Recent Advances in the Physical and Spectroscopic Properties of Polypyrrole Films, Particularly Those Containing Transition-Metal Complexes as Counteranions

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The results of recent investigations of polypyrrole (PPy) films using a variety of physical and spectroscopic techniques are reviewed. The physical techniques discussed include conductivity and X-ray diffraction measurements; the spectroscopic techniques reviewed comprise optical, electron paramagnetic resonance (EPR), and Mössbauer spectroscopies. After consideration of the historical background, applications, and the growth mechanism of PPy, a review of the nature of the charge carriers and the structure is presented. The data reported for a subclass of PPy films containing transition-metal complexes as counteranions are given special emphasis.

Introduction

Most polymers are electrically insulating, and this property is exploited in many of their applications (e.g., insulation for copper wires). In the past 15 years a number of new organic polymers have emerged which are electrically conducting. These "conducting polymers" have generated a large amount of interest in the field of "synthetic metals". The ultimate goal in the study of conducting polymers is the preparation of a material that possesses the mechanical and processing properties of a polymer and the electronic properties of a metal or semiconductor. Figure 1 shows the structures of four of the most widely studied conducting polymers in their neutral forms. The extended π-conjugated backbone is a common feature of the structures, but this alone is not sufficient to produce appreciable conductivity; partial charge extraction (partial oxidation) is also required. This is usually achieved by chemical or electrochemical means.

Polypyrrole (PPy) is the subject of the present review. This material is one of the most stable of the known conducting polymers and also one of the easiest to synthesize. Consequently it is being researched vigorously in both academic and industrial organizations. PPy was the subject of reviews by Diaz et al.,[1,2] Street,[3] and Malhotra et al.[4] in the 1986–88 period. PPy also received attention in part of a review of conducting polymers by Kanatzidis.[5] The biosensing properties of PPy, as well as its template synthesis within the pores
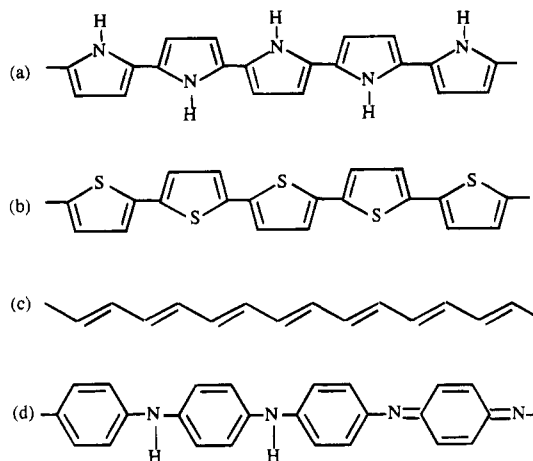

Figure 1. Structures of neutral (a) PPy, (b) polythiophene, (c) polyacetylene, and (d) polyaniline.

of nanoporous membranes and subsequent use to immobilize enzymes, have been reviewed recently by Bartlett[6] and Martin,[7] respectively. A large amount of work has been performed on this material since 1988, and new counteranions have been incorporated. In addition, a number of the earlier theories have been challenged.

PPy may be prepared by chemical or electrochemical oxidation. Recent examples of the former may be found in the work of Meijer et al.,[8] Zotti et al.,[9] and Zerbi et al.[10] This review concentrates on electrochemically prepared PPy. In this method, pyrrole, and an electrolyte salt are dissolved in a suitable solvent and the solution subjected to anodic oxidation. One of the

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advantages of the electrochemical method is that the growth rate and film thickness are easily controlled; the instantaneous growth rate is proportional to the current, and the thickness to the time integral of the current over the growth period. A disadvantage is that the properties of PPy are influenced by a number of variables (e.g., solvent composition, monomer concentration, electrolyte concentration, applied potential, current density, preparation temperature, and the nature of the electrode material). To obtain films with reproducible properties that can be compared from laboratory to laboratory, it is vital that considerable care and attention to detail are exercised.

The oxidation potential of PPy is lower than that of the monomer,[11] and thus the polymer is simultaneously oxidized during polymerization. Consequently counteranions from the electrolyte are incorporated into the growing polymer in order to maintain electrical neutrality. PPy typically contains between 20 and 40 mol % of counteranion. Therefore it is reasonable to expect that the physical properties of the material will be influenced by the nature of the incorporated counteranion (which is, itself, invariably an insulator).

The proportion of pyrrole units that are believed to be in the positively charged (+1) state (i.e., the extent of oxidation) is usually inferred from the level of counteranion incorporation in the polymer (e.g., the extent of oxidation of the pyrrole moiety in $PPyClO_4$ with a formula of $(C_4H_3N)(ClO_4{}^-)_{0.25}$ is +0.25). The positive charges on the PPy chains are delocalized over a number of pyrrole units (each positive charge is delocalized over four pyrrole units in the above example). Hence the polymer moiety is partially oxidized. The concentration of charge carriers in PPy is approximately 5 orders of magnitude higher than that usually found in inorganic semiconductors.[5]

The following section consists of a historical survey of PPy. This is followed by discussions of the present applications and the growth mechanism of the material. Its structural and charge-transport characteristics are then reviewed. The final three sections consist of discussions of the optical, electron paramagnetic resonance (EPR), and Mössbauer spectroscopic studies of PPy.

Background and Incorporation of Transition-Metal Complex Counteranions

In 1916, Angeli[12] obtained a black precipitate from acidic solutions containing pyrrole and hydrogen peroxide. The product was insoluble in organic solvents and was called "pyrrole black". McNeill et al.[13] first reported the semiconducting properties of PPy in 1963. McNeill and his Australian group prepared PPy by the pyrolysis of tetraiodopyrrole. These workers reported the conductivity of PPy as 0.005–1.0 S/cm and found that exposure to water vapor and oxygen caused a decrease in the conductivity.[13] This work has, unfortunately, been generally overlooked in the literature.

PPy was first electrochemically prepared by Dall'Olio et al.[14] in 1968 using aqueous sulfuric acid. The polymer was obtained as a powdery deposit and a

conductivity of 8 S/cm reported. In 1979, Diaz et al.[15] electrochemically prepared thick free-standing films of PPy with good electrical and mechanical properties. The latter work produced an enormous amount of interest in PPy. The material could be conveniently prepared, and it was soon realized that the electrochemical method facilitated incorporation of a variety of counteranions into the polymer. PPy films containing $BF_4{}^-$, $ClO_4{}^-$, $PF_6{}^-$, polymeric, and sulfonated counteranions have attracted the greatest attention in the literature.[16-39] These films have been examined using a variety of techniques, including cyclic voltammetry,[16,19,20,26,34,36] elemental analysis,[16,20,25] conductivity measurements,[16,18-21,26-28,32,33,35-38] X-ray diffraction,[19,21,25,28] scanning tunneling microscopy (STM),[22-24] and SEM,[16,18,20,33] as well as infrared,[17,26,28] optical,[17,19,20,26] X-ray photoelectron,[29-31] and EPR[17,28,39] spectroscopy. Some of these techniques are considered in more detail later. The counteranions listed above are invariably purchased commercially and, for the purposes of this review, are termed "classical counteranions".

When compared to the literature concerning PPy containing classical counteranions, relatively few studies have dealt with PPy containing anionic transition-metal complexes. These "nonclassical counteranions" are usually not available commercially and must be synthesized. The investigation of PPy containing transition-metal complexes is a little studied area of research that provides considerable opportunity for im-

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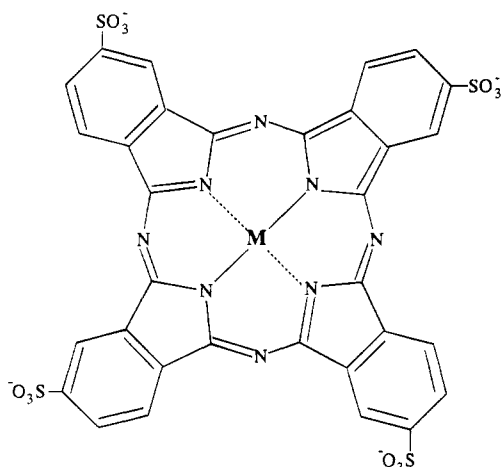
1084   *Chem. Mater., Vol. 7, No. 6, 1995*

Reviews

Figure 2. Structure of tetrasulfophthalocyanine metal chelates, $M^{II}PcTs^{4-}$ (M = Co, Cu, and Ni). Hydrogen atoms not shown.

Figure 3. Structure of $M^{III}EDTA^-$ (M = Co and Cr). Hydrogen atoms not shown.

proving our understanding of this rather intractable material. One advantage of employing transition-metal complexes is that the paramagnetic metal ions can act as in-built spectroscopic probes in techniques such as EPR and Mössbauer spectroscopy. Thus it is possible to obtain information concerning the counteranion environment, and the structure of the material.[40,41] Transition-metal complexes are also suited to an investigation of the relationship between the counteranion structure and the physical properties of PPy.

The earliest reported study of PPy containing a tetrasulfonated metallophthalocyanine (MPcTs) concerned PPyFePcTs.[42] In that work, the ability of the material to catalyze, electrochemically, the reduction of oxygen was examined. Several other papers on PPyMPcTs have been published,[19,43–52] although the majority of these have focused on the electrochemical properties of the films. The structure of $M^{II}PcTs^{4-}$ appears in Figure 2. We have recently studied the physical and spectroscopic properties of PPyMPcTs (M = Co, Cu, Fe, and Ni) prepared using both aqueous and nonaqueous solutions.[40,53] The conductivities of these materials were found to rapidly decrease upon exposure to air. As a reason for this, it was suggested[40] that the large size of the MPcTs counteranions produced packing inconsistencies within PPyMPcTs which facilitated the
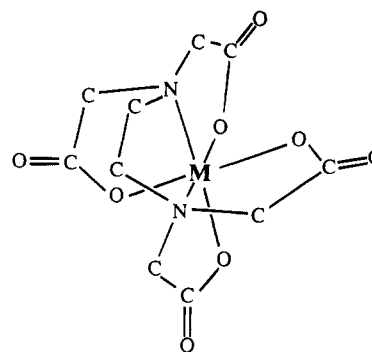
chemical attack of the polymer backbone by atmospheric oxygen.

A conductivity of about 50 S/cm was reported by Hahn et al.[54] for PPy containing $FeCl_4^-$. These workers noted that the conductivity of this material decreased more slowly upon exposure to air, than did $PPyBF_4$. Walton et al.[43] reported a conductivity of 0.01 S/cm for PPy containing 1,1′-ferrocenedisulfonate. This material contained Fe(II), stabilized by the polymer. Takakubo[55] investigated the effect of the preparation conditions on the conductivity of PPy containing tris-oxalato complexes such as $Cr(C_2O_4)_3^{3-}$, and reported values in the range 10–70 S/cm. It was found that the conductivity increased as the temperature of preparation decreased. We have extended this work to include a range of $M^{III}(C_2O_4)_3^{3-}$ counteranions[56] where M = Cr, Fe, Co, Al and have studied the films, grown both in aqueous and in propylene carbonate solution, by a range of structural and spectroscopic techniques. The conductivity values were in accord with Takakubo[55] and fairly independent of the metal ion employed. The room-temperature conductivities of the Cr- and Al-containing films showed long-term stabilities similar to that displayed by PPyPTS (where PTS is the *p*-toluenesulfonate counteranion) prepared using similar conditions.

A conductivity of 15 S/cm was also reported for the ethylenediaminetetraacetate derivative, PPyCoEDTA, by Takakubo.[55] We recently studied the physical and spectroscopic properties of PPyMEDTA (M = Co, Cr, and Fe) and found that the conductivities of these materials were dependent on the nature of the incorporated metal ion.[41] The structure of $M^{III}EDTA^-$ appears in Figure 3. The conductivities of PPyCrEDTA and PPyFeEDTA initially increased after exposure to air and then stabilized.[41] In this regard, these films were superior to PPyPTS prepared under similar conditions. It was proposed that spherical counteranions of moderate size (such as $MEDTA^-$) were effective in retarding the rate of chemical attack of the polymer backbone by oxygen.

We have recently incorporated a range of other M^{II}-(tetradentate) counteranions into PPy where M = Cu, Ni and tetradentate = N,N'-alkylene (or arylene) bis-(5-sulfosalicylaldehydeimine) (N_2O_2 donor) or N,N'-alkylenebis(oxamido) (N_2O_2 or N_4 donors) chelating groups. The conductivities were generally in the range

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Reviews

Chem. Mater., Vol. 7, No. 6, 1995 1085

0.1–0.2 S/cm at 295 K. In addition, the long-term conductivity stability of some of the films was very good.[57]

Kaye et al.[58] observed conductivities in the range of 15–30 S/cm for PPy films containing $Ni(mnt)_2^-$ and $Pd(mnt)_2^-$ (mnt represents the S-donor chelate 1,2-dicyanoethylene-1,2-dithiolene). These workers noted that the tendency for the conductivities of PPy{Ni-$(mnt)_2^-$} and PPy{$Pd(mnt)_2^-$} to decrease upon exposure to air was less than that of $PPyBF_4$. It was proposed that $Ni(mnt)_2^-$ and $Pd(mnt)_2^-$ acted as solid-state redox buffers, maintaining a potential within the films between those at which the counteranions donate and accept electrons, thereby slowing the oxidative process responsible for the loss in conductivity.

Erlandsson et al.[59] had earlier shown that the BF_4^- counteranion undergoes an irreversible reaction within $PPyBF_4$ upon exposure to oxygen and water vapor. This reaction is most likely responsible for the poor stability of the conductivity of $PPyBF_4$ noted by both Kaye et al.[58] and Hahn et al.[54] above.

The physical and electrochemical properties of PPy films containing heteropolytungstate counteranions ($SiW_{12}O_{40}^{4-}$, $PW_{12}O_{40}^{3-}$, and $P_2W_{18}O_{62}^{6-}$) have been studied by Bidan et al.[60] and Sung et al.[61] The former workers reported a maximum conductivity of 2.6 S/cm, and both groups noted that the films tended to retain their counteranions during electrochemical cycling. Bélanger et al.[62,63] extensively studied PPy films containing tetrathiomolybdate and molybdenum trisulfide and reported a conductivity of 0.026 S/cm.[63] Ikeda et al.[64] examined the ability of PPy containing $MTPPS_4$ (M = Co, Fe, and Mn) ($TPPS_4$ = *meso*-tetrakis(4-sulfonatophenyl)porphyrin) to reduce oxygen electrochemically. These workers found that the catalytic activity for oxygen reduction was pH dependent.

PPy films containing transition-metal cyanide complexes have also received attention.[65–68] Zagorska et al.[65] reported that the conductivity of PPy{$Fe(CN)_6^{4-}$}, measured as 1–3 S/cm, decreased by about 60% when exposed to air for about 30 days. Edge et al.[66] reported a conductivity of 17 S/cm for PPy{$Pt(CN)_4^{2-}$} and noted that the films had good mechanical properties. These workers found that the material contained square planar $Pt(CN)_4^{2-}$ counteranions which were not strongly bonded to the polymer chains. The effect of the growth conditions on the conductivity of PPy{$Ni(CN)_4^{2-}$} was subsequently studied by Cervini et al.[67] and a maximum conductivity of 122 S/cm reported. Some of the polymer

films exhibited good conductivity stability, losing only about 7% of their initial conductivity after 50 days of exposure to air. The infrared spectrum of PPy-{$Ni(CN)_4^{2-}$} showed that the C≡N stretching frequency of the incorporated $Ni(CN)_4^{2-}$ species was about 70 cm^{-1} higher than that found for the free $Ni(CN)_4^{2-}$ counteranion. It was suggested that in PPy{$Ni(CN)_4^{2-}$} the cyanide groups interacted with the PPy backbone. Cervini et al.[68] also investigated the effect of the growth conditions on the conductivity of PPy{$Au(CN)_2^-$}. A maximum conductivity of 303 S/cm was reported. This value is one of the highest conductivities reported for PPy containing a transition-metal complex. X-ray diffraction studies suggested that, within PPy{$Au(CN)_2^-$}, the PPy chains were preferentially aligned parallel to the plane of the electrode surface.

The anionic transition-metal complexes discussed above are electrostatically bound to the charged PPy moiety. Bidan et al.[69] synthesized a copper complex $[Cu(dpp)_2]^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) containing two entwined dpp ligands covalently attached to pyrrole units. Electropolymerization of the complex produced an electrically conductive film which could be reversibly de- and remetalated. It was suggested that the redox-active metal center acted as an electron relay during the oxidation of the pyrrole moiety. These workers have subsequently demonstrated that a range of transition-metal ions can be incorporated into PPy using the above ligand system.[70] This interesting approach offers an alternative method for the incorporation of transition-metal complexes into polypyrrole.

PPy composites have also received attention in the literature. PPy has recently been electrochemically polymerized onto a high-temperature superconductor.[71,72] It was found that PPy produced a reversible modulation of the superconducting transition temperature of $YBa_2Cu_3O_{7-\delta}$. Interestingly, it was suggested that superconductivity may have been induced in the volume of the polymer in intimate contact with the superconductor.[71] The latter publication appears to be representative of a developing trend where the properties of PPy composite materials are attracting an increasing amount of interest.[73–77]

Applications of PPy

The commercial applications of conducting polymers have been recently reviewed by Miller.[78,79] A brief discussion featuring recent applications involving PPy is given below.

Conducting polymers are suited to a variety of applications. They possess semiconducting or metallic

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Table 1. Examples of Commercial Products Containing PPy

product	manufacturer (country)
electrolytic capacitor[a]	Matsushita/Panasonic (Japan)
conductive coating for textiles[a]	Milliken and Co. (USA)
static dissipation wrist rest[a]	B. J. K. Computer Accessories (USA)
plating bath for Cu deposition on printed circuit boards[a]	Atotech (Germany and USA) and Blasberg (Germany)
PVC/PPy composites	A. C. and T. (France)
conducting powder	A. C. and T. (France)
shapable conducting films[a]	Ciba-Geigy (Switzerland)
electronic nose	Neotronics (U.K.)

[a] From ref 79.

conductivity, have low density and good flexibility, and are often redox active. The uses proposed include transport of electricity (conducting polymer wires), light-emitting diodes, electrodes in rechargeable batteries, electrochromic displays, gas sensors, biosensors, and radar avoidance coatings. Many conducting polymers (including PPy) change their optical properties when electrochemically reduced and thus are candidates for electrochromic displays and "smart windows". Table 1 shows some of the products containing PPy.

The conductivity of PPy is sensitive to gases and vapors. (This property is not unique to PPy and has been observed in other conducting polymers[80].) A vapor sensor containing PPy has recently been commercialized by Neotronics.[81] The sensor uses an array of conducting polymers and has the ability to differentiate between odors from a variety of sources. It is anticipated that the principal application will be the quality control of beers in breweries.[82]

The most commercially successful use of a conducting polymer involves PPy-assisted copper deposition onto printed circuit boards.[79] This process involves the chemical polymerization of pyrrole onto the printed circuit board followed by electrolytic plating of copper. The process is more efficient and environmentally friendly than that previously employed. In fact, every second piece of consumer electronics produced in Europe[83] contains PPy.

It is evident from the above discussion that PPy has many commercial uses. Given the continuing interest of large companies such as Milliken,[84] its commercial prospects appear promising. However, the stability of its electrical conductivity, particularly at elevated temperatures, needs to be improved in order for its full potential to be realized.

Mechanism of Formation of PPy

The mechanism of growth for PPy is of fundamental interest. A diagram of the generally accepted mechanism for the electrochemical polymerization[1] appears in Figure 4. The initiation step involves the anodic oxidation of monomers in the vicinity of the anode. The radical cations then dimerize and deprotonate. The occurrence of the dimerization step has been supported by the work of Andrieux et al.,[85] in which the early stages of electrochemical polymerization were investi-
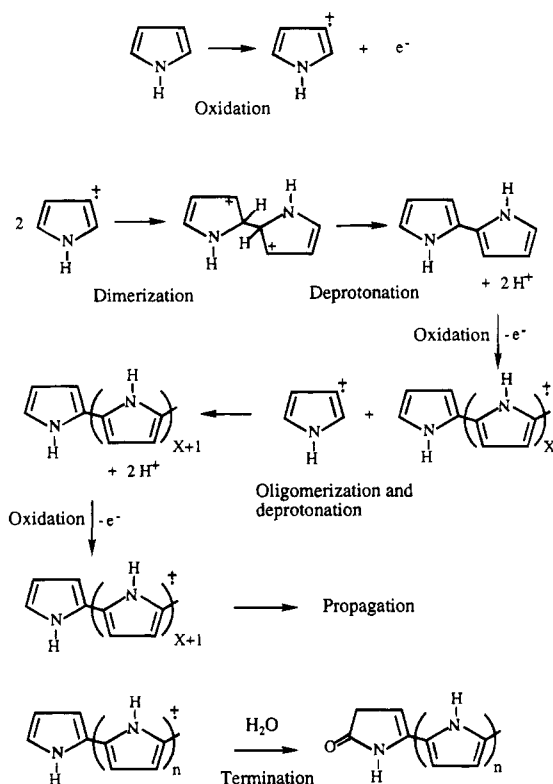

Figure 4. Mechanism for the electropolymerization of pyrrole. No attempt has been made to balance the last reaction.

gated by means of fast double potential step chrono-amperometry. After the deprotonation step, the dimer is reoxidized and couples with another radical cation. Deprotonation and reoxidation follow, and the process continues with the formation of oligomeric species. Once the chain length of the oligomers exceed the solubility limit of the solvent, precipitation occurs and nuclei deposit on the anode.[86] UV–visible spectroscopic studies have suggested that quiescent solutions may contain oligomers with up to nine pyrrole units.[87] The rate of polymerization is limited by the diffusion of monomers to the anode surface during the propagation stage. Recent work[88] has shown that the growth of the deposited PPy chains occurs exclusively through the addition of pyrrole monomers. The mechanism responsible for the change from an oligomeric to a monomeric based deposition (after nucleation) remains to be determined. The termination reaction is not known in detail but could involve nucleophilic attack by water on the polymer chains (see Figure 4).[1] The deprotonation steps in the above mechanisms are believed to produce an acidic environment in the region of the anode.[89,90]

Wei et al.[91,92] have proposed an alternative mechanism to that described above and shown in Figure 4. These workers found that the introduction of small

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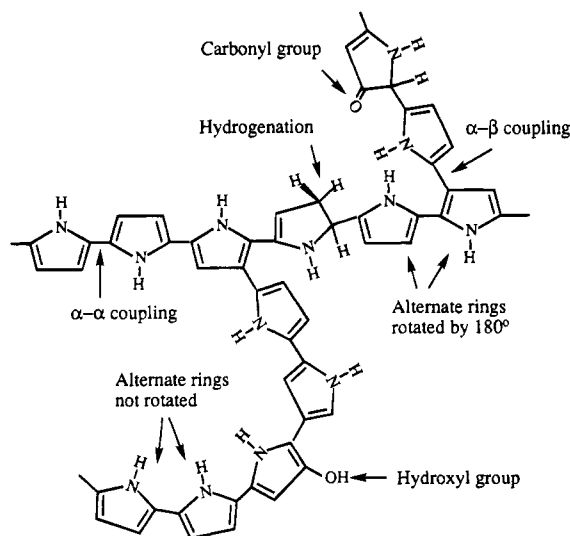
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Figure 5. Diagram showing various defects in the structure of PPy.

quantities of 2,2'-bipyrrole to a solution containing pyrrole significantly increased the rate of polymerization. Moreover the electropolymerization occurred at potentials higher than that required to oxidize 2,2'-bipyrrole but lower than the oxidation potential of pyrrole. This suggested that oxidized pyrrole monomers were not involved in the propagation reaction. An equivalent effect was observed in the case of thiophene,[92] and a mechanism proposed whereby the propagation step involved the electrophilic substitution of radical cations to neutral monomers. It was implied that a similar mechanism was operative for the polymerization of pyrrole. An attractive feature of the electrophilic substitution mechanism is that the coupling of identically charged monomers is not involved during the initial stages of polymerization. However, the question of whether electrophilic substitution is the dominant mechanism of polymerization in the absence of added oligomers remains unresolved. It is important to note that anodic potentials higher than the oxidation potential of pyrrole are required to maintain the electropolymerization in the absence of added oligomers.[2] Thus a constant supply of oxidized pyrrole monomers is required, suggesting that the mechanism originally proposed[1] is dominant.

Structure of PPy

The insolubility of PPy in all solvents has obstructed molecular weight determination by conventional methods. However, the molecular weight of poly(β,β'-dimethylpyrrole) perchlorate, PBDMPyClO$_4$, has been estimated as approximately 100 000 by means of radiochemical techniques.[93] Infrared, X-ray photoelectron spectroscopy (XPS), and NMR spectroscopy studies of PPy have established that the polymer contains several types of defects.[89,90,94] Some of these are illustrated in Figure 5. Overoxidation is a major source of chemical defects involving oxygen, and both carbonyl and covalently bonded hydroxyl groups are produced as a consequence of electropolymerization in the presence

of water.[89,94] Overoxidation is the electrochemically driven attack of the polymer chains by nucleophilic species (e.g., water), and occurs when the anodic potential is higher than the oxidation potential of the polymer. Since the oxidation potential of PPy is lower than that of pyrrole,[11] overoxidation of PPy is an inevitable consequence of film growth in the presence of nucleophiles. Aliphatic hydrogen groups are believed to be produced through the addition of hydrogen to the pyrrole ring under the acidic conditions of electropolymerization.[90] Coupling through the β position of the pyrrole ring is also likely to be an important source of structural defects.[17,90,95] The presence of nonalternating pyrrole rings will cause a deviation from chain linearity. In consideration of the above, it is clear that chemical and structural defects are important in PPy. They can have a significant influence on properties which are sensitive to structural order and charge transport, e.g., X-ray diffraction and electrical conductivity.

Determination of the precise molecular structure of PPy has been frustratingly obstructed by its amorphous nature. Geiss et al.[96] investigated PPy by means of electron microscopy and obtained diffuse electron diffraction patterns. These workers proposed a monoclinic unit cell containing linear chains of pyrrole rings, with alternate rings rotated by 180°. Nogami et al.[97] recently investigated the structure of uniaxially oriented PPyPF$_6$ films by means of X-ray diffraction and suggested that the unit cell was either monoclinic or triclinic; a linear chain structure was also assumed by these authors.

Mitchell et al.[98] conducted the first extensive study of PPyPTS by means of X-ray diffraction. These workers have performed the majority of the X-ray diffraction studies of PPy and invariably examined the film using two orthogonal orientations which correspond to reflection and transmission geometries. They found[98] that the positions of the maxima obtained for PPyPTS using reflection and transmission geometries were different. Consequently, PPyPTS was identified as an anisotropic material. (The positions of maxima obtained in reflection and transmission geometries are identical for an *isotropic* material.) By comparing the d spacing ranges observed for PPyPTS with those normally found in polymers and aromatic molecules, Mitchell et al.[98] established that PPyPTS consisted of layers of PPy chains whose planes were parallel to the plane of the electrode surface.

Mitchell[99] has pointed out that the practice of calculating d spacings from Bragg's law is not valid for amorphous polymers. Nevertheless, this remains a common practice concerning PPy.[21,25,40,41,100] It should be noted that the d spacings calculated in this way are in fact approximations. More precise values require a structural model for the basic unit, which is not yet available for PPy. This is a problem which requires attention in future studies.

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Neutron scattering has also been applied by Mitchell et al.[101] to the study of PPyPTS. They established that PPyPTS consists of PPy layers intercalated with sheets of PTS⁻. In addition it was found that few counteranions resided within the PPy layers and that the PTS⁻ species were well dispersed on a molecular scale within the counteranion layers.

The influence of the counteranion on the structure of PPy has been investigated in some detail.[102] It was found that when PPy was prepared from aqueous solution, anisotropic counteranions (i.e., planar aromatic counteranions) and spherical counteranions promoted anisotropic and isotropic structures of the polymer respectively. Two basic structures—a layered ordered structure and a more open disordered arrangement—have been identified for PPy. It was suggested that the adherence of the planar PPy chain to the electrode surface depended on the distribution of the negative charge of the counteranions; spherical counteranions led to a disruption of the smooth growth face on a molecular level, while anisotropic species (e.g., PTS⁻) aided its retention.[102] The above work clearly established that the structure of the counteranion considerably influences the structure of PPy.

Kassim et al.[103] have recently found that the structure of PPy containing camphor sulfonate, PPyCS, exhibits considerable anisotropy. This is despite the fact that this counteranion is nonplanar and appears to contradict the earlier work discussed above. A model was proposed to explain this behavior which considered the hydrophobic nature of the counteranion.[103] According to the model, counteranions with a strongly hydrophobic character (such as camphor sulfonate) are usually located near the electrode surface and therefore promote the growth of the PPy chains (with which they are closely electrostatically associated) parallel to the electrode plane. Conversely, hydrophilic counteranions, such as SO_4^{2-}, tend to reside in the bulk of the solution, and so polymer growth is not constrained to the electrode plane. While the above model does explain why the PPy chains tend to grow parallel to the electrode plane in PPyCS, it does not explain why the plane of these predominantly coplanar chains should lie parallel to the electrode plane.

PPy chains are intrinsically planar except when certain defects are present within the chains.[102] Table 2 lists the structurally important defects identified by Mitchell et al.[104] and gives their effects on the structure of the polymer. Clearly an increase in the concentration of defects within PPy chains causes both a decrease in the chain order (through a loss in chain linearity) and anisotropy (through a loss of chain coplanarity). This is consistent with the observation that the degree of anisotropy of PPyPTS decreases when the polymerization temperature employed during film growth increases.[105]

Warren et al.[21] and Buckley et al.[100] have also examined PPy by X-ray diffraction. A wide variety of counteranions was employed in both studies. Warren
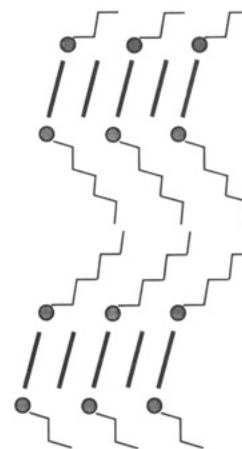

Figure 6. Idealized structure of PPy–"tenside salts", viewed along the PPy chain axis. The short lines represent PPy chains, zig-zag lines are the alkyl chains of the tensides. The circles represent $-SO_3^-$ or $-OSO_3^-$ groups. Adapted from ref 25.

Table 2. Effects of Chain Defects on the Structure of PPy[a]

	type of chain trajectory		
type of coupling	planar and linear	planar and nonlinear	non-planar
α–α coupling with alternating units rotated by 180°	×		
α–α coupling with nonregular 180° rotation of alternating units		×	
α–β (3,5) coupling		×	
α–β (4,5) coupling			×
β–β coupling			×
nonaromatic bonding			×

[a] Data taken from ref 104.

et al.[21] concluded that substituted benzenesulfonate and long alkyl chain counteranions promoted the highest degree of order. Wernet et al.[25] used X-ray diffraction to study the structure of PPy containing a variety of alkyl sulfonates and alkyl sulfates (the so-called "tensides"). These workers found a linear relationship between the length of the alkyl chain and the measured d spacings (obtained from the low-angle X-ray diffraction maxima) and proposed a structural model for these materials (shown in Figure 6). The structure consists of stacked PPy chains separated by counteranion aggregates (since these counteranions are amphiphilic, the aggregates may be thought of as solid-state micellar structures). The presence of counteranion aggregates in PPyMPcTs and PPyMEDTA has also been suggested.[40,41] The structure depicted in Figure 6 is considered to be "liquidlike" in that only short-range order is exhibited.[25]

In recent years, STM has provided considerable insight into the structure of thin films of PPy (i.e., films with a thickness of less than 1 μm). Helical chains of PPy have been observed in PPy containing PTS⁻ and poly(4-styrenesulfonate).[22,24] (The helical structures were unlikely to have been defects in the oriented graphite electrodes as they were also observed within PPy films grown on gold electrodes[106]). Salaneck et al.[107] and Vork et al.[108] had suggested the existence of helical chains of PPy several years earlier. However,

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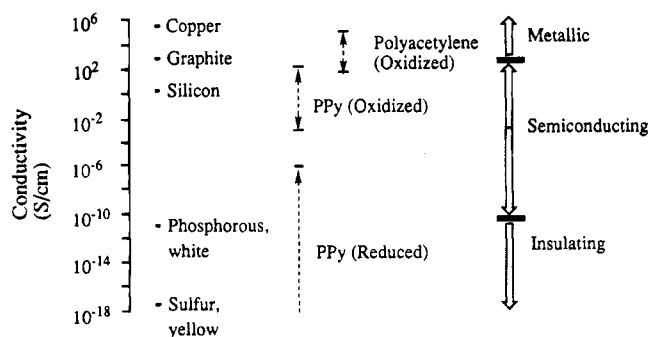
Conductivity (S/cm) scale:

- 10^6 — Copper
- 10^2 — Graphite
- — Silicon
- Polyacetylene (Oxidized) — Metallic
- PPy (Oxidized)
- 10^{-2} — Semiconducting
- 10^{-6}
- 10^{-10} — Phosphorous, white
- PPy (Reduced) — Insulating
- 10^{-14}
- 10^{-18} — Sulfur, yellow

Figure 7. Room-temperature conductivity ranges of PPy, polyacetylene, and other materials.

Street et al.[3] disagreed with this proposal, favoring the linear chain structure shown in Figure 1a. It remains to be established whether the helical chains observed in the thin films also occur in thick films of PPy since Kiani et al.[109] have noted that the X-ray diffractograms, obtained from thick films of PPyPTS, do not exhibit all the characteristics expected for a helical polymer structure. Thus while the structure of some PPy thin films has been determined, the structure of thick films is not yet fully understood. However, it appears reasonable to assume, for the present, that thick films of PPy generally comprise of linear chains of pyrrole rings, with alternate rings rotated by 180°. This assumption then raises the prospect of a change in the growth mechanism (as the film thickness increases) from one which initially favors the formation of helical chains to one where the formation of linear polymer chains is dominant.

Polarons, Bipolarons, and Charge Transport in PPy

The room-temperature conductivities of several materials, as well as those of PPy and polyacetylene, are shown in Figure 7. It can be seen that reduced PPy is poorly conducting. The conductivity values for oxidized PPy are generally comparable to that of silicon.

The electrical conductivity of a material is proportional to the product of the concentration of charge carriers (electrons, holes, and ions) and their mobilities.[110] The concentration of charge carriers in PPy may be altered by changing the extent of oxidation. Thus, electrochemically reduced PPy contains few charge carriers. The carrier mobility may be thought of as a measure of the ease with which the charge carriers move through the material, and it is sensitive to the level of structural order present. Structural and chemical defects within PPy reduce the level of structural order present compared to that in an ideal "defect-free" material. Thus defects decrease the conductivity through a decrease in mobility. In this context, it is interesting to note that the theoretical conductivity of perfectly aligned defect-free polyacetylene[5] is believed to be greater than 10^6 S/cm.

Charge transport in PPy is made up of two components;[111] intrachain charge transport, which occurs along the polymer chains and, in a system such as

PPyPTS, requires little energy, and interchain charge transport which involves the hopping of the charge to neighboring chains, a process which requires considerably more energy. Thus the total resistivity (which is the reciprocal of the conductivity) is the sum of the resistivity due to interchain transport and that due to intrachain charge transport. The total resistivity of PPy is usually dominated by the interchain component.

Variable-temperature conductivity measurements provide important information about the charge carriers in a material and allow metallic and semiconducting behavior to be distinguished. For PPy films which are not highly conducting (i.e., with a room-temperature conductivity of less than approximately 100 S/cm), the temperature dependence of the conductivity usually follows[53,111−114] that predicted by the Mott variable range hopping model below room temperature (i.e., ln $\sigma \propto T^{-1/n}$, where σ is the conductivity and $n = 4$ for three-dimensional hopping[115]). However, other models have been shown to give more satisfactory fits for data obtained from highly conducting polypyrrole films.[116] The Mott variable range hopping model was derived for amorphous semiconductors and considers the movement of charge carriers between localized states which have energies comparable to the Fermi energy. The conduction process is thermally assisted (via phonons), and the charge carriers hop along a path such that the activation energy required to reach the next site is a minimum. A major problem with the application of this model to PPy is that the density-of-states values deduced[53,117] have often exceeded the upper limit of 0.03 states eV^{-1} monomer^{-1} deduced from the early EPR susceptibility measurements.[118] (Kohlman et al.[113] have recently reported values of 0.2 and 0.8 states eV^{-1} monomer^{-1} for PPyPTS and PPyPF$_6$, respectively). This discrepancy has been attributed to the fact that the Mott variable range hopping model does not consider intrachain charge transport.[117] Shen et al.[117] extended the model to include an intrachain charge-transport contribution and obtained density of states values of 1×10^{-3} and 4.8×10^{-5} states eV^{-1} monomer^{-1} for PPyClO$_4$ and PPySO$_4$ respectively.

The conductivity of PPy is influenced by a number of experimental variables. Satoh et al.[119] found that, for PPyPTS, an applied potential of 0.6V (versus the SCE) gave the highest conductivity and that materials with high conductivities were obtained using solutions containing high electrolyte concentrations (i.e., concentrations of NaPTS greater than 0.80 M). The effect of monomer concentration on the conductivity of PPy was recently examined by Stankovic et al.[36] They found that films with optimum conductivity were produced only when a pyrrole concentration of greater than 0.3 M was present in the growth solution. The concentration of

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water in the growth solution has been found to affect significantly the conductivity of PPy prepared using acetonitrile and propylene carbonate.[36,37] Omastová et al.[37] suggested that the optimum concentration of water corresponded to about 1 wt %. Several workers have examined the influence of the preparation temperature, and it is usually the case[55,105,120] that improved conductivities are obtained at temperatures below about 10 °C. This is probably due to the generation of fewer chemical and structural defects at lower temperature. Yamaura et al.[121] have established that the incorporation of large counteranions into PPy decreases its conductivity. These workers suggested that large counteranions increased the separation of the PPy chains, thereby presenting a greater obstacle to interchain charge transport.

The influence of the basicity of the incorporated counteranion on the conductivity of PPy has been studied by Kuwabata et al.[122] and Zotti et al.[123] The former workers examined PPy containing a series of substituted carboxylate counteranions and found that the conductivity was a function of the pK_a of the parent acid of the counteranion. It was proposed that the electrostatic attraction between the counteranion and the positive charges of the polymer chain was strongest for basic counteranions; the latter obstructing charge transport and thus decreasing the conductivity. A related, rather elegant study by Zotti et al.[123] showed that various counteranions could be substituted into PPyPTS films by means of counteranion exchange. This method has the advantage of preserving the original structure and morphology of the polymer moiety and enables the effect of the substituted counteranion on the conductivity to be clearly determined. (The ability of PPy films to exchange counteranions has also been studied by Yamaura et al.[124] and Schlenoff et al.[125]) Zotti et al. found that highly basic counteranions (e.g., OH⁻) caused the greatest decrease in the conductivity[123] on account of their large energetic obstacle to charge transport and electrostatic pinning of the positive charge carriers in the polymer. The above work clearly established that the basicity of the incorporated counteranion strongly influences the conductivity of PPy.

Charge transport within PPyPTS has generally been considered to be anisotropic in nature. This view originated from measurements which showed that the conductivity parallel to the film plane was much greater than that normal to the film plane.[105] Measurements normal to the film plane were made by means of the two-probe method. Recent work by Kiani et al.[126] has shown that the conductivity of PPyPTS is isotropic even though the structure is anisotropic. Data obtained from the two-probe method were found to be dominated by contact resistances and therefore considered unreliable. The existence of an *isotropic* conductivity within a structurally anisotropic material was ascribed to a short effective chain length due to defects and structural
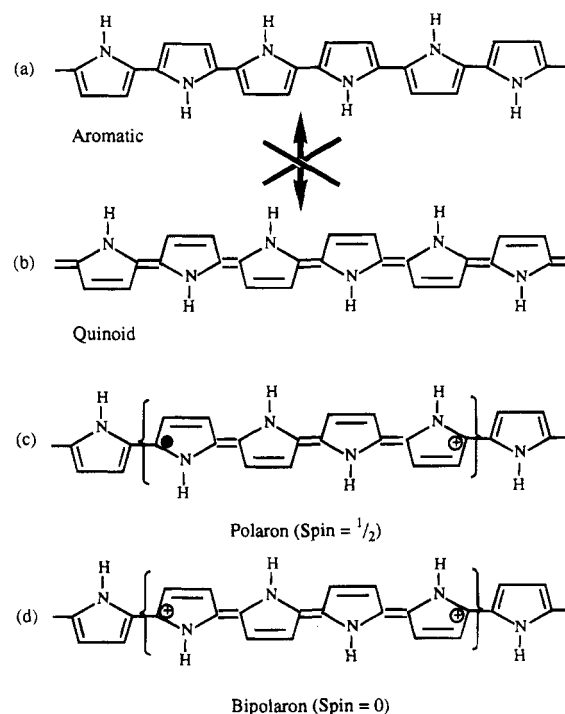

Figure 8. Structures of the resonance forms of PPy (a and b) as well as a polaron (c) and bipolaron (d). The charges depicted are delocalized over the whole region of the polaron or bipolaron.

disorder within the plane of the film. These factors greatly decreased the conjugation length and hence the contribution of intrachain charge transport to the overall conductivity parallel to the film plane. Consequently, interchain charge transport was dominant in all directions, and the conductivity was isotropic.

The nature of the charge carriers within PPy has attracted considerable interest. It was determined early that they were "spinless" and had a positive sign.[127,128] Thus, the charge carriers were not unpaired electrons. The charge carriers were subsequently identified as a new entity, called "bipolarons" (see below). The resonance structures of PPy (shown in Figure 8a,b) are not energetically equivalent. The energy of the quinoid structure has been calculated to exceed that of the aromatic form by 0.4 eV per ring.[129] Thus, PPy possesses a nondegenerate ground state. Upon extraction of negative charge from a neutral segment of chain (i.e., via partial oxidation), a local deformation to the quinoid structure is favored because this structure has a lower ionization potential than the aromatic form.[129] The spatial extent of the geometric modification is limited, being determined in the first instance by a balance between the energy gained from the decrease in the ionization energy (upon formation of the quinoid structure) and the local increase in the $\pi + \sigma$ energy.[129] This energy balance causes the positive charge and unpaired electron to have limited separation and move in unison. In combination with the quinoid structure, the positive charge and the unpaired spin are referred to as a "polaron" and may be considered as a radical cation. The structure of a polaron is shown in Figure 8c. The term

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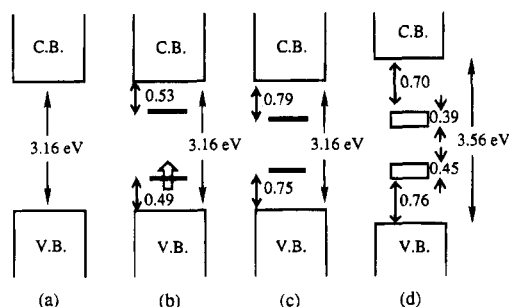(129) Brédas, J. L.; Themans, B.; Andre, J. M.; Chance, R. R.; Silbey, R. *Synth. Met.* **1984**, *9*, 265.

Reviews

Chem. Mater., Vol. 7, No. 6, 1995 1091

Figure 9. Electronic energy diagrams for PPy at various extents of oxidation. The band diagram for the neutral polymer is shown in (a). The extent of oxidation of PPy increases from (a) to (d). Polaron and bipolaron levels are shown in (b) and (c) respectively. In the heavily oxidized polymer, (d), the bipolaron levels have formed bands. C.B. and V.B. are labels for the conduction and valence bands respectively. Data taken from ref 131.

"polaron" has been borrowed from solid-state physics, where it refers to an electron and its local electrostatically induced lattice deformation.[130] However, a polaron in solid-state physics is not the same as a polaron in PPy because the latter is one-dimensional and involves a conjugated π-system. Electronic energy diagrams for PPy at various stages of oxidation appear in Figure 9. Formation of a polaron induces two states within the bandgap, which have bonding and antibonding character (Figure 9b). The unpaired electron (represented by the large arrow in Figure 9b) occupies the bonding state and the polaron has a spin of one-half ($S = \frac{1}{2}$).

When another electron is removed from a PPy chain that already contains a polaron (i.e., upon additional oxidation), there are two possible outcomes; another polaron may be generated on a different segment of the chain, or the existing polaron may be ionized to form a bipolaron. Theoretical calculations have suggested that the latter process is favored energetically.[131] However, this conclusion has been challenged.[132] Nevertheless, it appears certain that bipolarons play an important role in the charge transport within PPy. The structure of a bipolaron (which is a dication) is shown in Figure 8d. The positive charges move in a unified manner, achieved by a rearrangement of the double and single bonds. The modifications of the bond lengths associated with the bipolarons are larger than those associated with the polaron, and thus the bipolaron states lie further from the band edges[129] (Figure 9c). The lower energy bipolaron state is empty, and so the species has a spin of zero ($S = 0$). As more bipolarons are generated (through additional oxidation), the energies of the species overlap and bipolaron bands appear within the gap. The diagram shown in Figure 9d corresponds to about 33 mol % doping, close to the upper limit normally found in electrochemically oxidized PPy. Theoretical calculations have indicated that, in contrast to polyacetylene, the bandgap of PPy does not close upon 100% doping.[133] Consequently, theory suggests that it is not possible for PPy to exhibit metallic conductivity (i.e., a negative temperature coefficient of conductivity). However, it is

noted that the latter behavior has, in fact, been reported recently[114,134] for PPyPF$_6$ below about 20 K.

In addition to the intrachain bipolarons discussed above, it has recently been proposed[135] that polarons on adjacent PPy chains undergo efficient transverse coupling to yield interchain "transverse bipolarons". These weakly bound bipolarons help to reconcile the low spin densities reported for PPy (e.g., 1 spin/1000 monomers[135]) with the expectation of a much higher polaron concentration. The proportion of the total charge that is carried by transverse bipolarons remains to be determined. Only intrachain bipolarons are considered in the discussion that follows.

The precise conjugation lengths of the polaron and bipolaron remain unresolved. Early theoretical work suggested four pyrrole units.[131] However, Christensen et al.[136] recently suggested that the polaron extends over 12 monomer units. It is likely that chemical defects have a strong influence on the conjugation lengths, which may therefore depend sensitively on the preparation conditions. Thus well-defined defect-free pyrrole oligomers may provide a reliable estimate of the maximum number of pyrrole units over which polarons and bipolarons extend in electropolymerized PPy. Zerbi et al.[10] have recently reported the delocalization limit of pristine unsubstituted oligopyrroles as 7−9 pyrrole units.

There is considerable uncertainty surrounding the processes involved in the hopping of bipolarons from one chain to another. Presumably a bipolaron either hops as a unit, or dissociates into two polarons prior to hopping. The former process appears to have some theoretical support.[129]

Optical Spectral Studies on PPy Films

Street et al.[17] noted that the optical spectra of both oxidized and reduced PPy were sensitive to oxygen. Yakushi et al.[137] subsequently recorded the spectra of PPyClO$_4$ at various stages of reduction to neutral PPy. A strong absorption observed at 2.7 eV for the fully oxidized polymer was ascribed to a $\pi-\pi^*$ transition. However, this absorption was later attributed to a transition from the valence band to the antibonding bipolaron band (see below).

The spectra obtained by Yakushi et al.[137] were reinterpreted a year later by Brédas et al.[131] In the latter work, the theoretical energies for the transitions involving the polaron and bipolaron states were calculated. The spectrum of the fully reduced sample was dominated by the $\pi-\pi^*$ transition, which occurred at 3.2 eV. Three low-energy absorptions (at 0.7, 1.4, and 2.1 eV) were also apparent in the spectra at low doping levels and were attributed to transitions involving the polaron states.[131] The absorption previously observed in the spectra at 1.4 eV vanished upon additional doping. Brédas et al.[131] attributed this observation to the formation of bipolarons, since the bonding bipolaron state is unoccupied and no optical transitions are possible. The bipolaron states broadened upon ad-

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ditional doping, forming bands which produced two intense absorptions in the spectrum (at 1.0 and 2.7 eV).[131] The maximum due to the $\pi-\pi^*$ transition is weak in the fully oxidized polymer and occurred at higher energy. The overall agreement between the number, and energies, of the transitions predicted by the theoretical model and those observed in the spectra[131] supported the existence of polarons and bipolarons within PPy.

Yakushi et al.[138] subsequently performed a similar study on PBDMPyClO4. The spectra presented were similar to those obtained earlier for PPyClO4, but the absorption at 1.4 eV was absent. This absence was attributed to the greater extent of order believed to be present in PBDMPyClO4, which favored the conversion of polarons to bipolarons. The presence of the methyl groups in the β positions of pyrrole prevents the formation of defects involving $\alpha-\beta$ coupling.

Skaarup et al.[139] recently reexamined the optical spectra of electrochemically reduced PPyClO4. Interestingly, the spectra of their electrochemically reduced "pure" PPy films did not contain the feature noted by Brédas et al.[131] at 1.4 eV, indicating that polarons were not present in their reduced films. It was argued that the presence of polarons was determined by the conjugation length of the polymer chains, which was in turn dependent on the level of impurities (or defects) present. According to Skaarup et al.,[139] short conjugation lengths favored the formation of polarons. It was suggested that the level of polarons present within PPy was a function of the preparation conditions and polarons were considered to not be an intrinsic feature of PPy.

Well-defined oligopyrroles have been the subject of UV–visible spectroscopic studies by Meijer et al.[8] and Zotti et al.[9] Both sets of authors reported that the absorption maximum corresponding to the $\pi-\pi^*$ transition underwent a bathochromic shift with increasing oligomer length. Zotti et al.[9] deduced that an infinite defect-free chain of PPy would exhibit a $\pi-\pi^*$ transition of 2.81 eV. Defects in the chain decrease the extent of delocalization and increase the transition energy. Thus the value of 2.81 eV serves as a benchmark for the quality of PPy films (when examined in the reduced state).

Kuwabata et al.[19] examined the UV–visible spectra of PPy containing aromatic counteranions with different numbers of sulfonate groups and found that the energy of the bipolaron absorption increased as the number of sulfonate groups on the counteranion increased. Thus an increase in the negative charge of the counteranion caused a decrease of the conjugation length of the bipolarons in the polymer chain.

Only the absorption bands due to the polymer moiety were apparent in the spectra discussed above. This is a common (but not universal) feature of the published spectra of PPy and is due to the strongly absorbing nature of the polymer moiety. Absorption bands due to the counteranion are observed only when this species has a high molar extinction coefficient. The UV–visible spectrum of PPyCoPcTs (and PPyFePcTs) exhibited absorption bands[40] due to the phthalocyanine moiety

(which has a molar extinction coefficient[140] of the order of 10^5 M^{-1} cm^{-1}). This enabled information about the counteranion to be obtained; the presence of a band characteristic of aggregated CoPcTs^{4-} showed that some of the counteranions were aggregated within PPyCoPcTs.

EPR Investigations of PPy

The radical species located on the PPy chains have been the subject of a number of EPR investigations. Bolto et al.[141] first examined PPy in 1963 by means of EPR spectroscopy. A sharp resonance was observed in the $g = 2$ region, its line width being sensitive to oxygen. This sensitivity was attributed to the formation of a charge-transfer complex between oxygen and PPy. Twenty years later, Scott et al.[127] investigated the effect of oxygen on electrochemically reduced PPy by means of simultaneous EPR and conductivity measurements. The changes in the conductivity and spin intensity were found to be largely unrelated. It was concluded that the EPR active paramagnetic species were not the charge carrying species in PPy. The charge carriers were identified as spinless bipolarons. From the g values and line widths of the EPR signals (2.0025–2.0028 and 0.2–3.0 G respectively), Scott et al.[127] concluded that the paramagnetic species responsible for the EPR signal in PPy were delocalized π-radicals and resided in the π-conjugated system.

In addition to the early report of Bolto et al.,[141] several other workers reported that the EPR signal of PPy was sensitive to oxygen and air.[17,104,142,143] Mitchell et al.[104] noted that the line width of PPyPTS decreased by 25% when the spectrum was recorded under high vacuum. The broadening of the signal in the presence of air was attributed to an interaction between the free radical sites and the oxygen diradical. Mitchell et al.[104] attributed the EPR signal to paramagnetic species arising mainly from chemical defects.

Genoud et al.[144] conducted an in situ investigation of the changes in the spin intensity of PPy upon electrochemical charge injection. They found a correlation between the concentration of the paramagnetic species and the charge injected during the doping process. In contrast to the work of Brédas et al.,[131] it was concluded that, at low doping levels, the probability of bipolaron formation was low.[144] The paramagnetic species in PPy were attributed to polarons and not accidental defects. It was suggested that both polarons and bipolarons coexisted within PPy. Zhong et al.[145] conducted an in situ investigation of the electrochemical redox properties of PPy in aqueous solutions by means of EPR and Raman spectroscopy. It was found that the polaron was the stable intermediate species between the fully oxidized and reduced states of PPy. In a related study, a simultaneous EPR and ac impedance investigation of PPy was performed by Waller et al.[146] They observed

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Reviews

Chem. Mater., Vol. 7, No. 6, 1995 1093

a correlation between the conductivity and polaron concentration at low doping levels and concluded that both polarons and bipolarons contributed to the charge transport within PPy and that the notion of spinless conductivity was invalid for this material.

The work referred to above has generally shown that polarons contribute to the EPR signal of partially oxidized PPy. There is also evidence that neutral π-radicals are responsible for the EPR signal of electrochemically reduced PPy.[127] For a given sample, the proportions of the signal due to neutral π-radicals and polarons probably depend on the preparation conditions (which govern the extent of defects) and the extent of oxidation (which influences the polaron concentration).

Only a few groups have reported EPR spectra of PPy containing transition-metal complexes,[65,147,148] and our own work provides the only EPR spectra in which the signal of a paramagnetic metal ion is observed.[40,41,53,149] In the spectra of PPy prepared using $FeCl_3$ and $Fe(CN)_6^{3-}$, the radical signals originating from the PPy moiety are usually weak.[65,147,148] Han et al.[148] proposed that the weak signal intensity of $PPy\{Fe(CN)_6^{z-}\}$ (where $z = 3$ and/or 4) was due to a spiralled PPy structure in which the counteranions promoted the formation of bipolarons. An alternative explanation is that paramagnetic $Fe^{III}(CN)_6^{3-}$ species were present which caused a decrease in the signal intensity originating from the polymer moiety by means of spin–spin relaxation (see below). In a separate experiment, Han et al.[148] also noted that as the level of incorporation of $Co^{II}Cl_4^{2-}$ (which is also paramagnetic) into PPy increased, the EPR signal intensity originating from PPy diminished drastically.

The EPR spectra of PPyFeEDTA and of a composite counteranion material, PPyFe/CoEDTA, appear in Figure 10. Resonances are present in the spectra with g values of 2.0, 4.2, and 9.3. The radical species located on the PPy chains give rise to the signal at $g = 2.0$. The features at $g = 4.2$ and 9.3 are due to high-spin Fe(III) and confirm the presence of the paramagnetic transition-metal complex (FeEDTA$^-$) in each material. CoEDTA$^-$ contains low-spin Co(III), which is diamagnetic and therefore EPR silent. An interesting feature of the spectra (Figure 10) is that the intensity of the signal due to the radical species increases when the content of paramagnetic Fe(III) species decreases. From this, and related data,[40,41,149] a magnetic interaction has been proposed for PPy containing paramagnetic counteranions. This interaction is between the unpaired electrons of the polymer and those residing in the paramagnetic metal ion contained within the incorporated counteranion and has been ascribed to spin–spin relaxation.[149]

Mössbauer Spectroscopic Investigations of PPy Films

Daroux et al.[150] reported what was probably the first Mössbauer spectrum of PPy and there have been several
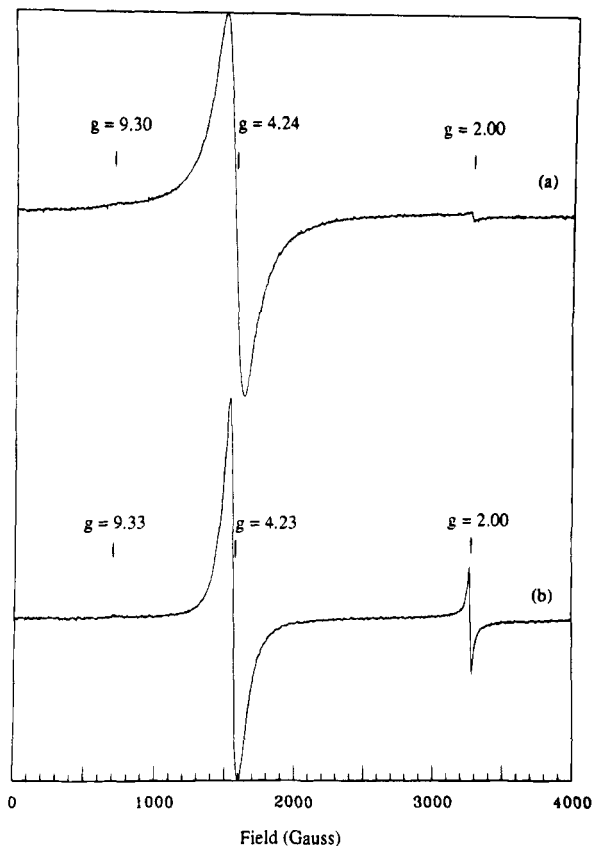

Figure 10. X-band EPR spectra of (a) PPyFeEDTA and (b) PPyFe/CoEDTA showing effective g values (Taken from ref 41). Spectra recorded at 100 K.

since, most of which have been limited to PPy containing the Mössbauer active ions $FeCl_4^-$, $Fe(CN)_6^{4-}$, $SnCl_5^-$, and $SbCl_6^-$. The majority of these studies have been carried out by a group centered at the Technical University of Warsaw.[65,151-155]

Several conducting polymers (including PPy, poly(1-methylpyrrole), polyacetylene, and poly(p-phenylene)) containing $FeCl_4^-$ have been prepared, and their Mössbauer spectra recorded.[152,153] It has been reported that the quadrupole splitting value is highest for $FeCl_4^-$ incorporated into PPy,[152,153] and this was attributed to a large distortion of the counteranion within the PPy matrix. Budrowski et al.[153] ascribed this distortion to hydrogen bonding between the chlorine atoms and the hydrogen atom located at the 1-position of the pyrrole ring. These workers also examined the effect of aging on the Mössbauer spectrum, and found that the quadrupole splitting value of the Fe(III) species decreased with exposure time. It was suggested that water molecules, absorbed from the atmosphere, decreased the extent of hydrogen bonding and counteranion distortion. In addition, it was proposed that some of the $Fe^{III}Cl_4^-$ species were converted to hydrated $Fe^{II}Cl_2$ upon aging.

It has been reported that PPy containing $FeCl_4^-$ and $SnCl_5^-$ does not exhibit resonant absorption at room temperature.[154,155] This is because the Mössbauer lat-

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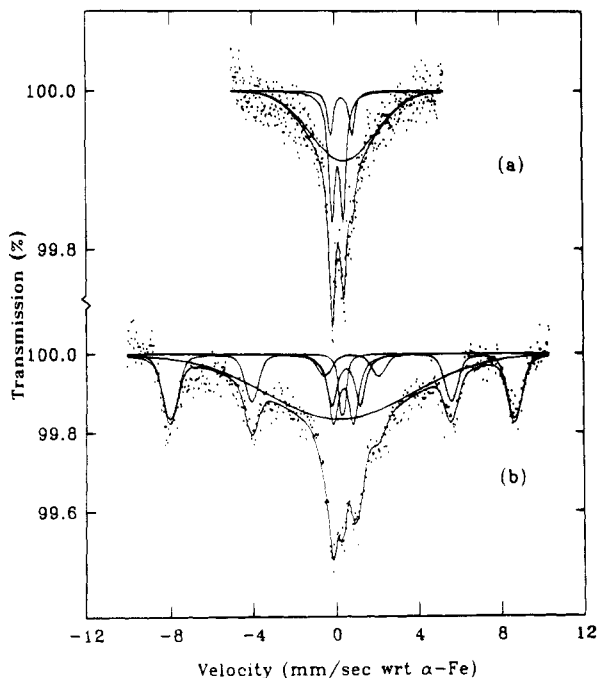
1094 *Chem. Mater., Vol. 7, No. 6, 1995*

Reviews

Figure 11. Mössbauer spectra of PPyFeEDTA obtained in zero applied field at (a) room temperature and (b) 4.2 K. Spectra calibrated using α-iron at room temperature (for details of subspectra see ref 41).

tice temperatures of PPy{FeCl$_4^-$} and PPy{SnCl$_5^-$} are much lower than room temperature (125 and 105 K, respectively[151]). These low values have been attributed to a "loose" bonding between the polymer chains and the inserted counteranions.[155] Presumably the hydrogen bonding mentioned above is insufficient to prevent the FeCl$_4^-$ counteranions from undergoing large vibrations within the polymer matrix at room temperature.

It has recently been shown that resonant absorption at room temperature is sometimes present in PPy containing Mössbauer active nuclei. The Mössbauer spectra of PPyFeEDTA recorded at room temperature and 4.2 K appear in Figure 11. These spectra have been discussed in detail elsewhere.[41] The spectrum of PPyFeEDTA clearly exhibits resonant absorption at room temperature (Figure 11a). Similarly, the spectrum of PPyFePcTs has also been reported to exhibit resonant absorption at room temperature.[40] The iron nuclei are coordinated to relatively large chelates (cf. FeCl$_4^-$) in both of these materials. Large counteranions provide a more rigid molecular environment for the iron nuclei (when incorporated into PPy), with the result that the iron–chelate bonding then dominates over the weaker polymer–counteranion bonding. Therefore higher Mössbauer lattice temperatures result leading to resonant absorption at room temperature. Accordingly, resonant absorption at room temperature should also be observed for PPy containing other anionic iron macrocycles.

Mössbauer spectroscopy may also provide information concerning the distribution of counteranions within PPy. The low-temperature spectrum of PPyFeEDTA (Figure 11b) exhibits pronounced magnetic splitting with a well-defined sextet as well as a central region consisting of a nonmagnetic signal. The former originates in iron nuclei (and hence counteranions) that are well separated from each other, while the nonmagnetic signal shows that some of the iron nuclei are closely associated.

Thus Mössbauer spectroscopy has revealed that the FeEDTA$^-$ counteranions reside in both a dispersed and an aggregated state within PPyFeEDTA. Like EPR, it is also a technique capable of revealing fine details such as the presence of mixtures of electronically distinguishable counteranion environments or intrinsic contamination.

Conclusion

PPy has been and continues to be the subject of a considerable amount of research worldwide. It is clear that this material represents an important class of conducting organic polymer. However, as described above, uncertainties still persist concerning the structure and charge-transport mechanism within PPy.

It is clear from the above discussion that the structure of PPy is dependent on the nature of the incorporated counteranion. When prepared using aqueous solution, there is convincing evidence that anisotropic films are produced when the counteranion has a planar shape. However, there is also some evidence that the hydrophobic nature of the counteranions is important. Consequently the structure within thick films of PPy and the factors that determine it require more attention.

It is also clear that the conductivity of PPy is strongly influenced by the incorporated counteranion. This result is not surprising as the counteranions can interact electrostatically with the charge carriers. A secondary effect on carrier mobility arises from the counteranions' ability to influence the structure of the polymer. While the effect of the counteranion on the environmental stability of the conductivity of PPy has received some attention, more work is required if the full potential of this material is to be realized.

PPy films containing transition-metal complexes have received a modest amount of attention in the literature, and this area of research remains relatively unexplored. The work performed in our laboratory has shown that some of these counteranions yield materials with interesting spectroscopic properties, high conductivity, and improved environmental stability. These counteranions have enabled us to use novel spectroscopic techniques such as EPR and Mössbauer spectroscopy. These techniques have revealed, for instance, the presence of two distinct environments within PPyMPcTs and PPyMEDTA. It is suggested that the existence of isolated and aggregated counteranions is probably a general feature of PPy. In addition, there is strong evidence of a magnetic interaction within PPy films containing paramagnetic counteranions. Additional study of this effect using low-temperature EPR spectroscopy and variable-temperature magnetic susceptibility measurements is warranted. Such research may yield a detailed picture of the magnetic interactions between the various spin systems present. Thus there is an urgent need for new PPy–transition-metal complex systems to be prepared and for their physical and spectroscopic properties to be explored.