Physical and Spectroscopic Studies of Polypyrrole Films Containing Tetrasulfonated Metallophthalocyanine Counterions Prepared from Nonaqueous Solution

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A range of polypyrrole films containing tetrasulfonated metallophthalocyanines (PPyMPcTs, M = Co and Fe) as counterions, prepared electrochemically from propylene carbonate solution, have been characterized in detail. The room-temperature conductivity values (0.1–0.8 S/cm) are lower than those determined on the well known *p*-toluenesulfonate system, PPyPTS (20–80 S/cm), prepared here under similar conditions, and this is due, in part, to the difference in size of the counterions. The conductivity of PPyPTS, a form of polypyrrole normally regarded as environmentally stable, was shown to be sensitive toward atmospheric oxygen and water. The conductivity of PPyMPcTs films decreased even more rapidly due to destructive oxidation by oxygen plus the effects of water vapor. By using a competitively doped film PPyCoPcTs/PTS, it was shown that part of the conductivity decrease in PPyCoPcTs was actually reversible and associated with the uptake of water vapor. In attempting to discover the reasons for conductivity differences and stability differences in these films, it was found that the morphology of growth surfaces of PPyMPcTs (M = Co, Fe, and Ni), as viewed by scanning electron microscopy, was dependent on the nature of M. The morphology of the anode surface of PPyCoPcTs was also quite different from that normally reported for films of PPy. Spectroscopic techniques, some of which (EPR and Mössbauer) have been rarely used to probe the counterions of PPy, show subtle phenomena such as the presence of both aggregated and monomeric forms of CoPcTs within PPyCoPcTs, the monomeric form being strongly electrostatically coupled to the cationic polymer. Mössbauer effect studies on PPyFePcTs indicated the coexistence of a high-spin Fe(II) species as well as various spin states of Fe(III). Previous reports of this system have clearly underestimated its molecular complexity.

Introduction

The semiconducting properties of polypyrrole (PPy) were first recognized, in Australia, by McNeill et al. in 1963.[1] The importance of the "electrochemical approach" to polypyrrole synthesis was established by Diaz et al.[2] in 1979, and since then considerable interest has been shown in this class of conducting polymers. This is, in part, due to the possible applications of these materials, which include rechargeable batteries and electrochromic devices.[3] The counterions which have been frequently used to prepare polypyrrole are ClO_4^-, BF_4^-, and *p*-toluenesulfonate (PTS^-). However, recent work employing $Ni(CN)_4^{2-}$ has shown that high conductivity is not limited to polypyrrole prepared using the inorganic counterions mentioned above.[4]

In many of the spectroscopic techniques applied to the study of polypyrrole, such as infrared spectroscopy, the signal originating from the counterion is masked by that of the polymer.[5] A relatively unexplored approach is to incorporate a counterion which contains a paramagnetic metal ion which can then act as a spectroscopic probe for techniques such as electron paramagnetic resonance (EPR). In our earlier work, preliminary EPR spectra of polypyrrole containing tetrasulfonated metallophthalocyanines (PPyMPcTs, M = Cu and Co), prepared from aqueous solution, were reported.[6] The earliest reported study of polypyrrole containing a tetrasulfonated metallophthalocyanine is that of Bull et al.[7] on PPyFePcTs. Since then, some further work has been conducted on this class of polypyrrole.[8–14] With one exception,[8] all of these polymers were prepared from aqueous solutions. In an attempt to improve the physical properties of the polymer, we have prepared PPyMPcTs (M = Co, Fe, and Ni) from propylene carbonate solution. The principal aims of the present work were to: (1) Examine the factors that govern

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Table I. Atom Mole Ratios, Conductivities, and Preparation Conditions for Various Polypyrrole Films

polymer	no.	preparation conditions[a]	atom mole ratio[b]	mater balance, %	oxygen equiv[c]	oxidation state[d]	conductivity (S/cm)[e]
PPyPTS	1A	A	$(C_{4.00}H_{2.99}N_{1.00})(PTS)_{0.26}$	93.83	0.45	0.26	21–53
PPyPTS	1B	B	$(C_{4.00}H_{3.13}N_{0.95})(PTS)_{0.28}$	95.34	0.34	0.28	71–78
PPyPTS	1C	C	$(C_{4.00}H_{3.11}N_{1.00})(PTS)_{0.28}$	97.75	0.16	0.28	56–70
$PPyClO_4$	2	A	$(C_{4.00}H_{3.38}N_{0.86})(ClO_4)_{0.26}$	96.69	0.19	0.26	64–70
PPyCoPcTs	3	D	$(C_{4.00}H_{4.67}N_{0.96})(CoPcTs)_{0.094}$	87.91	1.28	0.38	0.084–0.12[f]
PPyFePcTs	4	D	$(C_{4.00}H_{4.05}N_{1.10})(FePcTs)_{0.093}$	83.71	1.79	0.37[g]	0.64–0.75[f]
PPyCoPcTs/PTS	5	E	$(C_{4.00}H_{3.07}N_{1.10})(CoPcTs)_{0.032}(PTS)_{0.27}$	94.74	0.49	0.40	28–35
PPyFePcTs/PTS	6	E					21–22

[a] A, 0.02 M TEAPTS (1A) or $TEAClO_4$ (2). B, 0.15 M TEAPTS. C, 0.15 M TEAPTS, temp = 23 °C. D, 5 mM $CoPcTsTBA_4$ (3) or $FePcTsTBA_4$ (4). E, 2.5 mM $CoPcTsTBA_4$ (5) or $FePcTsTBA_4$ (6) and 0.01 M TEAPTS. [b] Values normalized to carbon. [c] Oxygen equivalent of missing weight. [d] From C/S or C/Cl ratios. [e] Measured at room temperature after 24 h of air exposure. [f] Measured on samples not exposed to air. [g] Based on exclusive presence of Fe(II).

the stability of the conductivity of PPyPTS and PPyMPcTs in order to gain a better understanding of this property. Techniques such as elemental analysis, scanning electron microscopy, and X-ray diffraction were employed to characterize the polymers. In this regard it was hoped to identify some general conditions for the synthesis of PPy films with improved stability. The results are described in sections A–D. (2) Further explore the counterion environment of PPyCoPcTs using EPR and UV–visible spectroscopy. The results are described in sections E and F. (3) Use EPR, UV–visible, and Mössbauer spectroscopy to study the counterion environment and nature of FePcTs in PPyFePcTs. The results are described in sections E–G.

Experimental Section

Reagents. Pyrrole and 1-methylpyrrole (Aldrich) were distilled prior to use and stored at −18 °C under nitrogen in the absence of light. Propylene carbonate (Aldrich) was used as received and water was "milli-Q" quality. Tetraethylammonium *p*-toluenesulfonate (TEAPTS) was also used as received (Aldrich). $CoPcTsNa_4$, $FePcTsNa_3$, and $NiPcTsNa_4$ were prepared according to a modification of the method of Weber and Busch.[15] The tetrabutylammonium salts ($MPcTsTBA_4$, M = Co, Fe, and Ni) were synthesized by treating the appropriate sodium salt with tetrabutylammonium hydroxide. Dichloromethane was then used to extract the $MPcTsTBA_4$ from the aqueous solution. After drying the dichloromethane solution, the solid was precipitated by the addition of anhydrous diethyl ether. The solid was dried, *in vacuo*, over P_2O_5 overnight. It should be noted that the formulations $FePcTsNa_3$ and $FePcTsTBA_4$ do not explicitly include any axial ligands which are invariably present in Fe^{III} phthalocyanines. In the present compounds water, or hydroxide, ν(OH) bands were observed in the infrared spectra. The magnetic moments of these Fe^{III} compounds were in the low-spin d^5 region (1.9–2.5 μ_B), again suggestive of axial ligation.

Polymer Synthesis. Polymer films were grown on gold-plated stainless steel electrodes in a two-compartment cell in a controlled temperature bath (±1 °C). Unless stated to the contrary, all polymerizations were conducted at 0 °C. A constant potential (0.96 V unless otherwise stated) was maintained using either a Princeton Applied Research 174A or Bioanalytical Systems SP-2 potentiostat. The reference electrode (Ag/3 M NaCl(aq)) was separated from the bulk electrolyte by a sintered glass-frit arrangement. The half-wave potential of the ferrocinium-ferrocene couple (measured in 0.1 M tetrabutylammonium perchlorate/propylene carbonate) was 0.43 V relative to the above reference electrode, compared to 0.40 V relative to a saturated SCE. The charge passed during the film growth was monitored using a home-made coulomb meter, and film thicknesses were in the range 70–350 μm.

PPyMPcTs and PNMPyMPcTs (PNMPy represents poly(1-methylpyrrole)) were prepared from 1 vol % H_2O–propylene carbonate solutions containing 0.10 M pyrrole (or 1-methylpyrrole) and 5 mM of the appropriate $MPcTsTBA_4$ (M = Co, Fe, and Ni). Further details are given in Table I. The electrolyte was purged with nitrogen prior to polymerization and a nitrogen atmosphere was maintained over the solution throughout the synthesis. The films, which were easily removed from the electrode, were rinsed thoroughly with distilled water followed by propylene carbonate, and excess solvent was removed using fiberless tissue paper. Samples used for conductivity measurements were then subjected to dynamic vacuum at room temperature. Residual solvent was found to be completely removed by drying the films in dynamic vacuum at 120 °C for 24 h. PPyPTS, $PPyClO_4$, and PPyMPcTs/PTS (M = Co and Fe) were rinsed in a similar fashion to PPyMPcTs but were dried in dynamic vacuum at 120 °C for 24 h prior to further measurements. Prior to elemental analysis, all films were extracted with acetonitrile in a Soxhlet thimble, under nitrogen, for 24 h and subsequently dried in dynamic vacuum at 120 °C for the same period. The drying was performed immediately prior to analysis.

It was found that both PPyCoPcTs and PPyFePcTs were brittle in the dry "solvent-free" state, and it was only possible to measure their conductivities by allowing residual solvent to remain in the films (up to 60–70 wt %). Surprisingly, these films were found to have an unusual ability to retain large amounts of solvent within their structure and underwent significant shrinkage during solvent removal. It must be emphasized that only the conductivity data for PPyMPcTs (M = Co and Fe) and the Mössbauer data (PPyFePcTs) were obtained on polymers in this condition. All other data presented were obtained on dried films which were free of solvent.

Physical Methods. Elemental analysis was performed by the University of Otago microanalytical service (New Zealand) and Galbraith Laboratories (U.S.A.). Conductivity measurements were performed using a linear four-probe cell, which could be placed in an air-tight chamber. The conductivity ranges shown in Table I represent the minimum and maximum values obtained on four samples of each film for all of the polymers except 1A and 1B. In the case of 1A and 1B multiple preparations were undertaken, using identical conditions, and the range reflects the averages obtained for each batch. Scanning electron micrographs were obtained using a JEOL JSM-840A instrument operated at an accelerating voltage of 20 kV. X-ray diffraction studies were performed using Cu Kα radiation and a SCINTAG PAD(V) diffractometer. Reflection geometry was used exclusively. UV–visible measurements were made on thin films, grown on optically transparent indium–tin oxide electrodes, using a Shimadzu UV-265 spectrophotometer. EPR measurements (performed on films dried at 120 °C under dynamic vacuum for 24 h) were made using a Varian E12 spectrometer operating at X-band frequency (9.11 GHz). A specially constructed evacuable EPR tube enabled these measurements to be made under nitrogen where necessary. The Mössbauer spectra were obtained in the transmission mode using a ^{57}Co in Rh source. A cryostat enabled the temperature to be maintained at 4.2 K. All isomer shifts were calibrated against natural α-iron foil at room temperature. The curve fitting was performed using a least-squares procedure and employed Lorentzian line shapes.

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Results and Discussion

(A) Elemental Analysis. Elemental analysis of polypyrrole has frequently been complicated by the presence of surplus oxygen and hydrogen.[16,17] It is also apparent, from the literature, that the discrepancies between analysed and calculated values (based on the ideal C_4H_3N formula) generally increase when the molecular weight and complexity of the counterion increase.[18-20] Thus, the best analyses are frequently obtained for PPy containing simple inorganic anions such as BF_4^-, ClO_4^-, and PTS, although this is not always the case.[21] Table I shows the compositions, determined from the elemental analysis, for several of the polymers used in the present study. The extraction and drying procedures used ensured that the films contained negligible concentrations of residual electrolyte and solvent. However, examination of the data shows the presence of unidentified mass. Since electron microprobe examination showed the films to be chloride free, contamination from the reference electrode was excluded as the source of the unidentified mass; it was therefore probably an oxygen-containing species, as suggested by other authors,[17,18,22] and residual water.

Weight loss experiments performed in this laboratory and elsewhere[23] did not show any irreversible mass increase upon storage of PPyPTS in air for extended periods. It follows that any excess oxygen was incorporated during the electropolymerization. This is at first sight surprising, since a nitrogen atmosphere was maintained throughout the synthesis, and the solvent used contained only 1 vol % H_2O. However, a recent report has shown that PPy films grown from propylene carbonate solution, containing similar levels of water as those used here, were subject to chemical attack by the water to produce oxygen containing species.[24] Such a process could account for at least part of the unidentified mass in the present systems.

Salmon et al.[25] found excess hydrogen and residual oxygen in PPy films which had been prepared in acetonitrile–1% H_2O and dried at 110 °C. They attributed the excess to residual water not removed by the drying process. In the present case it is likely that a combination of electrochemically incorporated oxygen and residual water is present since almost all of the formulas indicate excess hydrogen. Some of the excess hydrogen may also be due to the presence of sp^3 hybridized C–H moieties and chain ends within the polymer.[16] The relatively high conductivities of the PPyPTS and $PPyClO_4$ films (see Table I) imply that not all of the excess oxygen is present in the form of carbonyl groups, because much lower conductivities than those reported in the present study would be expected. Therefore, it is likely that a significant portion of the electrochemically incorporated species are present in the form of covalently bound hydroxyl groups.[26]

The oxidation states of the pyrrole unit in the films containing PTS^- and ClO_4^- (films 1A–C and 2) are tightly grouped in the range of 0.26–0.28 and only slightly influenced by the preparative conditions. Surprisingly, the films containing CoPcTs and FePcTs (films 3 and 4) have higher oxidation states in the range 0.37–0.38. Similar values were reported for PPy containing tetrasulfonated metalloporphyrins.[27] The data show that, for the present polymers containing single counterions, factors other than molecular size determine the amount of counterion incorporated. It is noteworthy that PPyCoPcTs/PTS has the highest oxidation state of all the polymers studied and that the majority of the counterions present in the film are PTS. This is discussed further below.

(B.1) Conductivity of PPyMPcTs, PPyPTS, and $PPyClO_4$. The room-temperature conductivities obtained in the present study are shown in Table I. The conductivities of the PPyPTS and $PPyClO_4$ films (1 and 2) are comparable with those reported for similar polymers.[25,28] As mentioned in the Experimental Section, in order to measure the conductivities of PPyCoPcTs and PPyFePcTs (3 and 4), it was necessary to allow residual solvent to remain in the films. The conductivities of both were also found to be extremely sensitive toward atmospheric oxygen. The values quoted in the table were obtained on films which had been prepared and handled in the absence of oxygen, and are at the lower end of the range usually reported for PPyMPcTs when prepared from aqueous solutions.[6,9,13] Walton et al.[8] reported conductivities of 0.01–0.05 S/cm for their CuPcTs-rich PPy films prepared from acetonitrile and aqueous methanol solutions.

The conductivities of the PPyPTS/MPcTs films (5 and 6) lie in the range observed for PPyPTS prepared under similar conditions (i.e., film 1A). This is probably a result of the relatively low incorporation of MPcTs, as shown from the composition of film 5. This low incorporation is surprising, given that the electrolyte solution contained equal anionic concentrations of each species (bearing in mind that $M^{II}PcTs$ is formally a tetraanion). Walton et al.[8] observed a similar feature in their "competitively doped" $PPyClO_4$/CuPcTs films prepared from acetonitrile and suggested that this behavior was connected with solvation and solubility factors. However, in the present work the $MPcTsTBA_4$ complexes were freely soluble in propylene carbonate. A more probable explanation is that, in a competitive doping environment, smaller counterions more effectively compete for the available cationic sites of the growing polymer and are therefore preferentially incorporated.

For the PPyPTS films, both the conductivity data and the elemental data show only a slight dependence on the preparative conditions. In agreement with earlier studies[30] the films prepared using the higher TEAPTS electrolyte concentration (films 1B and 1C) had the highest conductivities. This is most likely the result of different morphological and structural factors.

When the conductivities of the single counterion films, prepared under similar conditions, are compared (e.g., 1A, 2, and 3), it can be seen that the conductivity decreases

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with increasing counterion size. A related result has been reported earlier[29] and is best explained as a barrier effect, i.e., the larger counterion presents a greater obstacle to interchain charge hopping and thus reduces the overall conductivity.

It is difficult to know with certainty why the conductivities of PPyMPcTs, noted here and elsewhere,[8,11] are an order of magnitude or more smaller than those of PPyPTS and $PPyClO_4$ when grown under similar conditions. A large number of factors can play a part in such differences and these can often be interrelated. The oxidation state of the pyrrole unit in the PPyMPcTs films (see Table I) is much higher than in the other two types, and presumably so also is the concentration of charge carriers (polarons and bipolarons). The much lower PPyMPcTs conductivity values presumably then reflect such factors as lower charge carrier mobilities and incorporation of residual propylene carbonate in the film. The use of PPyNiPcTs, which possessed reasonable mechanical properties in the solvent-free state, enabled an assessment of the latter effect to be made. It was observed that the conductivity of PPyNiPcTs fell by only 11% (i.e., from 0.056 to 0.050 S/cm) after an absorption of 33 wt % of propylene carbonate. From this, and the similarity between the conductivities of PPyMPcTs (M = Co and Fe) and the solvent-free version of PPyNiPcTs, it is evident that the low conductivities of PPyMPcTs compared to PPyPTS and $PPyClO_4$ cannot be attributed to residual propylene carbonate alone. It follows that the most prominent factor is the structural barrier effect described above and is due to the $MPcTs^{4-}$ counterion being larger than PTS^- and ClO_4^-.

(B.2) Effect of Air and Oxygen on the Conductivity of PPyPTS. Polypyrrole has been reported to be a stable polymer, i.e., the conductivity is unaffected by short-term exposure to air.[5,23] However, our previous work showed that the conductivity of PPyMPcTs (M = Cu, Co, and Ni), prepared from aqueous solution, rapidly decreased when the films were exposed to the atmosphere.[6] To examine this behavior in the absence of possible complications originating from the metallomacrocycle (see below), a detailed study of the effect of air and oxygen on the well-known PPyPTS system was undertaken. The polymer was prepared and handled under nitrogen using a glovebox. Figure 1 shows that exposure to dry oxygen results in an increase in conductivity, while exposure to air results in an initial decrease followed by a gradual recovery. A mass increase of approximately 3% was measured for an identical film when exposed to air, in agreement with the observations of Wynne et al.[23] By analogy with polyacetylene, the conductivity increase upon exposure to oxygen is attributed to the formation of a charge-transfer complex, possibly involving O_2^-.[31] The magnitude of the increase was dependent upon the film composition, the more highly oxidized films (e.g., 1B) showing smaller increases. Oxygen sensitivity of this type has been reported for electrochemically reduced PPy films[32] but to our knowledge has not been reported for "as made" electrochemically oxidized PPy.

The initial decrease in the conductivity of the film when exposed to air could be explained by the uptake of water vapor from the atmosphere. The gradual recovery is attributed to the formation of the charge-transfer complex with oxygen. It is likely that the polar water molecules are attracted to both the SO_3^- groups of the PTS counterion and the cationic polymer chain. Apart from increasing the separation of these components, it is plausible that a partial electron donation from the water molecule to the polymer occurs,[33] thereby lowering the oxidation state and conductivity of the latter.[34]

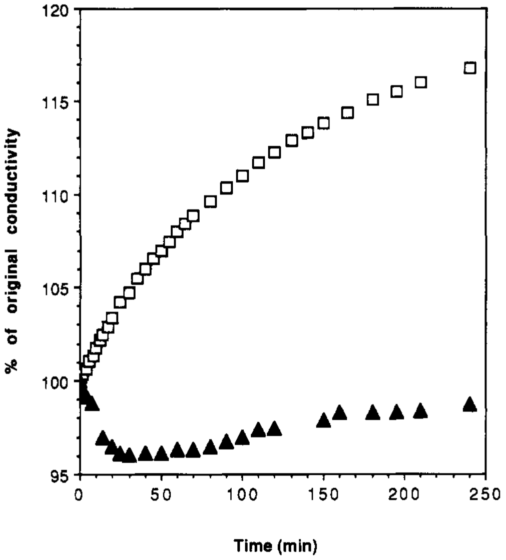

Figure 1. Effect of oxygen (□) and air (▲) on the conductivity of PPyPTS. Film prepared using method A from Table I.

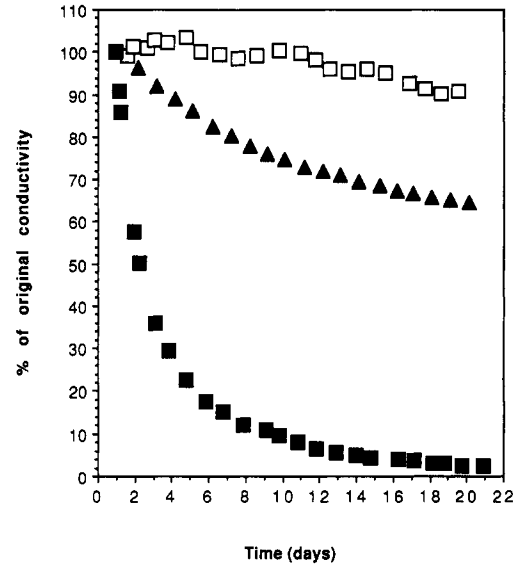

Figure 2. Conductivity versus time of exposure to laboratory air for PPyPTS (□), PPyCoPcTs/PTS (▲), and PPyCoPcTs (■). PPyPTS, PPyCoPcTs/PTS, and PPyCoPcTs prepared according to methods A, E, and D respectively (see Table I).

(B.3) Environmental Stability of the Conductivity of PPyMPcTs, PPyPTS/MPcTs, and PPyPTS. The variation of conductivity during the first three weeks of exposure to air of PPyPTS, PPyPTS/CoPcTs, and PPyCoPcTs is shown in Figure 2. The PPyPTS/CoPcTs film possessed good mechanical properties in the solvent-free

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(34) Separate experiments showed that exposure of PPyPTS to a H_2O/N_2 atmosphere caused a decrease in conductivity.

state which enabled the complete removal of solvent to be carried out prior to the experiment. At the end of the experiment the conductivity of PPyPTS was 91% of the initial value, while those of PPyCoPcTs/PTS and PPyCoPcTs were 65 and 2.5% respectively. Clearly the incorporation of CoPcTs into polypyrrole renders the conductivity of the film unstable to the laboratory environment, contrary to the findings of earlier reports.[9,10] Similar behavior was also observed for PPyFePcTs and PPyFePcTs/PTS. While this result is disappointing from an application viewpoint, it is also important since it shows that the counterion incorporated into polypyrrole directly influences the electrical stability of the polymer. If it can be ascertained what characteristics of the MPcTs counterion produce this lack of stability then the beginnings of criteria may be established for the selection of counterions that will enable improvements in the stability of the polymer to be achieved.

One possible explanation for the poor stability of PPy containing MPcTs (M = Co and Fe) is that the metallophthalocyanines catalyze the irreversible oxidation of the polymer radicals by oxygen. This idea is consistent with the observation that tetrasulfonated cobalt phthalocyanine is an effective catalyst for the autoxidation of thiols by molecular oxygen.[35,36] Further, the process is most efficient for CoPcTs bound in cationic polymers.[37] However, our earlier studies on PPyMPcTs (M = Cu and Ni)[6] showed that the conductivities of these polymers also decreased rapidly upon exposure to air. Since CuPcTs and NiPcTs would not axially bind oxygen (a necessary step in the proposed mechanism), it appears unlikely that a direct metallophthalocyanine-catalyzed oxidation of polypyrrole occurs. Separate experiments, on PPyMPcTs films exposed to dry oxygen, showed that oxygen was the major source of the conductivity decrease observed upon exposure to the atmosphere.

To investigate the reversibility of the conductivity decrease in PPyPTS/CoPcTs, the film was held at 120 °C at rotary pump pressure for 24 h, after ageing for 20 days at room temperature. The conductivity recovered approximately 30% of the total lost as a result of ageing, i.e., the conductivity was 75% of the initial value measured after 24 h of air exposure. Similar behavior was observed for PPyPTS/FePcTs, while PPyPTS consistently failed to show any recovery. EPR experiments conducted on PPyCoPcTs heated under similar conditions revealed the loss of axially coordinated water (see below). A possible explanation is that axially bound water increases the separation between MPcTs counterions and the polypyrrole chain and thereby increases the energy required for interchain hopping of the charge carriers. Such a process would be expected to be reversible. Therefore the conductivity decrease observed for polypyrrole films containing metallophthalocyanines consists of a reversible and an irreversible part. The former appears to involve water vapor, while the latter is the dominant effect and involves oxygen.

The results presented above suggest that it is the large size of the macrocycle itself that is responsible for the poor stability of PPy containing MPcTs. It follows that the incorporation of MPcTs into PPy leads to a structure in which the irreversible oxidation of the PPy chains is facilitated. The large size and rigidity of the counterion would be expected to produce spaces within the structure, through packing inconsistencies, which would provide avenues for chemical attack on unobstructed segments of chain.

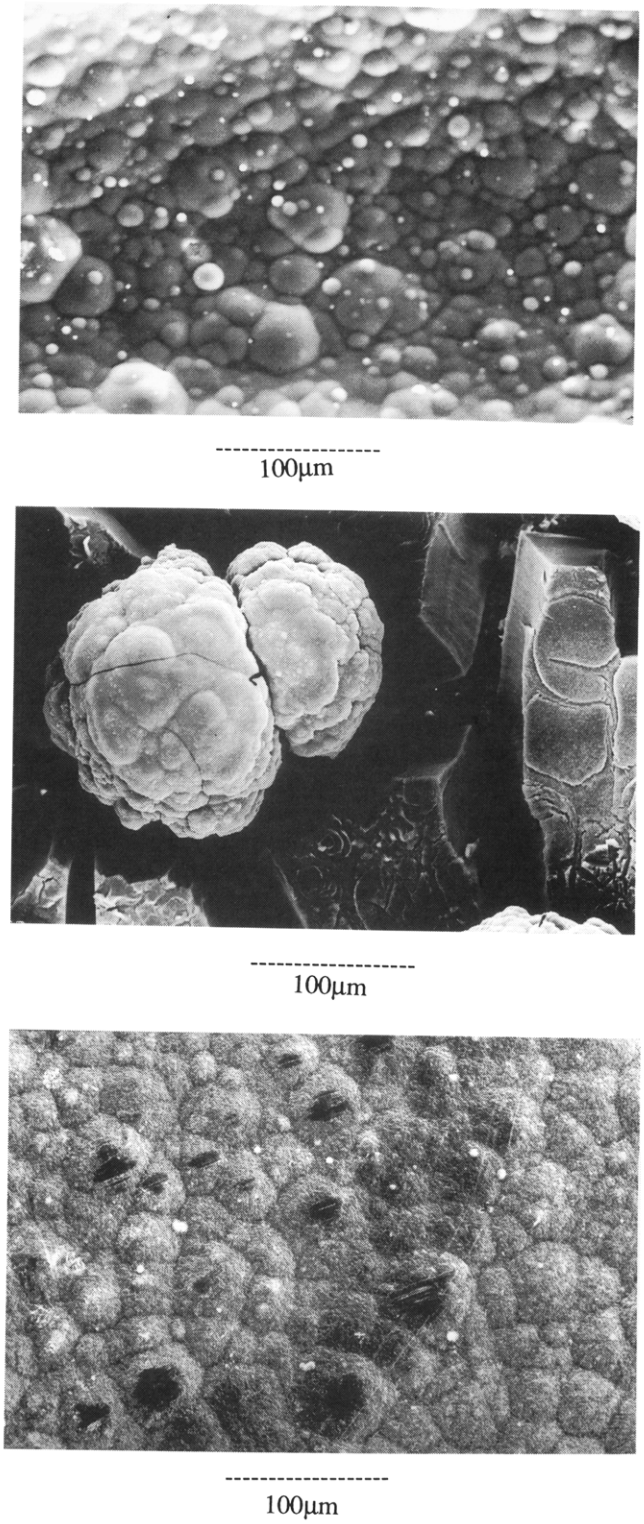

Figure 3. Scanning electron micrographs of the growth surfaces of (a, top) PPyCoPcTs, (b, middle) PPyFePcTs, and (c, bottom) PPyNiPcTs.

(C) Morphology. Scanning electron micrographs of the growth surfaces of PPyMPcTs (M = Co, Fe, and Ni) are shown in Figure 3. Examination of these surfaces

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reveals that the choice of metal has a substantial effect on the morphology. The growth surface of PPyCoPcTs consists of overlapping hemispheres, a feature that has frequently been observed for polypyrrole.[25,38] In contrast, the PPyFePcTs surface is mostly smooth, with occasional excrescences. The growth surface of PPyNiPcTs bears a resemblance to that of PPyCoPcTs, although the hemispheres appear more regular and fibrous in the former. These observations lead to the conclusion that the metal ion, in MPcTs, plays an important role in the growth of PPyMPcTs when prepared from propylene carbonate solution. To our knowledge a dependance of this type has not been reported previously.

The anode surface of PPy films (i.e., the surface of the film in contact with the anode) has frequently been reported as featureless. However, for PPyCoPcTs this is not the case (see Figure 4a). The morphology may be described as an "interconnected fibrillar array" and was reproducibly observed for PPyCoPcTs films when prepared according to the method given in the Experimental Section. The precise sizes and shapes observed depended on the preparation conditions. A micrograph of a section that had fortuitously fractured across the top of the fibrils suggests that they are hollow (Figure 4b). It is tempting to attribute this morphology to a specific interaction between CoPcTs and pyrrole; however, a similar but less regular morphology can be seen in the scanning electron micrographs of $PPyClO_4$ reported by Chiu et al.[39] An alternative explanation is that this morphology is a consequence of film shrinkage that occurs as a result of observation under the high vacuum of the scanning electron microscope. Further studies of the origin and possible applications of this unusual morphology are in progress.

A portion of the fracture surface of PPyCoPcTs is shown in Figure 4c. This surface suggests brittle fracture. The fine texture is not obscured by plastic flow. Apart from the "riblike" structure, which is only observed in PPyCoPcTs films, the micrograph also shows an area of more uniform texture. The former may be a manifestation of the fibrillar array structure observed on the surface. Alternatively, both types of structure could be a result of differences in crack propagation speeds during the fracture process.[40]

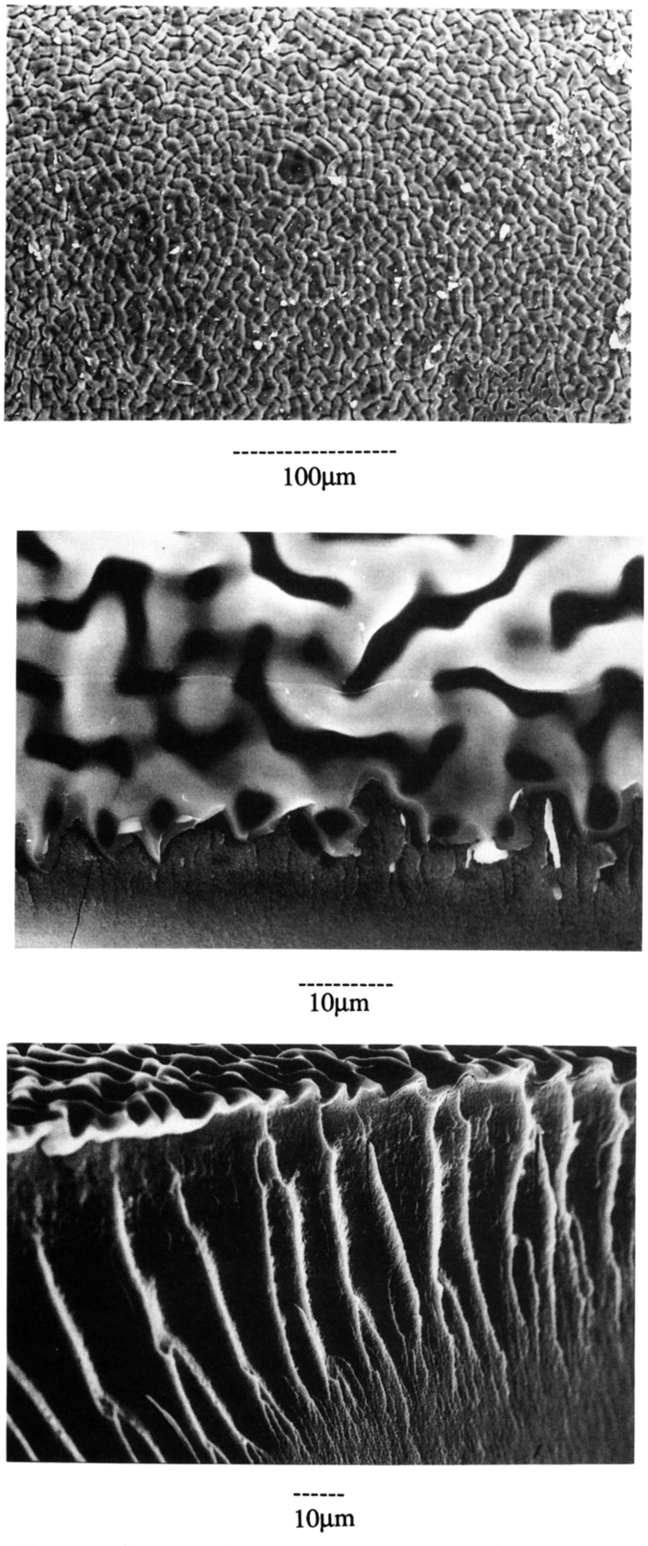

Figure 4. Scanning electron micrographs of PPyCoPcTs showing (a, top) anode surface, (b, middle) hollow ends of the fibrils, and (c, bottom) fracture surface obtained using liquid nitrogen.

(D) X-ray Diffraction. X-ray diffractograms of PPyPTS, PPyMPcTs (M = Co and Fe), and PNMPyCoPcTs are shown in Figure 5. Relevant tabulated data appear in Table II. Broad scattering maxima are present in all of the polypyrrole diffractograms, indicating that the underlying structures are largely amorphous. However, useful information can be extracted from the shapes and positions of the maxima. The diffractogram of PPyPTS (Figure 5a) shows maxima at $2\theta = 6°$ and 21.5° with a shoulder at $2\theta = 25°$. The low-angle maximum is attributed to scattering from PTS counterions,[23,41] while the shoulder at $2\theta = 25°$ originates from face-to-face pyrrole rings.[20,23] The origin of the maximum at $2\theta = 22.5°$ is less certain and is a subject of disagreement.[20,23,41,42] For PPyMPcTs, the diffractograms show a shoulder around $2\theta = 20°$ and a maximum located at $2\theta = 24°$. Thus, the diffractograms of both PPyPTS and PPyMPcTs consist of overlapping maxima in the $2\theta = 18–28°$ range and, although the relative intensities of these overlapping maxima differ, there is a similarity in their positions. Therefore the structures of the two materials (PPyPTS and PPyMPcTs) appear related on a molecular level. Since

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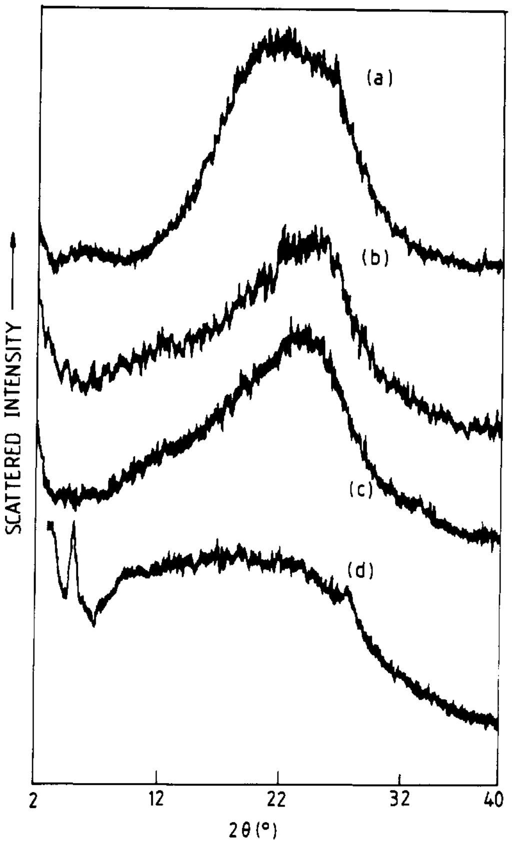

Figure 5. X-ray diffractograms of (a) PPyPTS (preparation A in Table I), (b) PPyFePcTs, (c) PPyCoPcTs, and (d) PNMPy-CoPcTs. Films were dried at 120 °C in dynamic vacuum for 24 h prior to measurement.

Table II. X-ray Diffraction Data[a]

polymer	2*θ*°	*d* (Å)[b]
PPyPTS[c]	6.0 br, w; 21.5 br, st; 25.0 sh, m	14.7, 4.1, 3.6
PPyCoPcTs	11.5 sh, w; 20.0 sh, w; 24.0 s, m	7.7, 4.4, 3.7
PPyFePcTs	11.5 sh, w; 20.0 sh, w; 24.0 s, m	7.7, 4.4, 3.7
PNMPyCoPcTs	5.2 s, m; 10.0 sh, w; 27.5 sh, w	17.0, 8.8, 3.2
$CoPcTsNa_4$	10.0 br, w; 27.5 s, st	8.8, 3.2
$CoPcTsTBA_4$	5.0 br, m; 9.5 s, st; 22.0 s, st	17.7, 9.3, 4.0

[a] st = strong, m = medium, w = weak, s = sharp, br = broad, and sh = shoulder. [b] Evaluated from Bragg equation. [c] Prepared according to method A (see Table I).

the diffractograms of PPyCoPcTs and PPyFePcTs are almost identical, it can be assumed that their structures are similar. The fact that the high-angle region of PPyMPcTs is reasonably well defined is consistent with the presence of a relatively ordered structure.[41] If this were not the case, broad ill-defined scattering maxima would be observed, as is the case for PNMPyCoPcTs (Figure 5d). The highly disordered structure in this polymer presumably originates from the incompatibility of a planar counterion and a twisted polymer chain.[43]

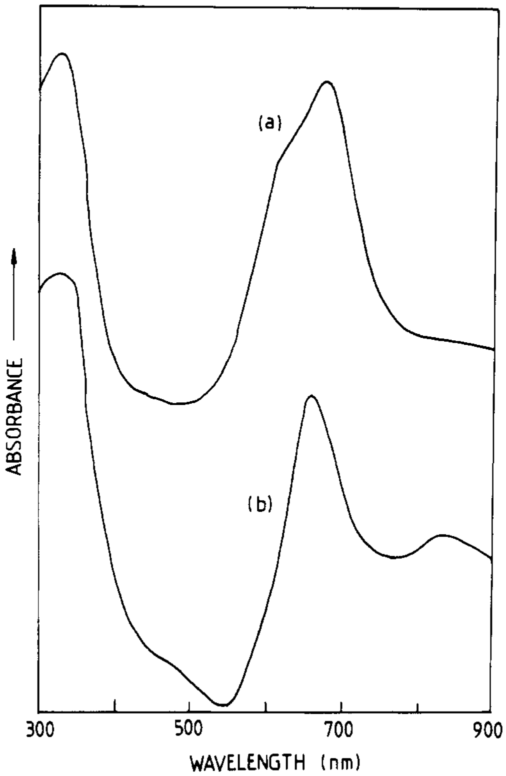

Figure 6. UV–visible spectra of (a) PPyCoPcTs and (b) PPyFePcTs.

Table III. UV–Visible Absorption Maxima (nm)[a]

$CoPcTsNa_4$[b]	321		570 (sh)	631	659	
PPyCoPcTs	330			630 (sh)	677	
PNMPyCoPcTs	326			630 (sh)	677	
$FePcTsNa_3$[b]	325		580 (sh)	631	664	
PPyFePcTs[c]	330	460 (w)	600 (sh)	659	839	
PNMPyFePcTs[d]	330		600 (sh)	659	684	880 (vw)

[a] sh = shoulder, w = weak, and vw = very weak. [b] Measured in water at a concentration of 2×10^{-5} M. [c] Prepared using an applied potential of 1.3 V. [d] Prepared using an applied potential of 1.2 V.

The positions of the maximum and shoulders in the PNMPyCoPcTs diffractogram coincide with some of the maxima found for $CoPcTsNa_4$ and $CoPcTsTBA_4$ (Table II). This is despite the fact that the polymer was continuously extracted with acetonitrile for 24 h prior to the experiment. These maxima most likely arise from aggregated CoPcTs, presumably located in environments similar to those in the sodium and tetrabutylammonium salts, and are absent in the diffractograms of PPyMPcTs. However, a weak broad shoulder at $2\theta = 11.5°$ in the latter is assigned to MPcTs, possibly in an aggregated form. This assignment is based on the proximity to the $2\theta = 10°$ maxima in the CoPcTs salts, and the presence of aggregated CoPcTs in PPyCoPcTs as shown by UV–visible and EPR studies (see below).

(E) UV–Visible Spectra. The UV–visible spectra of PPyMPcTs (M = Co and Fe) are shown in Figure 6. Tabulated data appear in Table III. The spectra of the films are dominated by the $\pi \rightarrow \pi^*$ transitions of the phthalocyanine ring.[44] The spectrum of PPyCoPcTs is almost identical to that published for PPyCuPcTs by Choi et al.[14] and is very similar to that reported for PPyCoPcTs grown from aqueous solutions.[10] The absorptions at 630 and 677 nm are assigned to aggregated and monomeric CoPcTs, respectively.[45] The aggregate band was also present in films which had been extensively extracted (by Soxhlet technique) and is attributed to CoPcTs bound to the polymer lattice. Compared to the aqueous solution value, the monomer band is red-shifted by 18 nm in both PPyCoPcTs and PNMPyCoPcTs. Red-shifts in phthalocyanine and porphyrin bands have been reported for

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PPyCuPcTs[11] and PPyMTPPS$_4$ (Fe and Co sulfonated tetraphenylporphyrin).[27] We feel that these red-shifts are indicative of a strong electronic interaction between the macrocycle and the cationic polymer, rather than due simply to the chromophore being in solution and solid phases. The precise nature of the interaction is unclear. However, given that PNMPy is expected to be nonplanar,[43] significant overlap of phthalocyanine and polymer molecular orbitals would be unlikely and direct electron withdrawal from the macrocycle limited. An inductive effect involving the interaction of the SO_3^- groups of the phthalocyanine and the cationic polymer would be less dependent on the planarity of the polymer chain and could explain the equivalence of the red-shifts observed for PPyCoPcTs and PNMPyCoPcTs. Irrespective of the origin of the red-shift, the data show the presence of aggregated and monomeric counterion within PPyCoPcTs and PNMPyCoPcTs. The monomeric counterions would most likely be intercalated between the polymer chains.

The visible region of the spectrum of PPyFePcTs differs significantly from that of PPyCoPcTs. There is little evidence of the aggregate peak and a new peak is present at 659 nm. On the basis of Mössbauer spectroscopy (see below) and the fact that the thin films were green, the peak at 659 nm is tentatively assigned to Fe^{II}PcTs.[45,46] This implies that the polymer has reduced at least part of the FePcTs upon termination of electrodeposition. This is consistent with the fact that Co^{II}PcTs is present in PPyCoPcTs (see below) even though the electropolymerization was carried out at potentials high enough to generate Co^{III}PcTs at the anode.[47] For these reasons it is also unlikely that Fe^{IV}PcTs is present within the polymer.[47] The weak band at 460 nm in PPyFePcTs could be due to an axially coordinated Fe^{II}PcTs species.[45] The origin of the peak at 839 nm cannot be assigned unambiguously. One possibility is that it arises from transitions involving either the polaron or bipolaron bands of the polypyrrole moiety.[4] Alternatively, this peak could originate from charge-transfer transitions involving Fe^{III} and the phthalocyanine macrocycle.[48] However, the absence of this peak in both our solution spectra of FePcTs and that reported by Nevin et al.[45] lead us to favor the former, i.e., that the peak originates from the polypyrrole moiety.

The presence of Fe^{II}PcTs is unexpected since this species is known to be readily oxidized to Fe^{III}PcTs by oxygen.[15,49] Its presence implies that the polymer can stabilize the species. This could occur either by steric crowding of the axial sites of Fe^{II}PcTs or by an electrostatic effect.

(F) EPR Spectra of PPy and PNMPy Containing MPcTs (M = Co, Fe, and Ni/Co). The EPR spectra of predried PPyCoPcTs as a function of time of exposure to laboratory air are shown in Figure 7. The full spectrum is characteristic of a low-spin square-planar Co(II) complex with $g_{\parallel} = 2.01$ and $g_{\perp} = 2.27$. The spectrum also contains a resonance at $g = 2.00$ which is superimposed on the Co(II) signal. The broadness of the spectral features is ascribed to spin–spin interactions arising principally from aggregated CoPcTs.[50] This is most pronounced in the dry state (Figure 7a). As the polymer absorbs water and oxygen from the atmosphere the cobalt hyperfine structure becomes better resolved. This is observed in both the parallel and perpendicular regions of the spectra and is most likely the result of axial coordination of water to the Co(II) centers. By increasing the separation of neighboring CoPcTs molecules the spin–spin interactions would be decreased, and the associated line-broadening reduced. The spectra obtained in both the dry and hydrated states did not show any super-hyperfine structure, as might have been expected given the proposed coordination between Co(II) and the pyrrole nitrogen in PPyCoPcTs.[9] However, due to the presence of the broadening effects mentioned above, the data do not preclude its existence.

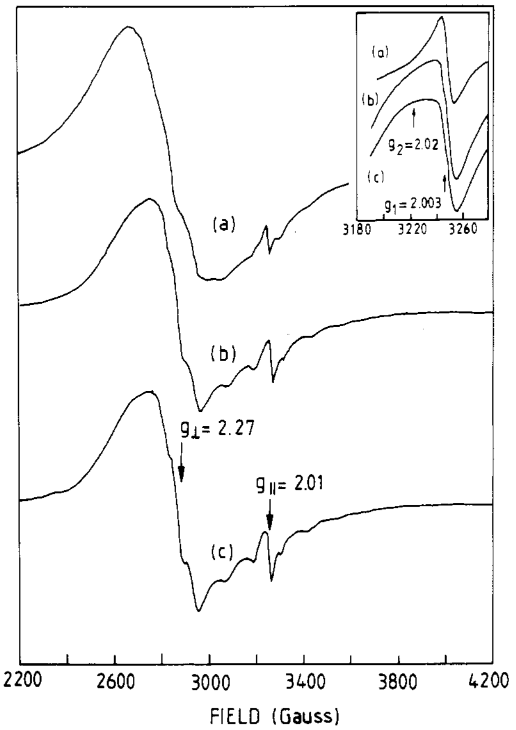

Figure 7. EPR of PPyCoPcTs, recorded at 100 K, as a function of air exposure. Initial spectrum obtained under nitrogen after 40 h of heating, in dynamic vacuum, at 120 °C (a). Same sample after 41 days of air exposure (b). Same sample after 135 days of air exposure (c). Inset shows expanded view of $g = 2.0$ region.

The behavior of the resonance located in the $g = 2.0$ region is unusual (see inset of Figure 7). The signal appears to consist of two components. The sharper line centered at $g = 2.003$ most likely originates in the paramagnetic species on the polymer chain, e.g., polarons. The broader component located at $g = 2.02$ is unlikely to be associated with polypyrrole. The intensity of this component could be reduced by heating in vacuum. Moreover, it was present in spectra recorded at 100 K but absent at room temperature. These features together with the general shape of the resonance are consistent with the presence of a Co^{III}PcTs–O_2^- species at 100 K.[51] The absence of the expected cobalt hyperfine structure for such a species is most likely a consequence of the broadening effects mentioned above. We suggest that the observed changes in the $g = 2.0$ signal reflect the build up of oxygen in the vicinity of the axial positions of CoPcTs. Upon cooling, a solid-state reaction occurs between the accessible oxygen and some of the CoPcTs counterions.

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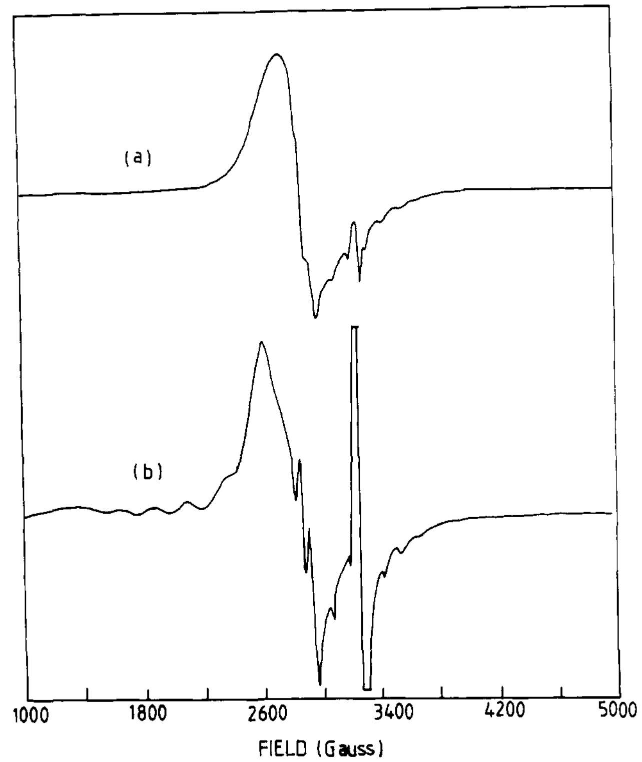

Figure 8. EPR spectra of (a) PPyCoPcTs and (b) PPyNiPcTs/CoPcTs.

Figure 8 shows the spectra for PPyCoPcTs and a PPyNiPcTs/CoPcTs counterion composite. Spectra obtained on identical samples which had been continuously extracted with acetonitrile and dried in vacuum were identical to those shown in the figure. Therefore, these spectra arise from MPcTs counterions bound to the polypyrrole matrix and not residual $MPcTsTBA_4$. The radical signal at $g = 2.0$, for PPyNiPcTs/CoPcTs, has a component originating from NiPcTs.[52] Dilution of CoPcTs with diamagnetic NiPcTs is expected to lead to a reduction in spin–spin broadening,[53] and the spectrum of PPyNiPcTs/CoPcTs shows extended hyperfine structure in the $g_\perp$ region (1000–3000 G) which is absent in PPyCoPcTs. This is strong evidence for a CoPcTs⋯NiPcTs interaction, suggesting that aggregates of MPcTs are present within PPyMPcTs. Such a result is not surprising, given the tendency of tetrasulfonated metallophthalocyanines to form aggregates in solution,[54] and complements the UV–visible data (see above). In our earlier work,[6] the EPR spectrum of PPyCuPcTs showed little hyperfine structure, and it is now believed that this polymer also contained a significant proportion of aggregated CuPcTs.

The spectrum of PNMPyCoPcTs is shown in Figure 9a. It differs considerably from that of PPyCoPcTs (cf. Figure 8a), and is dominated by the polymer radical signal at $g = 2.00$. This difference raises the possibility of some type of magnetic interaction between the polymer radical and the Co(II) unpaired electron, such that the signal intensity of the former is affected by the proximity of the latter. An interaction of this type was proposed for polyacetylene doped with $FeBr_3$.[55] Due to the increased CoPcTs–polymer separation expected in PNMPyCoPcTs, the interaction would be weaker and so the radical signal would be stronger. This interpretation must remain tenuous since other factors, such as different polaron/defect concentrations, may be present. However, with the exception of PPyNiPcTs/CoPcTs, all our polypyrrole films containing MPcTs (M = Co, Cu, and Fe) exhibited weak radical signals. Further work is underway to explore the behavior at lower temperatures and with different paramagnetic counterions.

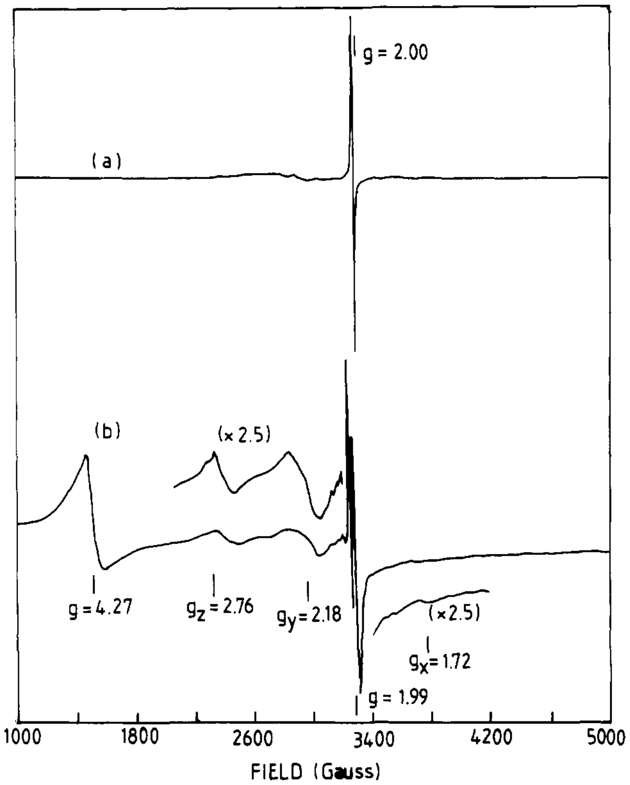

Figure 9. EPR spectra of (a) PNMPyCoPcTs and (b) PPyFePcTs.

The precise chemical nature of FePcTs prepared by the Busch method[15] has to this date never been completely resolved.[49,56] However, the EPR spectrum of PPyFePcTs is presented here since a paramagnetic signal attributable to Fe(III) was obtained (see Figure 9b). The presence of low-spin Fe(III) is indicated by the anisotropic portion of the spectrum containing $g_x = 1.72$, $g_y = 2.18$, and $g_z = 2.76$. However, these values are shifted relative to those reported for frozen DMF–H_2O glasses of FePcTs;[57] the shifts are attributed to the altered chemical environment of FePcTs within polypyrrole. Additional resonances observed with $g = 1.99$ and 4.27 were also present in the spectra of polycrystalline samples of $FePcTsNa_3$ (not shown). The former signal is tentatively assigned to a π-radical located on the phthalocyanine ring.[58] The presence of either a high-spin (rhombic symmetry)[59] or intermediate-spin[60,61]

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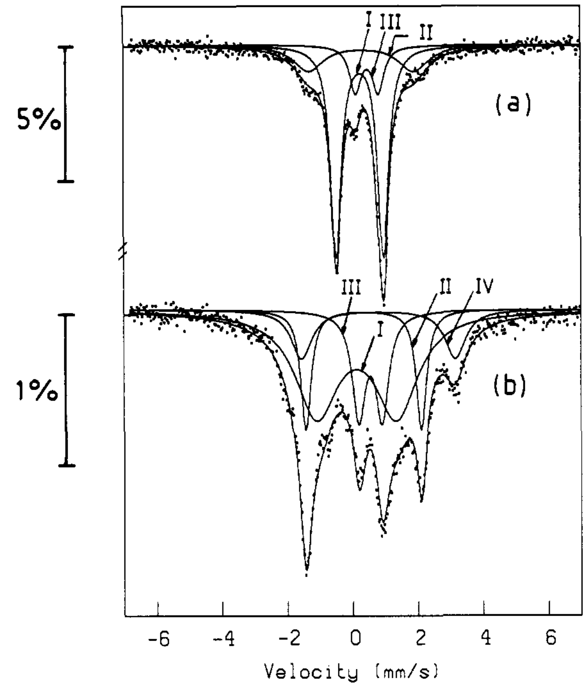

Figure 10. Mössbauer spectra of (a) $FePcTsNa_3$ and (b) PPyFePcTs. Spectra obtained at 4.2 K and zero applied field.

Fe(III) species is indicated by the resonance at $g = 4.27$. Such signals are often ascribed to impurity Fe(III) or partial decomposition products.[59] However, in the present case the species consistently survived multiple washings and extractions.

(G) Mössbauer Spectroscopy. Preliminary Mössbauer spectra of $FePcTsNa_3$ and PPyFePcTs are shown in Figure 10. Unlike the usual Mössbauer-active dopant systems studied in conducting polymers, e.g., $Fe(CN)_6^{3-}$, the Mössbauer spectrum of $FePcTsNa_3$ contains more than one iron species and is itself not fully understood.[56] In the present study, the spectrum of the precursor complex $FePcTsNa_3$ bears a strong resemblance to that reported for tetracarboxylated iron phthalocyanine(FePcTC).[62] The magnitudes of the isomer shifts (δ) and quadrupole splitting (ΔE_Q) for $FePcTsNa_3$ (Table IV) are consistent with the presence of ferric $S = {}^1/_2$, ${}^3/_2$, and ${}^5/_2$ spin states. The $S = {}^1/_2$ ferric species accounts for the majority of the iron species present in $FePcTsNa_3$. Not surprisingly, the spectrum of PPyFePcTs is complex. However, careful scrutiny reveals that the positions of all the peaks, except that at 3.12 mm s^{-1}, closely correspond to those present in $FePcTsNa_3$. Compared to both the sodium and tetrabutylammonium salts, the FePcTs incorporated into polypyrrole appears to have a much higher ferric $S = {}^3/_2$ content. However, care must be exercised in relating peak area to content because of the possibility of different Debye–Waller factors in each spin state. The values of the isomer shift and quadrupole splitting for this species are similar to those reported for $FePcTsH_3$ and FeTP-$PClO_4$ (see Table IV). The table also reveals that the quadrupole splittings of all three ferric species are higher for the FePcTs incorporated in polypyrrole than for the sodium salt. A high quadrupole splitting for polypyrrole containing $FeCl_4^-$ was observed by Kurcharski et al.[63] and was ascribed to a polymer–counterion interaction. In the present case the differences may be due to changes in the axial bonding and/or symmetry of the ligand field produced upon incorporation of the counterion into the polymer.

Table IV. Mössbauer Parameters for Various Iron Complexes

complex	T (K)	δ (mm s^{-1})[a]	ΔE_Q (mm s^{-1})	assignment[b]
$FePcTsNa_3$	4.2	0.24	1.45	I
		0.28	3.23	II
		0.46	0.70	III
$FePcTsTBA_4$	4.2	0.19	2.26	I
		0.36	0.53	III
PPyFePcTs	4.2	0.12	2.46	I
		0.34	3.55	II
		0.54	0.72	III
		0.79	4.72	IV
FePcTC[c]	77	0.170	1.236	I
		0.297	2.923	II
		0.557	0.816	III
$FePcTsH_3$[d]	77	0.33	3.34	II
$FeTPP(ClO_4)$[e]	4.2	0.38	3.50	II
$Fe(CH_3CO_2)(TPpivP)^-$[f]	4.2	1.05	4.25	IV

[a] Relative to metallic iron. [b] Assignments are as follows: I, $Fe^{III}(S = {}^1/_2)$; II $Fe^{III}(S = {}^3/_2)$; III, $Fe^{III}(S = {}^5/_2)$ and IV, $Fe^{II}(S = 2)$. [c] From ref 62. [d] From ref 56. [e] From ref 61, TPP^{2-} = Tetraphenylporphyrin anion. [f] From ref 64, $TPpivP^{2-}$ = pivalamide–picket-fence porphyrin anion.

The new line at 3.12 mm s^{-1} in the spectrum of PPyFePcTs is most likely coupled to the line centered at −1.44 mm s^{-1}. This doublet has an isomer shift in the range normally observed for high-spin ferrous. However, the quadrupole splitting is unusually large. It is noteworthy that a quadrupole splitting of 4.25 mm s^{-1} has been recently reported for a high-spin ferrous synthetic heme.[64] Consequently the new peak is tentatively assigned to a high-spin ferrous species, presumably $Fe^{II}PcTs$. The coexistence of ferric and ferrous iron has also been observed in polypyrrole chemically oxidized with $K_3Fe(CN)_6$.[65] Indeed, conducting polymers containing mixed valence iron species appear to be quite common.[66-68]

With the exception of the line at 3.12 mm s^{-1}, the lines in the spectrum of PPyFePcTs recorded at 4.2 K are also present in spectra obtained at room temperature (not shown). Therefore, the possibility that the spectral lines shown in Figure 10b are magnetically split appears remote. The absence of magnetic hyperfine structure at 4.2 K is unexpected since the EPR data tend to favor some type of magnetic interaction between the polymer radical and paramagnetic metal ions (see above). From these preliminary data it appears that the polymer radical does not strongly interact with the iron nucleus of FePcTs. This implies that either the polymer radical and the iron nucleus are not closely situated, or there is no suitable orbital pathway to allow them to couple. The spectrum of PPyFePcTs obtained in the solvent-free state was similar to that shown in Figure 10b with the exception that the relative intensities of the lines were altered. However,

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the isomer shifts and quadrupole splitting values were not significantly different to those appearing in Table IV. Future studies will include the use of applied magnetic fields in order to delineate any magnetic interactions.

Conclusion

From this work the following conclusions may be drawn:

(1) Despite the statements often found in the literature in regard to the good stability of PPyPTS, we have shown that the conductivity of pristine, electrochemically prepared, PPyPTS is sensitive to both oxygen and water vapor. Consequently, the conductivity of PPyPTS must now be considered to be dependent upon the composition of the environment. Further, the stability of the conductivity of PPy was also found to be dependent upon the incorporated counterion. The use of large MPcTs (M = Co and Fe) counterions appears to facilitate the destructive oxidation of the conjugated polymer backbone by oxygen. This work suggests that improved stability may be achieved through the use of either smaller counterions or counterions that possess sufficient conformational flexibility to be easily accommodated within the structure of polypyrrole.

(2) Two distinct counterion environments are present within PPyCoPcTs. The EPR spectra also suggest the presence of a magnetic interaction between the unpaired electrons of the polymer and the paramagnetic metal ion centers. In PPyCoPcTs, this interaction presumably involves the monomeric CoPcTs species which are intercalated between the polymer chains.

(3) EPR, Mössbauer, and UV–visible spectroscopy have revealed that PPyFePcTs is a far more complicated system than earlier reports[7,12] have indicated. It appears that this polymer contains both Fe^{II}PcTs and Fe^{III}PcTs.

Finally, it is noted that preparation from nonaqueous rather than aqueous solutions failed to produce any improvement in the mechanical or electrical properties of PPyMPcTs.

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