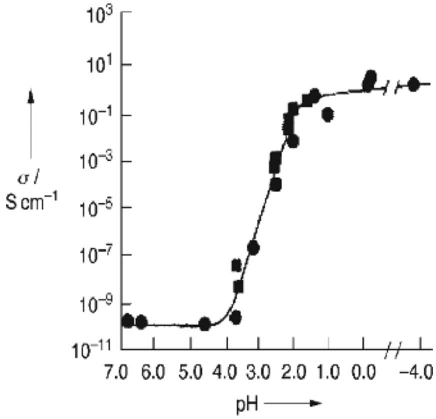

Figure 1.12 Conductivity of emeraldine base as a function of the pH of the HCl dopant solution as it undergoes protonic acid doping (● and □ represent two independent series of experiments). (Reproduced from *Angewandte Chemie – International Edition*, 2001, **40**, 2581; A. MacDiarmid, with permission from Wiley-VCH.)

nondoped base forms. Out of five forms of polyaniline, only the emeraldine salt form is conducting. Protonic acid doping occurs by proton addition to the polymer chain rather than by partial oxidation or reduction of the polymer π-system. The number of electrons associated with the polymer backbone does not change during the protonation step. Protonic acid doping of emeraldine base units with, for example, 1 M aqueous HCl results in complete protonation of the imine nitrogen atoms to give the fully protonated emeraldine hydrochloride salt. As shown in Figure 1.12, protonation is accompanied by a 9–10 orders of magnitude increase in conductivity, reaching saturation in *ca* 1 M

HCl [5, 78–80]. The process is reversed [78, 80, 81] when the protonated polymer is treated with aqueous alkali. Further, this behavior has been observed in other systems, such as poly(heteroaromatic vinylenes) [82].

In their doped, electronically conducting forms, ICPs typically possess positive charges (polarons or bipolarons) along their polymer chains, whose charge is balanced by the incorporation of anions. These anions may consist of a wide variety of chemical groups ranging from simple anions such as Cl^-, $HSO_4{}^-$, $ClO_4{}^-$, $NO_3{}^-$ [41], to bulkier species such as *p*-toluenesulfonate (*p*TS^-) or camphor-10-sulfonate (CSA^-) [55, 83, 84], to large polyelectrolytes such as poly(styrenesulfonate) [85–89], as well as amino acids and biopolymers, including proteins and DNA [90–93]. The incorporated anions provide a powerful additional element for tuning the properties of the resulting ICPs, giving rise to a wide range of properties and applications. The nature and extent of doping not only increase electronic conductivity of the polymer but also induce desired properties such as improved processability, environmental stability and special catalytic, optical or spectroscopic, and redox properties useful for optical pH sensors, heterogeneous catalysis, gas separation membrane, drug delivery and biosensors [62, 94, 95]. The nature of the dopant anion also strongly influences the morphology of the polymer [62]. Recently, it has been shown that the surfactant function of the dopant plays an important role in the formation of nanostructures [96, 97]. Wan *et al.* have reported that the morphology of polyaniline nanostructures prepared in the presence of inorganic acids is dependent on dopant structures [98].

Apart from oxidative and protonic acid doping processes, there are some doping processes where no counter dopant ion is involved, such as photodoping [99] and charge injection [100–102]. In photodoping, when the polymer is exposed to radiation of greater energy than its band gap, electrons are promoted across the gap. For example, in *trans*-polyacetylene, solitons are observed under appropriate experimental conditions [99]. After irradiation is discontinued, charge carriers disappear rapidly because of the recombination of electrons and holes. If a potential is applied during irradiation, then the electrons and holes separate and photoconductivity is observed. Charge injection is most conveniently carried out using a metal/insulator/semiconductor configuration involving a metal and a conducting polymer separated by a thin layer of a high dielectric-strength insulator. In the case of charge injection at a metal–semiconductor interface, the polymer is oxidized or reduced (electrons are added to π^*-band or removed from the π-band). However, the polymer is not doped in the sense of chemical and electrochemical doping, for there are no counterions. In the case of charge injection at a metal–semiconductor interface, electrons reside in the π^*-band and/or holes reside in the π-band only as long as a biasing voltage is applied. Because of the self-localization associated with the formation of solitons, polarons and bipolarons, charge injection leads to the formation of localized structural distortions and electronic states in the energy gap. This approach has resulted in the observance of superconductivity in a polythiophene derivative [100–102].

1.1.4 Synthesis

Intrinsically conducting polymers are generally synthesized *via* chemical or electrochemical oxidation of a monomer where the polymerization reaction is stoichiometric in electrons. However, several other synthetic approaches exist, such as photochemical-initiated or biocatalytic oxidative polymerizations using naturally occurring enzymes.

1.1.4.1 Chemical Synthesis

Chemical synthesis has the advantage of being a simple process capable of producing bulk quantities of ICPs on a batch basis. To date it has been the major commercial method of producing such materials. Chemical polymerization is typically carried out with relatively strong chemical oxidants like ammonium peroxydisulfate, ferric ions, permanganate or bichromate anions, or hydrogen peroxide. These oxidants are able to oxidize the monomers in solution, leading to the formation of cation radicals. These cation radicals further react with other monomers or *n*-mers, yielding oligomers or insoluble polymer. There are two main limitations of the chemical oxidation technique, both related to the limited range of chemical oxidants available. The counterion of the oxidants ultimately ends up as a dopant or codopant in the polymer. Hence it is difficult to prepare ICPs with different dopants. The limited range of oxidants also makes it difficult to control the oxidizing power in the reaction mixture and in turn the degree of overoxidation during synthesis. Both the type of dopant and the level of doping are known to impact upon final properties of the polymer such as molecular weight, crosslinking and, ultimately, conductivity.

1.1.4.2 Electrochemical Synthesis

The electrochemical synthesis of conducting polymers, first demonstrated with polypyrrole [103], has proven important in the development of the field. Using this approach, semiconducting polymers have been obtained from a wide variety of monomers including thiophene, furan, carbazole, aniline, indole, azulene and polyaromatic monomers such as pyrene and fluoranthene. In general, chemical oxidation provides ICPs as powders, while electrochemical synthesis leads to films deposited on a working electrode. A wide range of anodes may be employed, including platinum, gold, carbon and indium-doped tin oxide (ITO)-coated glass. The ITO-coated glass electrodes, being transparent in the visible/near-infrared region, are very useful for *in situ* spectral investigations involving absorption or circular dichroism of the deposited polymer films.

Table 1.1 shows a list of dopant ions and their source electrolytes which are currently being used in the electrochemical synthesis of conducting polymers. All of these dopant ions with the exception of the last two (marked by *) are anions and are associated with electrochemical oxidation of the polymers at the anode. Aizawa *et al.* [104] reported the first example of the reductive doping of an electrochemically synthesized polythioenylene film with cations like tetraethyl ammonium (Et_4N^+)

Table 1.1 List of dopant ions and their source of electrolyte[a] (Reprinted from *Materials Chemistry and Physics*, **61**, K. Gurunathan, A. V. Murugan, R. Marimuthu, U. P. Mulik, D. P. Amalnerkar, 173. Copyright (1999) with permission from Elsevier.)

Dopant ion	**Supporting electrolyte**
BF_4^-	$R_4N^+BF_4^-$, MBF_4
PF_6^-	R_4NPF_6, MPF_6
ClO_4^-	R_4NClO_4, $MClO_4$
Cl^-	R_4NCl, HCl, MCl
Br^-	R_4NBr, MBr
I^-	R_4NI, MI
AsF_6^-	$MAsF_6$
HSO_4^-	$MHSO_4/R_4NHSO_4$
$CF_3SO_3^-$	$MCF_3SO_3/R_4NCF_3SO_3$
$CH_3C_6H_4SO_3^-$	$MCH_3C_6H_4SO_3$
SO_4^{2-}	Na_2SO_4, H_2SO_4
(Et_4N^+)*	Et_4NPF_6
(Bu_4N^+)*	Bu_4NPF

[a] R = Alkyl; Et = Ethyl; But = Butyl; M = Metal (Li^+, Na^+, Ag^+, K^+).

and tetrabutyl ammonium (Bu_4N^+). They observed a red to green electrochromic transition as a result of cation doping.

The advantage of electrochemical polymerization is that by selecting an appropriate electrolyte, a much wider choice of cations and anions for use as 'dopant ions' is possible. Also, in electrochemical polymerization, doping and processing take place simultaneously with polymerization. However, in conventional methods, first polymer synthesis and doping are carried out, followed by processing. The electrochemical oxidation route also has greater control over the electrochemical potential of the system (thereby limiting overoxidation) and in turn the rate of polymerization as well as the film thickness.

1.1.4.3 Photochemical and Biocatalyzed Synthesis

Alternative routes to ICPs, including photochemical, are reportedly advantageous in some applications over the conventional chemical and electrochemical approaches. For example, pyrrole has been successfully polymerized to polypyrrole by irradiation with visible light using either $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) or $[Cu(dpp)_2]^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) as the photosensitizer and an appropriate electron acceptor (sacrificial oxidant) [105, 106]. Recently, the enzyme horseradish peroxidase has been used for the polymerization of anilines in the presence of hydrogen peroxide through oxidative free radical coupling reactions [91, 107]. The advantage of this synthetic approach is that the polymerization of aniline can be carried out at environmentally mild conditions compared to the chemical and electrochemical methods.

1.1.5 Processability

Over the last three decades, ICPs such as polythiophene, polypyrrole and polyaniline have attracted a great deal of research interest because their electrical, electrochemical and optical properties show great promise for commercial applications in rechargeable batteries, light-emitting diodes, electrochromic display devices, sensors, etc. In these applications, polymers are normally used as films or coatings, with different thicknesses, depending on the requirements of the application. Key hurdles to the use of these polymers in commercial products have been the lack of facile synthetic methods for producing useful quantities as well as simple approaches for processing bulk polymer into useful forms. In addition, the stability, including mechanical, thermal, conductivity (with time and at high temperature) and overoxidation, has been a concern.

The limitations in postsynthesis processability are due to the chain stiffness and interchain interactions that render these materials insoluble in common solvents. For example, polymers can become crosslinked, highly branched, or electrostatically crosslinked due to polaron/bipolaron charge interactions. The chemical or ionic crosslinking renders the polymer intractable. However, several approaches have been adopted to facilitate solution processability including:

(i) *Reduction of polymer to nonconducting state to remove interchain charge interactions.* A unique property of polyaniline is that in the deprotonated form, emeraldine base (EB), it is readily soluble in some solvents such as *N*-methylpyrrolidinone, dimethyl formamide and dimethyl sulfoxide [108]. Also, polyaniline has been processed without changing molecular structure in certain amines like pyrrolidine and tripropylamine [109], fluorinated solvents [110], acetic acid or in concentrated sulfuric acid, and other strong acids [111, 112].

(ii) *Substitution of alkyl chains (polypyrrole, polythiophene and polyaniline).* A major breakthrough in the field of ICPs was the synthesis of soluble and conducting poly(3-alkylthiophene) [113, 114]. These polymers have straight chain alkyl groups, such as hexyl, octyl, dodecyl and octadecyl, and a degree of polymerization ranging from 100 to 200, depending on the alkyl group. The neutral polythiophenes substituted by flexible and long alkyl side chains (with more than three carbon atoms) are rendered soluble in common organic solvents (chloroform, toluene, etc.) through reduced interchain interactions and favorable substituent–solvent interactions. However, steric interactions along the polymer backbone result in reduced orbital overlap and a corresponding lowered conductivity. Many attempts have been made to improve the processability of polyaniline by the introduction of an alkyl group on the *N*-substituent [115, 116] or alkoxy substituent [117, 118].

(iii) *Counterion induced processability.* Organic solvent solubility can be imparted to conducting polyaniline and polypyrrole salts by the incorporation of large functionalized protonic acids such as camphor sulfonic or dodecylbenzenesulfonic acid as a counterion during synthesis of these polymers [55, 83]. The long alkyl chains of the dodecylbenzene functional group lead to solubility in common solvents such as toluene, xylenes, decalin, chloroform, etc.

(iv) *Enzymatic synthesis*. Water soluble polyaniline [107, 119, 120] and polypyrrole [121] have been prepared using a template-guided enzymatic approach. Strong acid polyelectrolytes, such as sulfonated polystyrene, and strong acid surfactant molecules, such as sodium dodecylbenzenesulfonate, are used as templates because they provide a lower local pH environment for the formation of the conducting polymer.

(v) *Colloidal dispersions*. The most commercially successful method of producing processible forms of ICPs has been the aqueous colloidal dispersion route. In this approach, aqueous colloidal dispersions of conducting polymers have been prepared in the presence of a water-soluble polyelectrolyte such as polystyrene sulfonic acid [122] and polymeric stabilizers such as poly(vinyl alcohol-co-acetate), methyl cellulose, poly(vinyl pyrrolidone), poly(vinyl methyl ether), etc. and surfactant stabilizers [123, 124]. The polyelectrolyte and anionic surfactants act as the charge compensating dopant for the polymer and also render the resulting complex a colloidal dispersion as these polyelectrolyte and surfactants are themselves water soluble.

(vi) *In situ polymerization of metastable monomer–oxidant mixtures*. Selecting a chemical oxidizing agent with a formal potential near to, but below, the oxidation potential of the monomer, results in a metastable reaction mixture that polymerizes upon solvent evaporation. This behavior allows facile preparation of well defined conducting polymer films on any substrate [125, 126].

(vii) *Self-doping*. Recently, environmental concerns have placed restrictions on the commercial use of many organic solvents. These concerns in turn have encouraged the use of polymers that can be processed in aqueous media. ‘Self-doping’ is the most successful approach for increasing the solubility of conductive polymers in aqueous solution. When ionizable functional groups that form negatively charged sites are attached to the polymer chain to make the polymer conducting, it is referred to as ‘self-doping’ or when the group is an acid, ‘self-acid-doping’. The distinctive properties of self-doped conducting polymers are their water solubility, electroactivity and conductivity over a wider pH range (in the case of polyaniline), and thermal stability. The ionizable groups on the backbone give the polymer certain polyelectrolyte properties, i.e., these groups dissociate into aqueous solvent. The solubility of self-doped conducting polymers in aqueous solutions can be attributed to the hydrophilic interactions between the covalently attached ionized group on the polymer backbone and polar molecules of water. In water, the steric and ionic repulsive interactions overcome the interchain interactions and allow for the rapid solvation of polymer backbone.

1.2 SELF-DOPED CONDUCTING POLYMERS

Charge transfer doping and the associated changes in electronic properties of conjugated organic polymers [41] such as polyacetylene, polythiophene and polypyrrole, are well known. As discussed above, in such systems, the injection of charge into the delocalized π-electron system (either chemically or electrochemically) requires that dopants or counterions diffuse into the polymer during the charge injection process in order to maintain charge neutrality. In the case of polyaniline, doping can be achieved without electron transfer by protonation of the polymer (Figure 1.11). In this case as well, however, the doping process requires (and is limited by) diffusion of counterions into the structure to preserve charge neutrality. This reversible exchange of large anions between the active polymer mass and electrolyte limits many important characteristics such as electrochromic switching, charging rates, etc.

The driving force behind the extensive research on self-doped polymers has been to improve the processability in aqueous media, to increase the speed of electrochromic switching and to enhance the charge storage performance of polymer-based batteries. In 1987, Wudl *et al.* first reported the novel concept of 'self-doping' in conducting polymers [127, 128]. In this work, a self-doped conducting polymer was described as a conjugated polymer where a significant fraction of monomer units contained a covalently attached ionizable, negatively charged, functional group acting as a stable/immobile dopant anion. This principle of self-doping in a conjugated polymer is shown in Figure 1.13. As shown in the figure, by immobilizing the larger anion, upon oxidation, the smaller mobile proton or other monovalent cation is ejected from the polymer into the electrolyte to maintain charge neutrality. Due to the higher mobility of the smaller cations, the rate of the charging (redox) process is significantly increased. Sodium salts and acid forms of poly(3-thiophene ethanesulfonate) and poly(3-thiophene

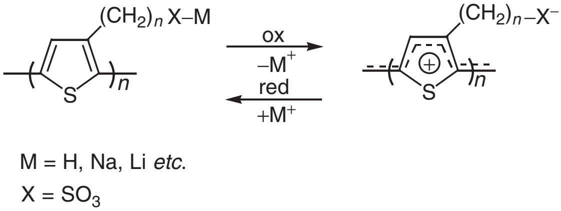

Figure 1.13 Oxidation–reduction reactions of polythiophene derivatives showing self-doping during the oxidation reactions. (Reprinted from *Synthetic Metals*, **20**, A. O. Patil, Y. Ikenoue, N. Basescu, N. Colaneri, F. Wudl, A. J. Heeger, 151. Copyright (1987), with permission from Elsevier.)

butanesulfonate) were the first self-doped conducting polymer materials to show water solubility in neutral (insulating) and doped (conducting) states [127]. The films cast from water solution exhibit electronic conductivity in the range of 10^{-7}–10^{-2} S/cm depending on the relative humidity. Since these polymers are prepared by the electropolymerization of 3-substituted thiophene monomers in the presence of 'foreign' electrolyte, various experiments and arguments were put forward to prove self-doping, including cyclic voltammetry experiments combined with pH measurements in organic solvents [129].

Following these initial reports, Havinga *et al.* electropolymerized a potassium salt of 3′-propylsulfonate 3′-propylsulfonate 2,2′:5′,5″-terthienyl in the absence of foreign electrolyte [130, 131]. In this case, the monomer itself acts as the electrolyte during electrochemical polymerization, resulting in solid evidence for self-doping. The self-doped poly(3′-propylsulfonate 2,2′:5′,5″-terthienyl) shown in Figure 1.14 is soluble in water. However, the polymer solutions are unstable. Ikenoue *et al.* reported the first chemical synthesis of self-doped polymer by chemically oxidizing sodium 3-(3′-thienyl)propanesulfonate using ferric chloride in an aqueous medium. This polymer shows self-doped behavior

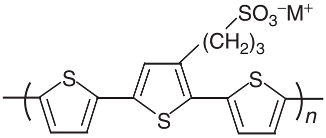

Figure 1.14 Chemical structure of self-doped poly(3′-propylsulfonate 2,2′:5′,5′-terthienyl). (Reprinted with permission from *Chemistry of Materials*, **1**, 650. Copyright (1989) American Chemical Society.)

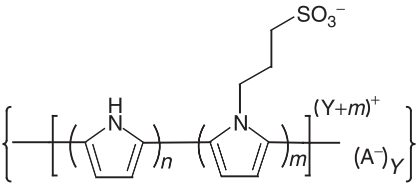

Figure 1.15 Chemical structure of self-doped poly(pyrrole-co(3-(pyrrol-lyl)propanesulfonate). (*Chemical Communications*, 1987, **621**, N. S. Sundarsan, S. Basak, M. Pomerantz, J. R. Reynolds. Reproduced by permission of the Royal Society of Chemistry.)

both in water and as a film [132]. The spin-coated films of poly(3-(3′-thienyl)propanesulfonate) exhibit faster optical switching response and higher stability.

This approach of introducing ionic substituents has been extended to other ICPs like polypyrrole [130, 133–135], polyaniline [136–138], polyphenylenes [139–142] and polyphenylenevinylenes [143]. For the polypyrrole system, the self-doping concept has been extended by Reynolds *et al.* [133, 134] and Havinga *et al.* [130, 135]. Reynolds *et al.* chemically polymerized the *N*-substituted pyrrole and potassium-3-(pyrrol-l-yl)propanesulfonate in aqueous solution with ferric chloride as oxidizing agent and electropolymerized it or copolymerized with pyrrole in n-$(Bu)_4NBF_4/CH_3CN$ or $LiClO_4/CH_3CN$ solution, electrochemically forming a poly{pyrrole-co(3-(pyrrol-lyl)propanesulfonate} (Figure 1.15). Havinga *et al.* polymerized the ring substituted pyrrole, sodium (3-pyrrolyl)alkanesulfonate (Figure 1.16), chemically in aqueous solution with ferric chloride as the oxidizing agent and electrochemically in acetonitrile without any electrolyte. These water soluble self-doped forms of polypyrrole have electronic conductivities in the range of 10^{-3}–0.5 S/cm and good stability under ambient conditions.

The first self-doped polyaniline was produced by Hany and Genies in 1989 [136] by heating the emeraldine salt of polyaniline in dimethyl sulfoxide with either 1,3-propane sulfone or 1,4-butane sulfone to produce the corresponding poly(aniline-*N*-propylsulfonic acid) or poly(aniline-*N*-butylsulfonic acid). However, these polymers had poor solubility and significantly lower conductivity (10^{-9} S/cm). In 1990, Yue and Epstein [137] and Bergeron *et al.* [138] reported the first water-soluble, self-doped, conducting polyaniline derivatives. The ring-sulfonated polyaniline (Figure 1.17 A) was prepared by the sulfonation of the emeraldine base of polyaniline with fuming sulfuric acid for 2 h at room temperature followed by precipitation

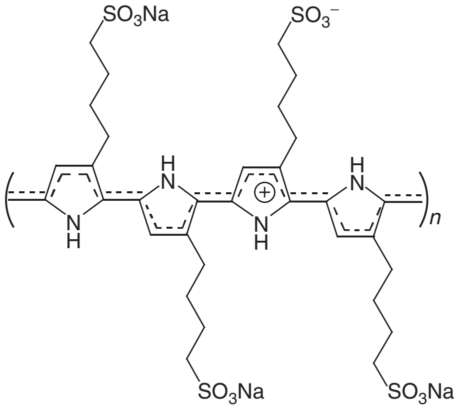

Figure 1.16 Chemical structure of self-doped poly(sodium (3-pyrrolyl)alkanesulfonate). (Reprinted with permission from *Chemistry of Materials*, **1**, 650. Copyright (1989) American Chemical Society.)

of the reaction product with methanol and acetone. In the resulting sulfonated polyaniline, only approximately half of aromatic rings contained sulfonate groups. This degree of modification was sufficient to compensate all positive charges of the protonated nitrogen sites in the emeraldine salt form of this polymer. The polymer obtained exhibited a significantly lower conductivity (approximately 0.1 S/cm) compared with unmodified polyaniline (typically 1–10 S/cm), however, the conductivity was independent of pH up to 7, unlike polyaniline. Electrostatic interactions prevent the proton from diffusing away from

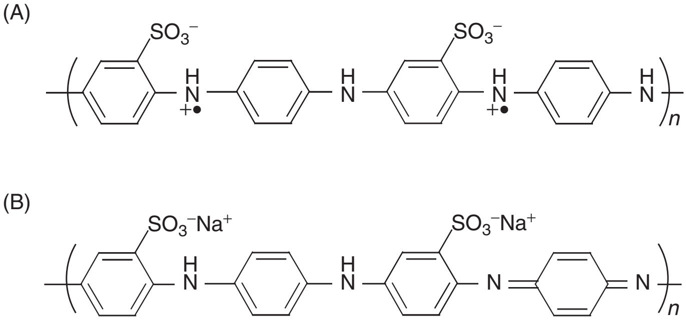

Figure 1.17 Chemical structures of (A) self-doped ring-sulfonated polyaniline and (B) dedoped (insulating) salt form of ring-sulfonated polyaniline. (Reprinted with permission from *Journal of the American Chemical Society*, **112**, 2800. Copyright (1990) American Chemical Society.)

the ring-bound, negatively charged, polymer chain. This high local concentration of protons in the vicinity of the polymer backbone has been claimed to be responsible for the retention of doping at neutral pH [137]. In contrast to the parent polyaniline, self-doped sulfonated polyaniline was found to be soluble in diluted aqueous base, forming the dedoped (insulating) salt form (Figure 1.17 B). Since these initial reports, many papers have been published, dealing with synthesis, properties and applications of self-doped conducting polymers.

1.3 TYPES OF SELF-DOPED POLYMERS

Self-doped conducting polymers have been generated by functionalizing the monomer (prepolymerization modification) and polymer (postpolymerization modification) with ionizable, negatively charged, moieties. These self-doped conducting polymer derivatives have been prepared with various functional groups such as sulfonic acid, alkyl and alkoxysulfonic acid, carboxylic acid, phosphonic acid, acetic acid and boronic acid. In general, two kinds of self-doped conducting polymer derivatives have been prepared. One of them contains ionizable functional groups (usually sulfonate), attached directly to the aromatic rings of the polymer backbone. The other kind contains ionizable functional groups, bound through a spacer consisting of alkane or aromatic groups to heteroatoms in the conjugated backbone. Some examples of polyaniline, polypyrrole and polythiophene derivatives are shown in Figure 1.18 ((**1**) [144], (**2**) [136, 138, 145] (**3**) [146, 147], (**4**) [148], (**5**) [149], (**6**) [150, 151], (**7**) [144, 152–154], (**8**) [147], (**9**) [148], (**10**) [155], (**11**) [147], Figure 1.19 ((**1**) [130, 135], (**2**) [156], (**3**) [157], (**4**) [158, 159], (**5**) [159], (**6**) [134] and Figure 1.20 ((**1**) [127–129], (**2**) [160], (**3**) [161, 162], (**4**) [163], (**5**) [164], (**6**) [165], (**7**) [166].

The common feature of all self-doped polymers is that the dopant is attached covalently to the conjugated backbone. Conducting polymers prepared with large dopants containing functional protonic acids, for example, camphorsulfonic acid, dodecylbenzene sulfonic acid, and polyelectrolytes or polymeric acids, are not technically self-doped polymers, although in many cases they can exhibit similar properties including solubility, pH stability, fast switching, etc. The lack of mobility associated with these large anions, as well as the fact that polyelectrolytes are entangled in the conducting polymer structure, make their expulsion difficult during the dedoping process. Consequently cations are incorporated to maintain electroneutrality. In 1992 Cao and Heeger *et al.* [55, 167] reported the concept of counterion-induced processibility

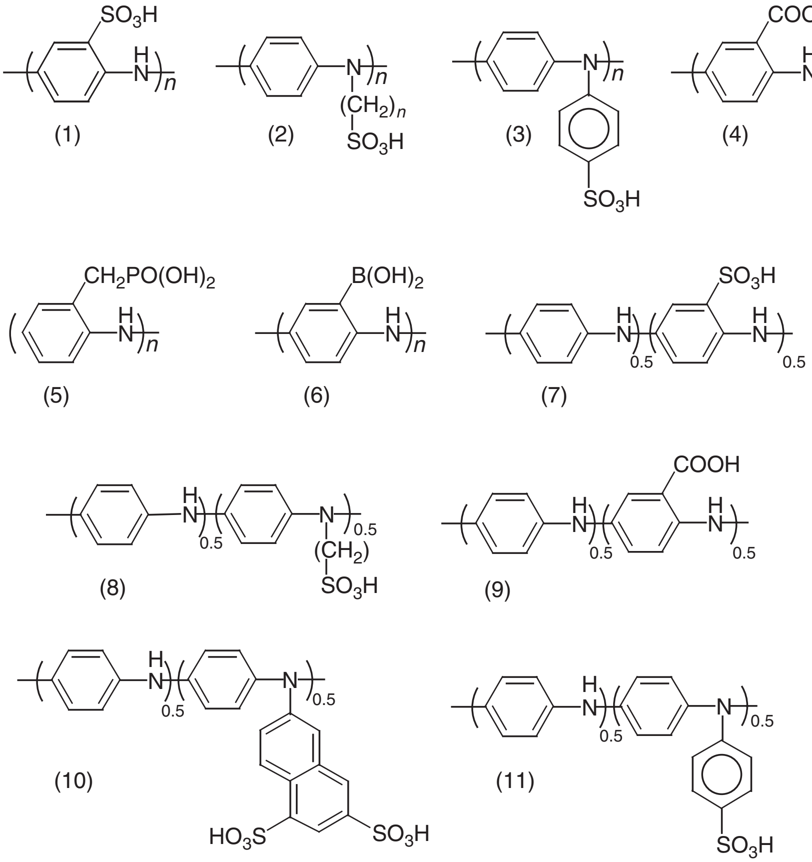

Figure 1.18 Various self-doped polyaniline derivatives.

of conducting polyaniline. Doping polyaniline with functionalized protonic acids renders the polymer conducting and soluble in common organic solvents such as xylene, decalin, chloroform or *m*-cresol. The polyelectrolytes or polymeric acids that have been used as dopants to prepare water-soluble conducting polymers include poly(ethanesulfonic acid) [85], poly(acrylic acid) [85, 86], poly(styrenesulfonic acid) [85, 86, 88, 89], poly(2(acrylamido)-2-methyl-1-propanesulfonic acid) [168] and poly(amic acid) [169]. These dopants can be incorporated into the polymer during either chemical or electrochemical polymerization or by doping in their aqueous solution. Recently, an enzymatic approach has been developed for the polymerization of aniline in the presence of a polyelectrolyte template such as poly(4-styrenesulfonate)

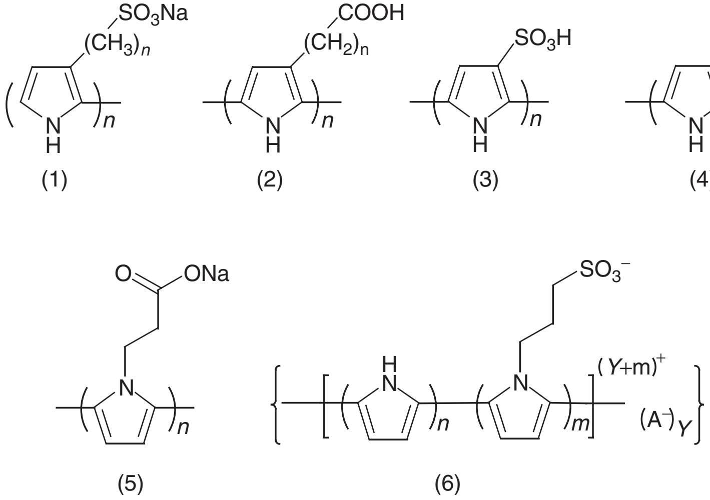

Figure 1.19 Various self-doped polypyrrole derivatives.

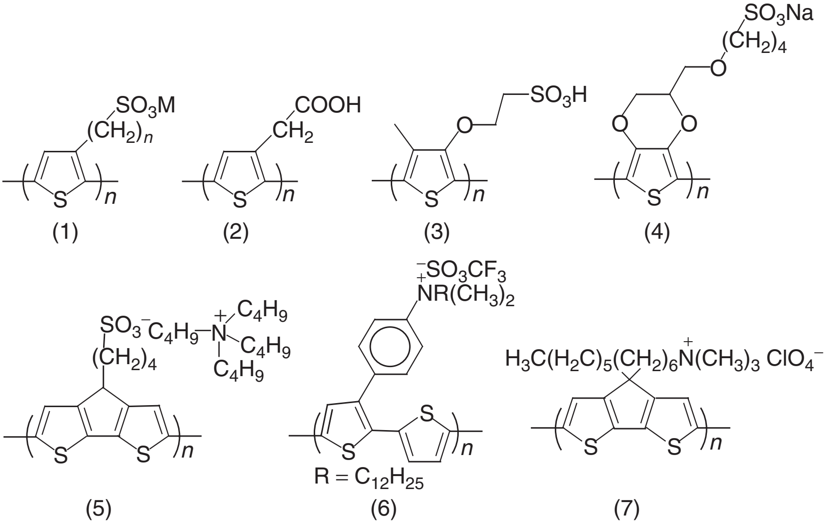

Figure 1.20 Various self-doped polythiophene derivatives.

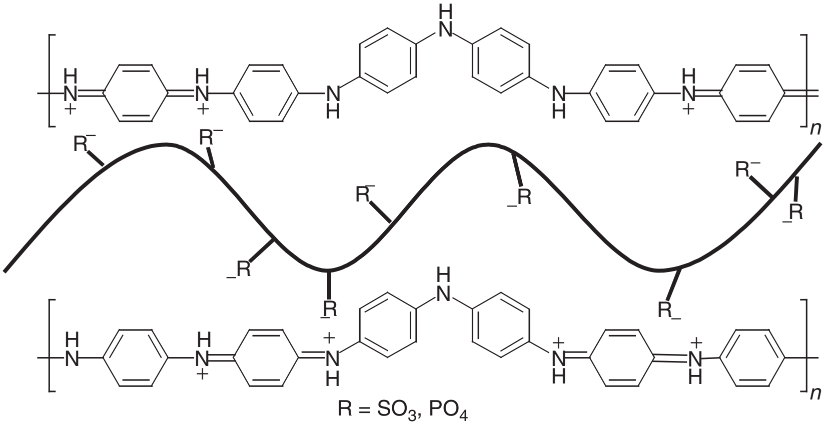

Figure 1.21 Complex formation of macromolecular polyelectrolyte template along with polyaniline chain. (Reprinted with permission from *Macromolecules*, **37**, 4130. Copyright (2004) American Chemical Society.)

or poly(vinylphosphonic acid) under mild aqueous pH 4.3 buffer conditions [107, 119, 120]. The polyelectrolytes act as a template upon which the aniline monomers and oligomers preferentially align themselves through electrostatic and hydrophobic interactions and form complex, as well as large, molecular counterions, which are integrated and essentially locked to the conducting polymer chains (Figure 1.21) [170], thus making doped (as synthesized) polyaniline water soluble. Similarly water-soluble polypyrrole [121] and water-dispersible poly(thieno[3,4-*b*])thiophene have been prepared in the presence of poly(styrenesulfonic acid) [122].

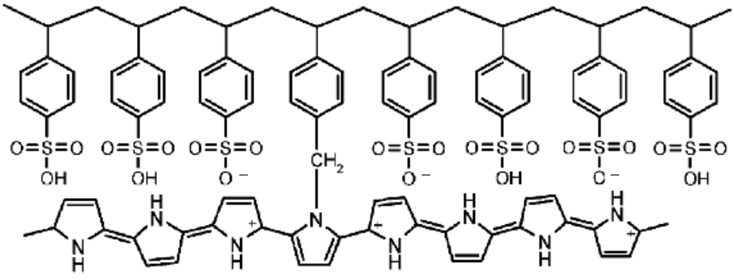

Figure 1.22 The structure of self-doped polypyrrole graft copolymer (Reprinted with permission from *Macromolecules*, **38**, 1044. Copyright (2005) American Chemical Society.)

Recently, Bae and Jo *et al.* prepared water-soluble self-doped polyaniline [171] and polypyrrole [172] graft copolymers. In their study, the polymeric dopant poly(styrenesulfonic acid) is covalently bonded to the conjugated polymer backbone as shown in Figure 1.22. Water-soluble moieties (sulfonic acid groups) that do not participate in self-doping, make polyaniline and polypyrrole graft copolymers soluble in water and polar organic solvents. The conductivities of these polymers are reportedly 4.8×10^{-1} and 1.2×10^{-1} S/cm, for polypyrrole and polyaniline copolymers, respectively. These conductivity values are higher than those of water-soluble conducting polymers prepared using polyelectrolytes as a template [170], and other benzene ring or nitrogen atom substituted water-soluble polyanilines [173–175].

1.4 DOPING MECHANISM IN SELF-DOPED POLYMERS

1.4.1 p-Type Doping

Self-p-doping is by far the most common type of doping found in the literature and there are many examples based on conjugated polymers derived from polyaniline [137, 152, 153], polypyrrole [130, 135], polythiophene [127–129] and polyphenylenes [139–142]. In general, when unsubstituted conjugated polymers are oxidized (p-doping), anions are incorporated to preserve charge neutrality in the materials as the positive charges develop along the polymer backbone. Upon reduction, or dedoping, the anions are ejected. In contrast, when a self-doped polymer is reduced, a cation must move into the polymer to charge compensate the immobilized anion. Upon oxidation that cation is ejected from the polymer. For example, in the case of self-doped polythiophenes with an alkanesulfonic acid substituent, upon electrochemical or chemical oxidation, charge transfer resulting in the generation of charge carriers occurs concomitant with the ejection of protons from the bonded dopant to maintain charge neutrality as shown in Figure 1.23 [176, 177].

The self-protonation of sulfonic acid ring substituted polyaniline (in emeraldine oxidation state) differs from the 'self-doping' mechanism of poly(3-(4-alkanesulfonate)thiophene shown in Figure 1.23 [127]. Figure 1.24 shows the oxidation of sulfonated polyaniline by ejection of electrons from nitrogen and dedoping of protons. The removal of protons produces negative charges on SO_3^-, which compensates positive charges of nitrogen. According to Epstein *et al.* [144, 153, 173], in

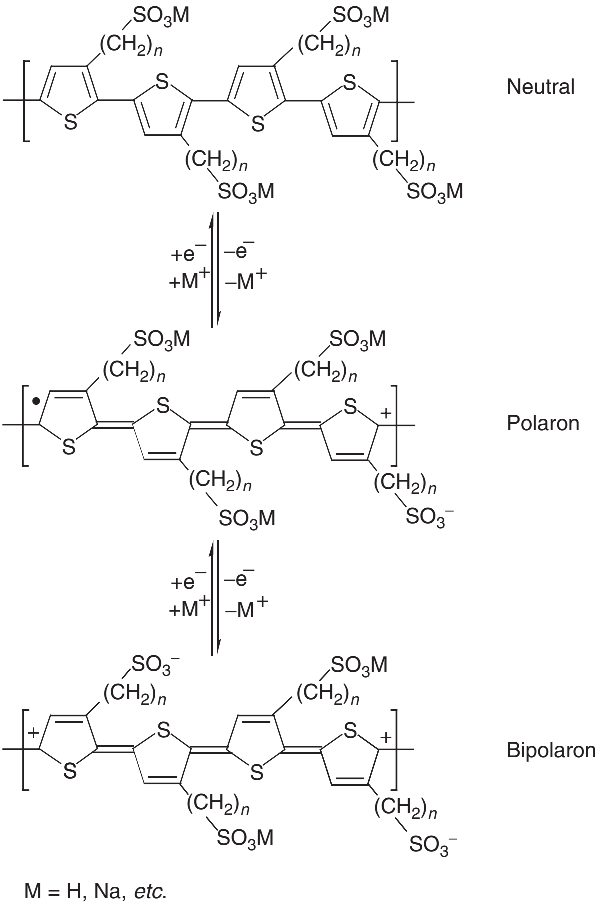

Figure 1.23 Chemical or electrochemical oxidation of polythiophene derivatives. (Reproduced from *Advanced Materials*, 1997, **9**, 1087, M. Leclerc, K. Faid, with permission from Wiley-VCH.)

the oxidized state of sulfonated polyaniline the positive charge carriers are more localized on nitrogen atoms than are those of the parent polyaniline emeraldine salt. This is due to strong electrostatic interaction between SO_3^- groups and cation radical nitrogen atoms or amine hydrogens to form five- or six-member rings, which are in an energetically favorable configuration as shown in Figure 1.25 A. This configuration can effectively localize the positive charge around the nitrogen atoms. The interaction between SO_3^- groups and cation radical nitrogen atoms or amine hydrogens is also likely take place between two adjacent chains (Figure 1.25 B) in addition to intrachain interaction shown in

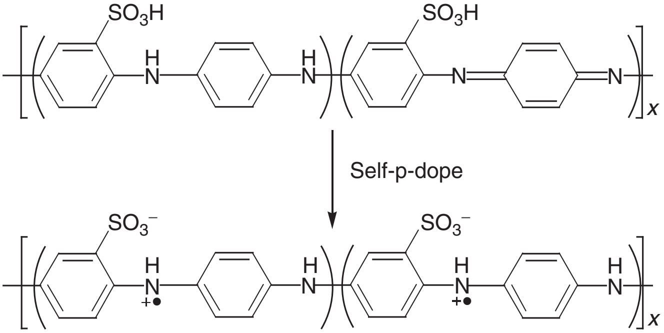

Figure 1.24 Structural changes of sulfonated polyaniline by oxidation. (Reprinted with permission from *Journal of the American Chemical Society*, **112**, 2800. Copyright (1990) American Chemical Society.)

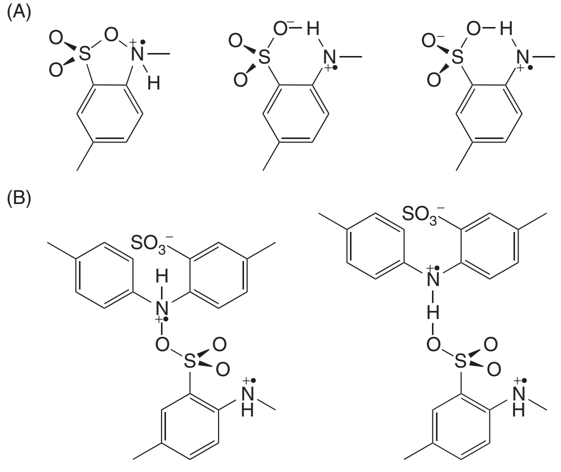

Figure 1.25 Intrachain (A) and interchain (B) interactions in sulfonated polyaniline. (Reprinted with permission from *Journal of the American Chemical Society*, **113**, 2665. Copyright (1991) American Chemical Society.)

Figure 1.25 A. These interchain interactions may play an important role in increasing the three-dimensionality of the charge and spin motion [153].

In contrast with its parent form, introduction of the –SO_3H group on the polyaniline backbone brings new acid–base chemistry within the polymer. The acid–base equilibrium can be changed externally either chemically or electrochemically. The conductivity of sulfonated polyaniline is independent of external protonation over a broad pH range. This clearly indicates that the internal acid–base chemistry in sulfonated polyaniline is not affected by the external medium within this pH range. In the case of highly sulfonated polyaniline, conductivity is pH independent in the range 0 to 12 [173]. This is likely due to the enhancement of the doping strength of protons from sulfonic acid groups on the imine nitrogen atoms by the formation of six-member-ring complexes. As a result, doped imines are more difficult to dedope. Even after exchange of protons with cations, the six-member ring conformation may still exist and thus imines may still be doped by weaker metal cation Lewis acids. Therefore, the polymer treated with alkaline aqueous solutions is still highly conducting.

1.4.2 n-Type Doping

All self-p-doped polymers contain covalently attached negatively charged counterions. However, in self-n-doped polymers, cationic sites act as dopant and are incorporated into the polymer. The concept of self-n-doping in conjugated polymers was introduced by Wudl *et al.* [178]. As shown in Figure 1.26A, the polymer poly(dipropargylhexylamine) was prepared from the cyclopolymerization of *N*-hexyldipropargylamine. Treatment of the polymer with methyl trifluoromethanesulfonate resulted in the corresponding poly(dipropargyl-*N*-hexyl-*N*-methyl ammonium triflate) as shown in Figure 1.26B. The UV-vis results of the methyl trifluoromethanesulfonated polymer clearly support n-doping. Upon reduction with sodium sulfide in tetrahydrofuran, the conductivity of methyl trifluoromethanesulfonated polymer ($<10^{-6}$ S/cm) was increased to approximately 0.1 S/cm. This polymer was reportedly environmentally stable. However, the polymer is electrochemically unstable, decomposing after a few cathodic cycles.

Ferraris *et al.* [165] chemically synthesized a processible, self-n-doped, poly(2-(2′-thienyl)3-(4-dimethyl dodecyl ammonium phenyl)thiophene triflate) using the monomer shown in Figure 1.27A. This polymer was reportedly soluble in *N*-methylpyrrolidone to a concentration of 53 mg/mL. Similarly, the polymer was prepared electrochemically in tetramethyl ammonium trifluromethane sulfonate. The polymer prepared chemically and electrochemically exhibited reversible redox behaviour in the p- and n-doping regions. The presence of bound cations to the polymer backbone provides the ability to p- and n-

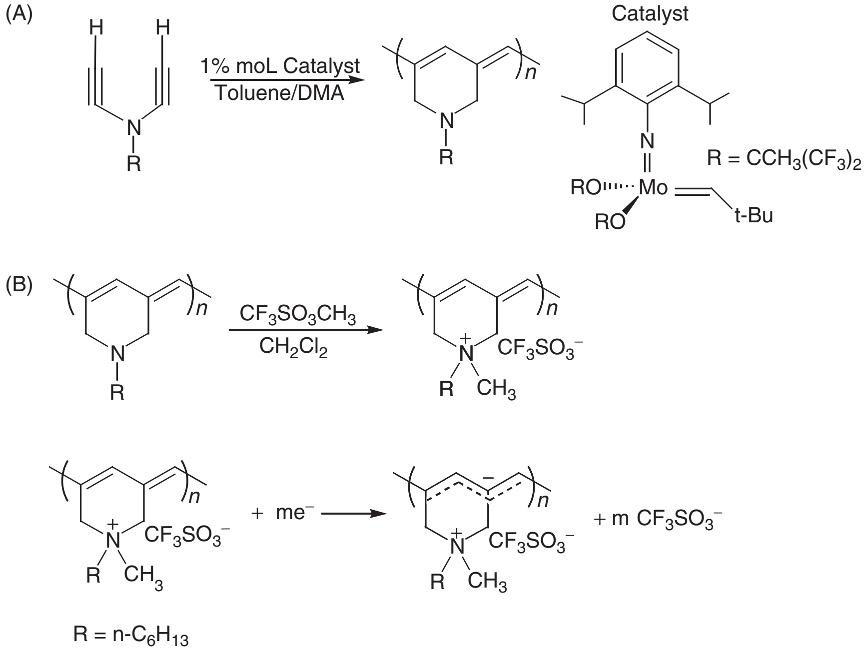

Figure 1.26 Synthesis of (A) poly(dipropargylhexylamine) and (B) poly(dipropargyl-*N*-hexyl-*N*-methyl ammonium triflate. (Reprinted with permission from *Chemistry of Materials*, 5, 1598. Copyright (1993) American Chemical Society.)

dope solely through the movement of anions. A comparison between a normal conducting polymer and a self-n-doped polymer shows that during the reduction (n-doping) process, normal polymers insert cations whereas self-n-doped polymers expel anions. Furthermore, this study was extended to a series of self-n-doped polymers derived from 3-(4-dimethyl dodecyl ammonium phenyl)thiophene triflate shown in Figure 1.27B [179].

Berlin *et al.* [166] reported the synthesis of n-doped polycationic polythiophenes using thiophene monomer functionalized with ammonium groups (see Figure 1.20 (7)). The polymer exhibits reversible p- and n-doping characteristics. The n-doping process and the associated expulsion of anions, is reportedly fast and independent of cation size, and the *in situ* conductivity is reportedly 2×10^{-2} S/cm. Kumar *et al.* synthesized a fully sulfonated n-doped polyaniline electrochemically using an acetonitrile–water (4:1) mixture [180]. The n-doping was confirmed

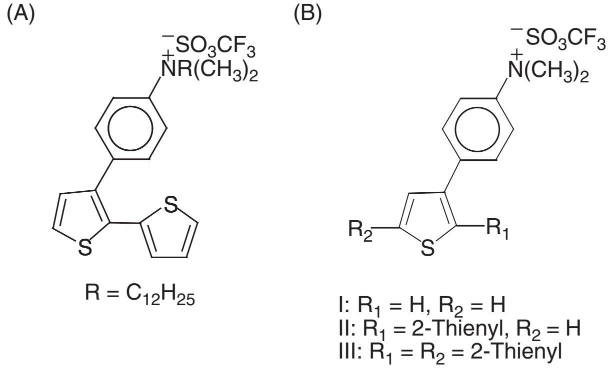

Figure 1.27 Structures of monomer based on phenylthiophene architecture. (Reproduced from *Polymer Preprints*, 1998, **39**, 137, 'Characterization of self-n-dopable polymers, A. A. Moxey, D. C. Loveday, I. D. Brotherson, J. P. Ferraris.)

by measuring *in situ* conductance of the polymer grown on a Pt twin wire electrode. Pei *et al.* [181] synthesized self-doped, n-type conducting polymers, poly(2-hydroxy-1-4-phenylene), sodium and tetrabutyl ammonium salts. Delocalization of the electrons associated with the side group oxygen anion onto the conjugated poly(*p*-phenylene) main chain occurs in the polymer generating intrinsic n-type carriers. This delocalization completely quenches the photoluminescence of the polymer, and increases the conductivity of the polymer by more than one order of magnitude. The conductivity of poly(2-hydroxy-1,4-phenylene) tetrabutyl ammonium salt is reportedly 5×10^{-9} S/cm. The low conductivity is attributed to the immobility of intrinsic charge carriers generated from side chain anion delocalization.

1.4.3 Auto Doping

Wudl and Heeger *et al.* prepared the self-dopable polymers poly(n-(3′-thienyl)alkanesulfonic acids) (P3TASH) and their sodium salts with alkane chain lengths ranging from 2 to 4 [127–129]. In an extension of this study, Ikenoue *et al.* found that poly(3-(3′-thienyl)propanesulfonic acid) (P3TPSH), which was obtained by exchanging the sodium ions in poly(sodium-3-(3′-thienyl)propanesulfonate) (P3TPSH) with protons using H^+-type ion exchange resin, was actually already self-doped, as evidenced by the presence of an additional optical absorption peak at 800 nm associated with the formation of polarons [132, 182, 183]. Since no electrical potential was applied to the system, 'ejection' or 'popping out' of protons was not expected to occur. Thus, the structure and doping mechanism of P3TASH was assumed to be different from that obtained by the electrochemical doping of P3TASH or its sodium salt. In order to distinguish between these two types of doping mechanism, the term 'auto-doping' or 'self-acid-doping' was first introduced by Ikenoue, Wudl and Heeger *et al.* They observed that P3TASH was extremely hygroscopic and hence the films of the polymer contained moisture. When the acid film was fully dehydrated, it turned greenish blue with a concomitant loss of conductivity; exposure to water vapor regenerated the original orange color. They therefore ascribed this aqueous solvatochromism to an acid–base reaction. In the presence of moisture, the acidic proton is solvated by water molecules. When water is removed by heating, the next most basic species able to accommodate the protons is the polythiophene backbone itself, as shown in Figure 1.28 [182]. Protonation of the backbone creates a polaronic residue on the polymer chain. This phenomenon is not observed for the sodium salts. Due to auto-doping, the sulfonic acid form of the polymer exhibits a higher conductivity in its electrochemically neutral state than the corresponding sodium salt.

The most detailed study of auto-doping in P3TASHs has been reported by Chen *et al.* [184]. In this report, they studied the structure and effect of the side chain length on the doping level of P3TASHs with alkanes containing two, six, and ten carbons, i.e., poly (2,3′-(thienyl)ethanesulfonic acid) (P3TESH), poly (2,3′-(thienyl)hexanesulfonic acid) (P3THSH), and poly (2,3′-(thienyl)decanesulfonic acid) (P3TDSH). The conductivities of the sulfonic acid derivatives are reported to be orders of magnitude higher than their sodium salts. The conductivity of P3TESH is reportedly two orders of magnitude higher than P3THSH. The important observation was that the spin density, as determined by electron spin resonance measurements, for the sulfonic acid forms is relatively high and comparable to that of poly(3-methylthiophene) doped by AsF_5^-. Electron spin resonance measurements of the aqueous solutions of P3TESH and P3THSH confirms the presence of large concentration of free spins, suggesting that the auto-doping or self-acid-doping is a redox process. Infrared spectra of P3TESH, P3THSH and their sodium

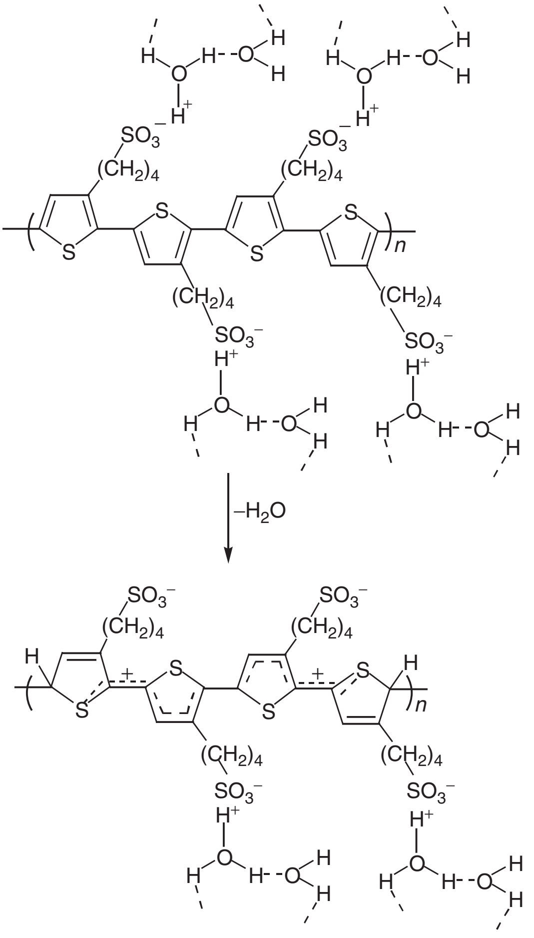

Figure 1.28 Auto-doping mechanism of P3TASH. (Reprinted from *Synthetic Metals*, **30**, Y. Ikenoue, N. Uotani, A. O. Patil, F. Wudl, A. J. Heeger, 305. Copyright (1989), with permission from Elsevier.)

salts (Figure 1.29) suggest that the structure of auto-doped P3TESH and P3THSH involves polaron/bipolaron and proton addition on α-carbons similar to nonsulfonated polythiophenes.

An important study was performed by these authors to investigate the sulfonic acid derivatives P3TESH and P3THSH by titrating them with base while monitoring the pH of the solution. The titration curves shown in Figure 1.30 exhibit a two stage variation in pH values for both polymers. It is suggested that the first stage involves neutralization with free protons (H_f^+) while the second stage involves proton

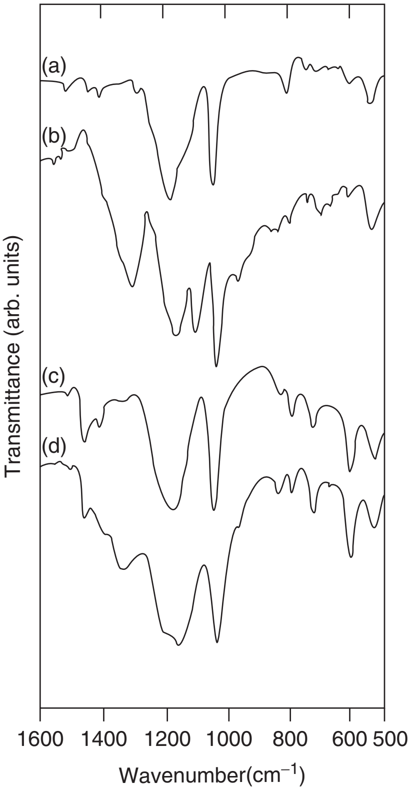

Figure 1.29 IR spectra of thin films at room temperature; (a) P3TESNa, (b) P3TESH, (c) P3THSNa and (d) P3THSH. (Reprinted with permission from *Macromolecules*, **26**, 7108. Copyright (1993) American Chemical Society.)

addition on α-carbons ($H_\alpha{}^+$). The ratios of $H_f{}^+$ and $H_\alpha{}^+$ are reported to be 48 % and 30 % for P3TESH and 61 % and 25 % for P3THSH, respectively. Surprisingly, 22 % and 14 % respectively of the anticipated protons ($H_m{}^+$) could not be detected by this method for P3TESH and P3THSH. The authors suggest that a percentage of the protons associated with the sulfonic acid derivatives oxidize the π-system of the polymer chain, which then either add to α-carbons or recombine to liberate hydrogen gas. The latter processes are considered responsible for the appearance of a large number of free spins. The doping level of P3TESH and P3THSH in aqueous solutions is reported to be sum of the fraction of $H_\alpha{}^+$ and $H_m{}^+$ and is 52 % and 39 %, respectively. The doping level of a particular poly(n-(3′-(thienyl)alkanesulfonic acid) is thus a function of the degree of protonation and the extent of the

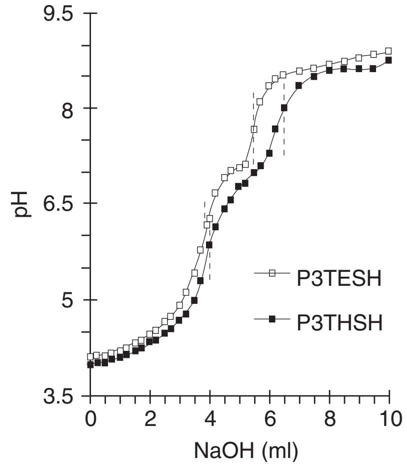

Figure 1.30 Titration curves of P3TESH and P3THSH with aqueous NaOH. (Reprinted with permission from *Macromolecules*, **26**, 7108. Copyright (1993) American Chemical Society.)

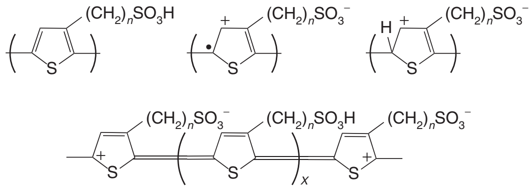

Figure 1.31 Basic units of poly(n-(3′-thienyl)alkanesulfonic acid). (Reprinted with permission from *Macromolecules*, **26**, 7108. Copyright (1993) American Chemical Society.)

redox process. It appears that the structures of auto-doped P3TASHs involve polaron/bipolaron with additional protons on some α-carbons of the rings resulting from redox processes and comprise four species as indicated in Figure 1.31.

1.5 EFFECT OF SUBSTITUENTS ON PROPERTIES OF POLYMERS

Functionalized conducting polymers were initially pursued as a means for overcoming issues of processibility. For example, the first conducting polymers discovered were insoluble, intractable, nonmelting and thus not processible. However, over the past several years, remarkable progress has been made towards improving the processability of these materials. To improve melt and solution processability of the stiff backbone, the standard approach consisted of substitution of flexible side chains (alkyl, alkoxy, etc.) to the main chain. This approach was first applied to polythiophene [185]. However, as is well known, the presence of substituents on the backbone of the conducting polymer can not only modify the processability but can also modulate the electrical, electrochemical, and optical properties of the resulting polymer. Similarly, in self-doped conducting polymers, substitution of ionizable anionic functional groups has a significant impact on various properties. The distinctive properties of self-doped polymers that differ from the parent polymers are discussed below.

1.5.1 Solubility

The insolubility or aggregation of doped conducting polymers in solution is believed to be due to increased rigidity of the polymer chains on doping and the increased polar interactions between the polymeric chains. The manifestation of electronic delocalization throughout a π-system requires that adjacent monomer units along the backbone be coplanar. This coplanarity tends to make the polymers inflexible and insoluble. The low solubility is most likely due to lack of conformational mobility in solution and due to efficient molecular packing or crystallization forces in the solid state. However, this problem can be overcome by structural modifications. Substituents along the polymer backbone can significantly increase the solubility by disrupting the packing forces in the solid state, and by providing new polymer solvent interactions. The substitution of long, flexible, pendant, alkyl or alkoxy chains to a rigid polymer backbone has induced solubility in polythiophenes [113, 114, 186], polyanilines [115–118], poly(phenylene vinylenes) [187] and polyphenylenes [188, 189] in common organic solvents. The conformational mobility of the side chains, which act as ‘bound solvent’ [190], provides enough entropic driving force to carry the rigid polymer chain into solution.

A distinctive property of self-doped polymers is their water solubility in the neutral (insulating) and doped (conducting) states. This solubility is due to the covalently attached negatively charged groups on the polymer backbone. Solubility allows a deposition of conductive and electroactive layers onto any, even a nonconducting, surface by a simple casting of self-doped polymers. Such layers could find numerous applications in diverse areas of technology. For example, in self-doped sulfonated polyaniline, with increasing sulfur to nitrogen ratio from 0.65 to 1.3, the solubility in water increases from 22 to 88 g/L [191]. Zotti *et al.* [164] reported the solubility of self-doped polythiophene *ca* 10 g/L.

1.5.2 DC Conductivity

While substituents on conjugated polymer chains can increase their processability, it is recognized that there is a tradeoff in terms of conductivity. This is a direct result of the fact that the properties that strengthen chain–chain interactions are also responsible for charge transport along the backbone of the polymer. For example, the twisting of polymer backbone via steric interactions decreases π-orbital overlap resulting in decreased conductivity [192, 193]. Grubbs *et al.* were able to strike a balance between these two properties using ring opening metathesis polymerization of monosubstituted cyclooctatetraenes [194]. This approach resulted in a single substituent on every eighth carbon in polyacetylene, resulting in a soluble polymer that retained a significant amount of its conductivity.

In self-doped polymers, the same steric effects associated with covalently attached groups are largely responsible for the decrease in the conductivity as a result of decreased interchain transport or reduced conjugation of the π-system [153]. Self-doped polyanilines (ring substituted or through a alkyl or aryl linker to nitrogen sites) have lower conductivity in the range of 10^{-2} to 10^{-9} S/cm than parent polyaniline ~1–10 S/cm [136, 138, 146, 149, 153, 173, 195–202]. However, for ring sulfonated polyaniline with 50 % and 75 % degrees of sulfonation, conductivity is comparatively higher than with other self-doped polyanilines, around 0.1 and 1 S/cm, respectively [153, 173]. Commercially available ring sulfonated polyaniline with a sulfonation degree of 100 % has been reported to have a conductivity of 0.02 S/cm [202], which is lower than for 50 % and 75 % degrees of sulfonation. This decrease in conductivity with increasing degree of sulfonation has been attributed to the higher degree of twisting of the phenyl rings relative to one another and increased interchain separation due to increasing density of sulfonate groups [202]. Unlike polyaniline, the conductivity of self-doped polyaniline is independent of pH within a broad range of 0–12 [173].

The highest conductivity of 65 S/cm for electrochemically prepared self-doped ring-sulfonated polypyrrole was reported by Sahin *et al.* [203]. However, conductivity decreases from 65 S/cm to 6.5 S/cm with increase in sulfonation (or S/N ratio) from 0.29 to 0.53. The conductivity of ring sulfonated polypyrrole is higher than alkylsulfonate ($0.5-10^{-3}$ S/cm) [135] and *N*-substituted self-doped polypyrroles ($10^{-4}-10^{-6}$ S/cm) [133, 134, 204, 205]. The spacer alkyl chains of sulfonic acid and *N*-substitution leads to a large decrease in the conjugation along the polypyrrole chain, and in turn conductivity decreases. The conductivities found for chemically prepared self-doped polypyrrole are lower than for the polymer prepared electrochemically. The conductivity of sulfonic-acid-substituted self-doped polythiophene and polypyrrole is higher than with carboxylic acid substituents, likely due to its relatively weak acidity [206]. The structure and effect of the side chain length on the doping level of poly(n-(3′-thienyl)-alkanesulfonic acid) with alkanes of carbon numbers two, six and ten has been reported and it was found that the doping level decreases as a function of chain length [184]. The lower doping level of poly(n-(3′-thienyl)-alkanesulfonic acid) with higher chain length was attributed to its higher oxidation potential due to shorter conjugation length.

1.5.3 Molecular Weight

The molecular weights of substituted polymers are typically low compared with parent polymers due to the bulky nature of the ring substituents, which can hinder polymerization; however, solubility in common organic solvent is increased. Dao *et al.* [193] have studied the effect of alkyl substituents on the molecular weight of polyaniline. The molecular weight of chemically prepared poly(2-methyl aniline) and poly(2-ethyl aniline) was reportedly 7000 and 5000 g/mol, respectively, which is 15-times lower than polyaniline (80 000) prepared under identical conditions. A similar effect of alkyl substituents was observed on molecular weights of polythiophenes [207, 208].

Although self-doped polymers are typically processible and retain most of their electronic and redox properties, the insolubility of the products under the polymerization conditions leads to premature termination of the polymerization reaction. This results in low molecular weight polymers. Post polymerization modification, in the case of sulfonated polyaniline, can get around this problem to some extent; however, there is a lack of control over the degree of sulfonation as well as the distribution along polymer chains. A breakthrough was achieved with a self-doped form of poly(anilineboronic acid), which is soluble under polymerization conditions and resulted in a high molecular weight polymer [151]. Gel permeation chromatography results indicated a number average molecular weight of 1 676 000 g/mol, a weight average molecular weight of 1 760 000 g/mol and a polydispersity of approximately 1.05.

1.5.4 Redox Properties

The structure and conformational changes of a conducting polymer backbone in the presence of substituents such as alkyl, alkoxy and halogens, etc. do not show a significant impact on the redox properties (redox switching, cycleability and stability at high pH) except for shifts in redox potentials. However, in self-doped polymers, ionizable, negatively charged, covalently bonded, functional groups act as intramolecular dopant anions that are able to compensate positive charges in the polymer backbone, thus replacing auxiliary solution dopant anions. This 'inner' anion doping determines many distinctive properties of self-doped polymers, setting them apart from their parent polymers. Among them, the electrochemical redox activity in pH neutral solutions seems to be of great interest. In contrast to polyaniline, which shows its redox activity at solution pH not exceeding 3 or 4, self-doped derivatives are active in a broad range of solution pH, extended to higher values [209], in some cases up to pH 12 [210, 211]. Therefore, the use of conducting polymer coated electrodes in such fields as electrocatalytic conversion of solution species [212] sensors and biosensors could be possible, even in weakly neutral solutions, with the use of self-doped polyaniline derivatives.

1.5.5 Electronic and Spectroscopic Properties

The addition of substituents on the backbone of conjugated polymers decreases the degree of coplanarity. The steric repulsions between adjacent side groups result in twisting of the chain and hence yield a reduction in conjugation of the rings in the polymer. The optical absorption spectroscopic studies of the substituted polymer have given an indication of the effective conjugation length of the double bonds in the main chain. There are many reports in the literature showing the shift in absorbance with the addition of substituents on the conjugated polymer backbone associated with decreasing chain length [192, 194]. Similar structural impact is expected with self-doped polymers in addition to the impact of the charge on polaron/bipolaron structures.

In self-doped polyaniline, sulfonic groups induce changes in the geometry of the polyaniline backbone [152], affecting the physicochemical properties of the polymer. Comparative electronic absorption spectroscopic studies have shown a hypsochromic shift of the $\pi-\pi^*$ transition on going from emeraldine salt (ES) to sulfonated polyaniline salt, and a bathochromic shift of the polaron band transition. This is consistent with a decreased extent of conjugation, because of an increase in torsion angle between adjacent phenyl rings with respect to the plane of the nitrogen atoms, caused by the repulsion between the sulfonic group and hydrogen atoms on the adjacent phenyl rings [152, 153]. Based on X-ray photoelectron spectroscopic investigations [154] indicating a higher proportion of positively charged nitrogens, it was concluded that the polaron of sulfonated polyaniline is more localized as compared with the conductive form of polyaniline.

1.5.6 Mechanical and Thermal Properties

Mechanical properties of conducting polymers are limited in general due to low molecular weight, limited branching and crosslinking. Thermal properties are largely limited by the volatility of the dopants. For example, polyaniline is known for its limited thermal stability and loss of conductivity at high temperature. From a chemical point of view, several processes take place in polyaniline upon heating: loss of dopant, oxidation of chains by oxygen, and cross-linking. Since the protonated polymer undergoes irreversible chemical modifications upon heating in air, its conductivity cannot be recovered by redoping [199, 213–217]. The thermal stability, together with conductivity at high temperature, are important properties for many commercial applications. For example, thermal stability is important for conductive coatings and electronic circuits as well as polymer electrolyte membranes for fuel cells. Attempts to improve thermal stability have focused on stabilizing the dopant, which is typically volatile. Thermal stability of self-doped polymers is expected to be better since the dopant moiety is covalently bonded to the polymer backbone. Han *et al.* [218] have reported that the thermal stability of self-doped propylthiosulfonated polyaniline is significantly higher than sulfonated polyaniline [219] and unsubstituted polyaniline. The covalently bonded electron donating mercaptopropanesulfonic acid constituent group on the polymer backbone reportedly stabilizes the aromatic benzenoid ring, thereby reducing the decomposition of the backbone. The propylthiosulfonated polyaniline retains its sulfonic acid groups up to ~260 °C [218], whereas sulfonated polyaniline begins to lose sulfonic acid groups at a much lower temperature of about 185 °C [219].

According to a recent report, the thermal stability of self-doped poly(anilineboronic acid) [220] is greater than that of HCl-doped polyaniline and other self-doped forms of polyaniline. This is due to a self-doped structure where the anion is immobilized in the form of a crosslink, resulting in conductivity up to 500 °C. This self-doped crosslinked structure is also responsible for enhanced mechanical properties including a hardness of 0.5 GPa [221].

1.6 APPLICATIONS OF SELF-DOPED POLYMERS

Conducting polymers are attractive materials for use in existing and emerging technologies due to their light weight, low cost and versatility compared with other standard conductors and semiconductors. Some examples of potential applications include rechargeable batteries, electrochromic displays and smart windows, light emitting diodes, toxic waste cleanup, sensors, field effect transistors and electromagnetic interference shielding, etc. Self-doped polymers are expected to play an important role in the technical implementation of conducting polymers since they can overcome many of the limitations associated with conducting polymers. For example, these polymers have proven to be an enabling step in the development of plastic electronic devices and biosensors.

1.6.1 Molecular Level Processing

The processing of ICPs into thin films is oftentimes extremely challenging due to their insolubility, intractability and infusibility. Therefore, the development and utilization of these polymers as active elements of thin film electronic and optical devices continues to be an intense area of research. These materials are generally manipulated into thin films *via* simple spin-casting techniques. However, it is becoming more apparent that better control over the molecular and supramolecular organizations of these materials is needed to exploit fully their novel optical and electrical properties. Recently, a new layer-by-layer processing technique involving the alternate deposition of adsorbed layers of oppositely charged polyelectrolytes from dilute solutions has emerged, as a variable means to manipulate polymers into multilayer thin films [222, 223]. This approach provides molecular level control over thickness and architecture of multilayer thin films, is remarkably simple to use, and is readily extended to a wide variety of polymers, including many different electroactive polymers.

Electronically conducting multilayers have been prepared by using oxidized polyaniline and polypyrrole as polycations [224–228]. Owing to their interesting electrical and optical properties, mono- and multilayers prepared from conducting polyelectrolytes should be interesting materials for potential application in the field of sensors, electrooptics and LED technology [162, 222, 229–231]. Water soluble self-doped conducting polymers have the attractive feature of producing uniform conducting coatings on any charged substrate with precise control of thickness, irrespective of form or size of the substrate, by simply dipping it into an aqueous polymer solution. There are only a few papers dealing with the fabrication and properties of multilayers prepared from self-doped conducting polymers. Rubner *et al.* were first to demonstrate that ultrathin conducting layers can be fabricated using carboxylic-acid-derivatized polythiophenes [223, 232–234]. Light-emitting diodes have been prepared by sequential adsorption of anionic and cationic poly(*p*-phenylene)s [235]. Lukkari *et al.* have shown that multilayers can be prepared from sulfonated poly(alkoxythiophene) and that the linear charge density of the conducting polymer, (i.e., its oxidation state) affects the multilayer formation [236]. They were the first to report on the all thiophene polyelectrolyte multilayers containing poly(3-(3′-thienyloxy)propanesulfonate) (P3TOPS) as polyanion and poly(3-(3′-thienyloxy)propyl triethyl ammonium) (P3TOPA) as polycation [237] as shown in Figure 1.32.

Sulfonated polyaniline has been used in the fabrication of multilayer heterostructures in light emitting diodes, the electrochemical control of electrolyte activity [238] and biosensors [239]. Recently,

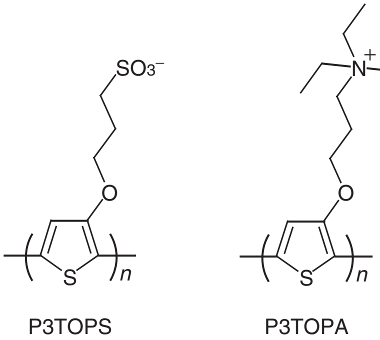

Figure 1.32 Structures of P3TOPS and P3TOPA. (Reprinted with permission from *Journal of the American Chemical Society*, **123**, 6083. Copyright (2001) American Chemical Society.)

nanoassemblies of sulfonated polyaniline multilayers have been formed [240]. Cao *et al.* [241] have shown the photovoltaic properties of a multilayer film based on highly sulfonated polyaniline and diazoresin. Torresi *et al.* [242] have used self-doped polyaniline multilayer films to prepare oxalate biosensors. Chan *et al.* [243] fabricated multilayer photovoltaic devices based on ruthenium containing poly(*p*-phenylenevinylene) and sulfonated polyaniline.

1.6.2 Transistors

The metal oxide semiconductor field effect transistor (MOSFET) is the most important device for very large scale integrated (VLSI) circuits such as microprocessors and memory devices [244]. Much research has explored the use of conducting polymers as an active material in field effect transistor devices; dedoped or doped conjugated polymers such as *trans*-polyacetylene [101], polythiophene [245], thiophene oligomers [246], poly(3-alkylthiophenes) [247, 248], polythienylene vinylene [249], poly(*N*-methylpyrrole) [250], polyaniline [251] and polynaphthalene vinylene or polyphenylene vinylene [252] have all been demonstrated as suitable materials for field effect transistor architecture. However, the performance of these organic devices has not been comparable with that of their inorganic counterparts due to low charge carrier mobility and relatively poor stability. Experiments have shown that the field effect mobility can be increased by two to three orders of magnitude by additional doping, confirming the fact that the carrier mobility in conjugated polymers depends strongly on doping [253–256]. Although the increased mobility is favorable when applications are considered, the threshold voltage V_t is also increased upon doping, and therefore the field effect transistor characteristics become more of the ‘normally on’ type [257]. To improve both carrier mobility and stability of conjugated polymer FET devices, Kuo *et al.* have fabricated water soluble, self-acid-doped, conducting polyanilines, poly(aniline-co-*N*-propanesulfonic acid aniline) (PAPSAH) and sulfonic acid ring substituted polyaniline MOSFETs (SPAN) [257]. The schematic cross sectional view of fabricated MOSFETs is shown in Figure 1.33. These field effect transistors have ideal current drain source (ds) voltage characteristics and their field effect mobilities can reach 2.14 (PAPSAH) and $0.33\,\mathrm{cm^2\,V^{-1}s^{-1}}$ (SPAN) (Figure 1.34). These values are reportedly close to those of amorphous silicon inorganic transistors ($0.1–1.0\,\mathrm{cm^2\,V^{-1}s^{-1}}$). Also, these field effect transistors are found to be environmentally more stable than those of other polyaniline field effect transistors.

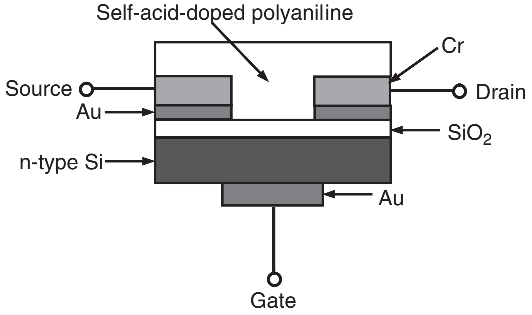

Figure 1.33 Cross sectional view of fabricated MOSFETs.

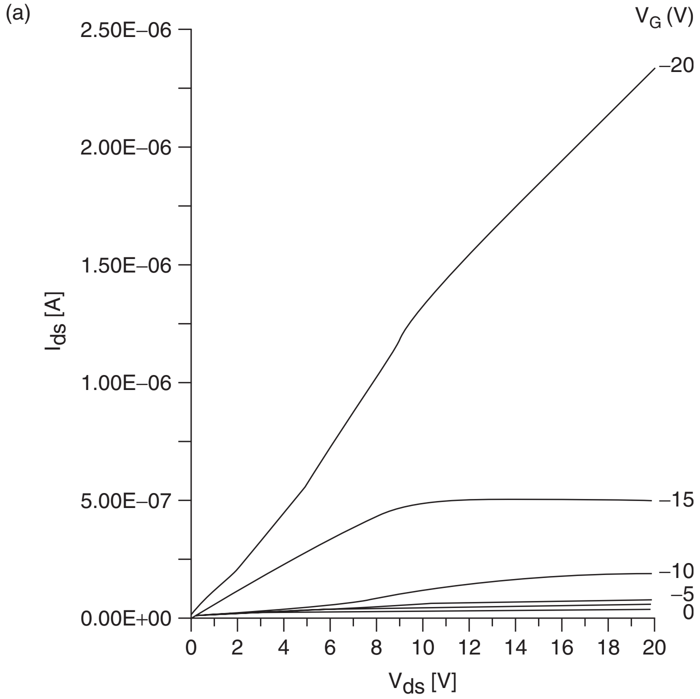

Figure 1.34 Drain-source current (I_{ds}) vs drain-source voltage (V_{ds}) characteristics of (a) SPAN (0.327 μm) and (b) PAPSAH (0.812 μm) MOSFETs at various V_{G}. The devices were exposed to air for two days prior to measurement. (Reprinted from *Synthetic Metals*, **93**, C. T. Kuo, S. A. Chen, G. W. Hwang, H. H. Kuo, 155. Copyright (1998), with permission from Elsevier.)

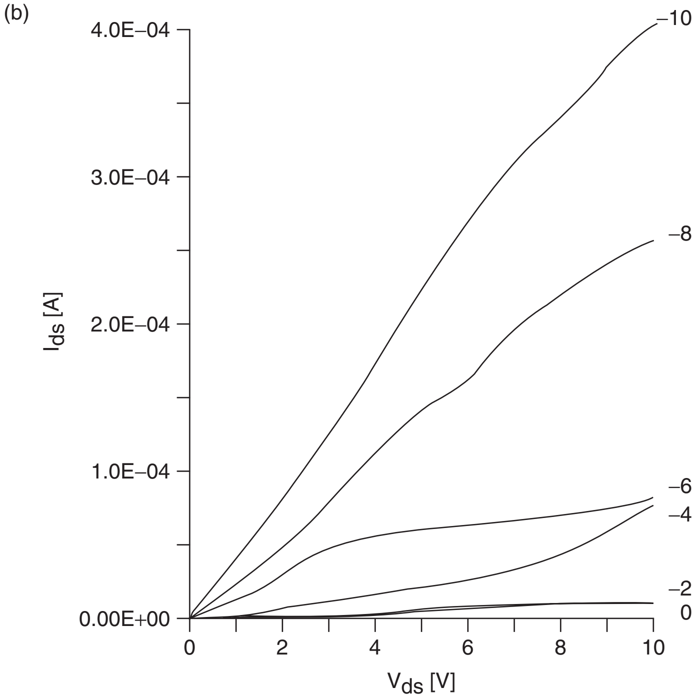

Figure 1.34 (*continued*).

1.6.3 Biosensors

Polyaniline is the conducting polymer most commonly used as an electrocatalyst and immobilizer for biomolecules [258–260]. However, for biosensor applications, a nearly neutral pH environment is required, since most biocatalysts (enzymes) operate only in neutral or slightly acidic or alkaline solutions. Therefore, it has been difficult or impossible to couple enzyme catalyzed electron transfer processes involving solution species with electron transport or electrochemical redox reactions of mostly polyaniline and its derivatives. Polyaniline is conducting and electroactive only in its protonated (proton doped) form i.e., at low pH values. At pH values above 3 or 4, polyaniline is insulating and electrochemically inactive. Self-doped polyaniline exhibits redox activity and electronic conductivity over an extended pH range, which greatly expands its applicability toward biosensors [209, 210, 261]. Therefore, the use of self-doped polyaniline and its derivatives could, in principle, enable the direct or mediated electron transfer between the polymer matrix and active centres of biocatalysts.

Karyakin *et al.* have developed a potentiometric glucose biosensor using self-doped polyaniline [262]. Self-doped polyaniline acts as a pH transducer exhibiting a stable potentiometric response of 70 mV/pH. Also, the self-doped polyaniline biosensor reportedly shows a three- to fourfold higher response compared with a glucose sensitive field effect transistor [263]. Chen *et al.* have used self-doped polyaniline as an ascorbate sensor [264]. Self-doped polyaniline has also been successfully utilized for enzyme immobilization in multilayers [265]. Rusling *et al.* [266] have shown enhanced electrochemical sensitivity to hydrogen peroxide by efficient wiring of the active enzymes with sulfonated polyaniline.

1.6.4 e-Beam Lithography

Electron-beam (e-beam) lithography allows the production of features much smaller than standard lithographic techniques, and as a result is expected to allow the production of increased memory capacity and more advanced large-scale integrated circuits. However, e-beam lithography has the serious disadvantage of positional errors arising from electrons accumulating in the resist and substrate during the e-beam writing process. Conducting polymers have been found to be useful in several lithographic applications [267, 268]; however, they are not sufficiently soluble in the conducting state, thus restricting their widespread use in lithographic applications. The processability of conducting self-doped polymers makes the material more convenient for lithographic applications. Ikenoue *et al.* have proposed a useful method for the coating of water-soluble, self-doped, polymers e.g., polythienylalkanesulfonate, as a charge dissipating top coat on the resist [269, 270]. This polymer has a variety of advantages including: (i) an electron conduction mechanism capable of giving an excellent shielding effect allowing fast e-beam writing speeds, (ii) good processibility for coating and removal of the polymer, and (iii) good film formation owing to high molecular weight. They suggest that the self-doped polymer is not only useful for the charge dissipation but is also useful for stabilizing the sensitivity of chemically amplified resist as an acidic polymer film. Watanabe and Shimizu *et al.* [196] have reported the use of self-doped polyaniline films to prevent charging during e-beam lithography and to improve post-exposure delay latitude for chemically amplified resists, and as a conductive bottom layer in multilevel resists. Charge buildup on the resist layer during plasma etching causes gate oxide leakage or breakdown due to plasma nonuniformities. This damage was reportedly reduced by using self-doped polyaniline.

1.6.5 Electrochromic Devices

Chromatic changes caused by electrochemical processes were originally described in the literature in 1876 for the product of the anodic deposition of aniline [271]. However, the electrochromism was defined as an electrochemically induced phenomenon in 1969, when Deb observed its occurrence in films of some transition metal oxides [272]. Electrochromism in polypyrrole was first reported by Diaz *et al.* in 1981 [273]. Electrochromism is defined as the persistent change of optical properties of a material induced by reversible redox processes. Electronic conducting polymers have been known and studied as electrochromic materials since the initial systematic studies of their electronic properties.

Electronic conducting polymer-based electrochromics have received increasing attention due to their potential for facile production, structurally controllable states, high contrast, fast switching speeds and the ability to be applied to flexible electrochromic devices [274–277]. In conducting polymers, the electrochromism, as well as the conductivity, is explained using band theory [276]. The doping of a conducting polymer modifies its electronic structure, i.e., introduces charge carriers, producing new electronic states in the band gap, thus allowing new electronic transitions resulting in color changes.

Self-doped polymers exhibit faster electronic and optical responses to changes in electrochemical potential relative to the parent polymers, and thus they are useful for fabricating electrochemical chromic displays. Ikenoue *et al.* reported the electrochromic fast switching behavior of self-doped poly(3-(3′-thienyl)-propanesulfonic acid). The polymer shows a considerably faster optical switching response (saturated within 50 ms) than does the well known polyisothianaphthene (saturated within 500 ms), and long term stability over 10 000 cycles [183]. Self-doped polyaniline derivatives gave reversible color changes in all-solid-state electrochromic windows assembled from an electrochromic poly(aniline-*N*-butyl sulfonate) and an ion conducting polymer electrolyte membrane. The all-solid-state electrochromic window responded to potential steps between +2.3 and −1.5 V by changing its color from green-blue to transparent yellow within 60 s. The color contrast and optical response of poly(aniline-*N*-butyl sulfonate) in contact with different polymer/electrolyte systems is reportedly a function of electrolyte composition [278].

Reynolds *et al.* [279] reported electrochromic behavior of self-doped propanesulfonated poly(3,4-propylenedioxypyrrole). The polymer has not only shown interesting electrochromic properties in the visible, but, upon doping, also exhibits a very strong absorption in the near infrared with changes in transmittance up to 97 %, extending the use of the polymer as the active layer in a visible/near infrared switchable device. Viinikanoja *et al.* [280] reported the electrochromism and pH-induced halochromism of self-doped poly(3-(3′-thienyloxy)propanesulfonate) multilayers.

1.6.6 Ion Exchangers

A unique property of self-doped polymers is their ability to act as a ‘charge controllable membrane’ with cation exchange abilities [133, 163, 281, 282], in contrast to the anion exchange properties of classical polymers, i.e., doped with small or free moving anions. Reynolds *et al.* [283] have reported the ion exchange properties of self-doped poly(3,6-(carbaz-9-yl)propanesulfonate). According to electrochemical analysis, the polymer has two separate oxidation states involving interactions of the polymer backbone with the covalently bound, self-doping, ion and counterions from the electrolyte, indicating that the polymer has the ability to act as a potential dependent, charge controllable, membrane with both cation exchange and anion exchange properties.

1.6.7 Rechargeable Batteries

Lithium secondary batteries are one of the most important applications of electronically conducting polymers. Conducting polymers such as polyaniline, polypyrrole and polythiophene are expected to be promising materials for the electrodes of secondary batteries because they are relatively stable in air and have good electrochemical properties. In the discharging cycle of these batteries, the electrons flowing from the lithium anode (negative pole) through an external electric circuit must be consumed at the cathode (positive pole). When used as the active mass of a positive electrode, a conducting polymer ensures efficient utilization of electrons by converting the oxidized form of the conducting polymer into the reduced form. Conversely, electrochemical oxidation of the reduced form takes place in the reverse charging cycle. Most of the common conducting polymers exchange anions during the charging and discharging processes. The reversible exchange of anions between active polymer mass and electrolyte limits many important characteristics such as the electric charge density (relative to the mass of a polymer), the maximum electric current available (due to limited rate of electrochemical processes including anion mobility), cycleability of the battery, storage characteristics, etc. The use of self-doped conducting polymers excludes the participation of anions in the charging–discharging process. Instead, the charge compensation occurs at the expense of lithium cation insertion or expulsion, and the increased efficiency of this process leads to a significant improvement of some characteristics of rechargeable lithium batteries [201].

Sulfonated polyanilines are typically used as the cathode in rechargeable batteries. They exhibit better chemical stability due to steric protection by the sulfonic group [145]. This fact reduces the degradation of the quinoid structure during oxidation, increasing the cycleability of the electrode. Also, the electrostatic environment provided by sulfonic groups decreases the participation of anions during the charge compensation process [284]. In lithium batteries, it is desirable that only lithium cations intercalate into the cathode, because this leads to the use of small amounts of electrolyte that only serves as a carrier for the cations to migrate/diffuse from the anode to the cathode, and this permits the fabrication of higher specific capacity batteries. A sulfonated polyaniline prepared by copolymerization of *o*-aminobenzenesulfonic acid and a relatively small amount of aniline reportedly exhibits a specific charge of approximately 47 Ah kg^{-1} in aqueous solutions (first redox process only) and over 80 Ah kg^{-1} in nonaqueous solutions (both redox steps) [285]. For a complete Li/sulfonated polyaniline cell with nonaqueous $LiClO_4$ electrolyte, specific charge of 52 Ah kg^{-1} and specific energy of 130 Wh kg^{-1} were calculated on the basis of experimental results. The specific energy of a sulfonated polyaniline–Li battery was *ca* 50 % higher than a PANi–Li battery [286]. Mousavi *et al.* [287] reported that the maximum capacity of a self-doped polyaniline–Zn battery is 146.4 Ah kg^{-1} and the specific energy 172.8 Wh kg^{-1} with coulumbic efficiency of 97–100 % over at least 200 cycles between 0.8 to 1.6 V.

1.6.8 Dip-Pen Nanolithography

Controlled patterning of conducting polymers at a micro- or nanoscale is the first step towards the fabrication of miniaturized functional devices.

Dip-pen nanolithography [288] is a promising new nanofabrication tool, which allows one to pattern molecules on a variety of surfaces with a coated AFM tip in a controlled fashion on a sub-100 nm to many micrometer scale [289, 290]. Recently, Mirkin *et al.* [291] fabricated nanopatterns of self-doped conducting polyaniline by dip-pen nanolithography using electrostatic interactions as a driving force (Figure 1.35). The water soluble self-doped polyaniline ‘ink’ is converted to its solid state after patterning. The smallest feature size generated with these polymer inks had a diameter of 130 nm. In this case, the electrostatic interaction between the charged polymer chains and the oppositely charged substrate acts as a primary driving force in the dip-pen nanolithography process. Others have utilized electrically biased electrodes to polymerize monomers on conducting substrates [292]. Mirkin’s approach differs from the literature approach in that no bias is required, and one can write on nonconducting substrates.

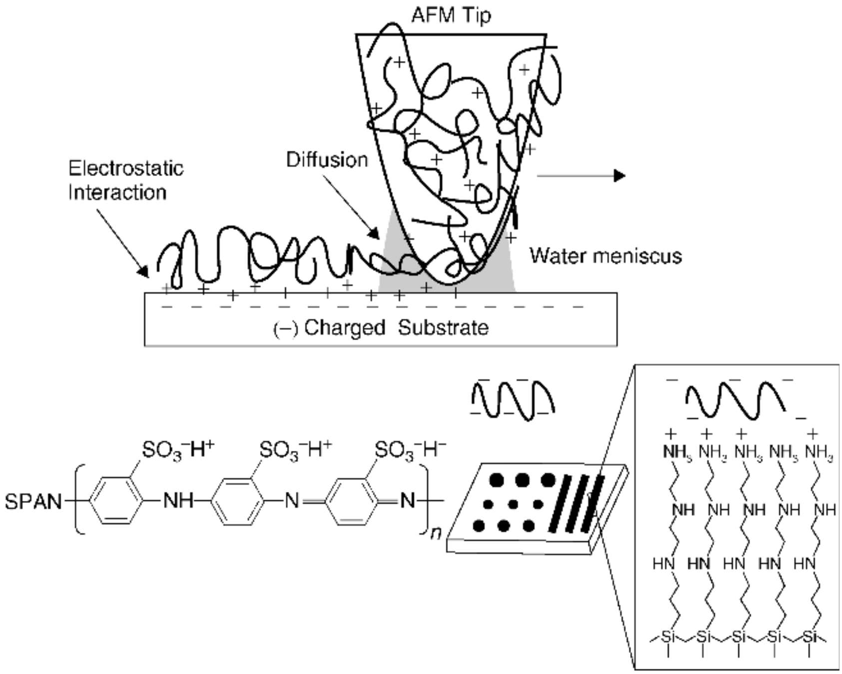

Figure 1.35 Schematic representation of dip-pen nanolithography for charged self-doped polyaniline. (Reproduced from *Advanced Materials*, 2002, **14**, 1474, J. H. Lim, C. A. Mirkin, with permission from Wiley-VCH.)

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