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Physical and Spectroscopic Studies of Polypyrrole Films Containing Transition-Metal EDTA Chelates

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Polypyrrole films containing transition-metal chelate counteranions, based on ethylenediaminetetraacetate ($EDTA^{4-}$) and cyclohexanediaminetetraacetate ($CDTA^{4-}$), have been prepared. The polymers (PPyMEDTA (M = Co, Cr, and Fe) and PPyMCDTA (M = Co and Fe)) have been characterized by elemental analysis, conductivity, X-ray diffraction, and TEM studies, as well as infrared, UV-visible, EPR, and Mössbauer spectroscopy. The conductivity of PPyFeEDTA and PPyCrEDTA initially increased upon exposure to the environment and then stabilized, while that of PPyCoEDTA initially increased and then decreased very slowly; this behavior is superior to that of the well-known *p*-toluenesulfonate system (PPyPTS). The conductivity, degree of order, and conjugation length of the polymers were dependent upon the nature of the incorporated counteranion. TEM investigations of thin films of PPyCoEDTA revealed some crystallinity, lattice fringes being observed. EPR spectroscopy showed that the coordination of $EDTA^{4-}$ within the counteranion of PPyCrEDTA was sexadentate. The low-temperature Mössbauer spectrum of PPyFeEDTA exhibited magnetic structure and indicated the presence of at least two counteranion environments. In addition to an aggregated form, a large proportion of the counteranions is well dispersed within the polymer matrix.

Introduction

Despite a vast amount of research, the precise structural arrangements within thick films of polypyrrole remain largely unresolved. Also, the factors that govern the environmental stability of the conductivity of the polymer await elucidation. The present study attempts to address these issues through the examination of the physical and spectroscopic properties of polypyrrole films containing transition-metal chelates.

The first extensive study of polypyrrole was conducted by McNeill et al. in 1963.[1] The polymer was prepared by the pyrolysis of tetraiodopyrrole, and subsequent examination identified polypyrrole as a semiconductor. The current interest in polypyrrole has its origins in the work of Diaz et al.,[2] in which it was shown that films with improved conductivity could be conveniently prepared by electrochemical synthesis. In this method, the polymer is oxidized during polymerization, and counteranions from the supporting electrolyte are incorporated to maintain electrical neutrality. Apart from the intellectual challenges that this relatively new polymer present, a significant driving force for the vast amount of research that has been conducted on polypyrrole is the potential for its application in devices such as rechargeable batteries and electrochromic displays.[3]

In a large proportion of the reported work, polypyrrole has been prepared containing "commercially available" inorganic counteranions, such as ClO_4^-, BF_4^-, and *p*-toluenesulfonate (PTS^-). In recent years, polypyrrole films containing unusual counteranions, such as $Pt(CN)_4^{2-}$,[4] tetrathiomolybdate,[5] and first-row transition-metal complexes,[6-9] have been prepared. Polypyrrole-containing polymeric and sulfonated aromatic counteranions have also been the focus of considerable interest.[10-14] Warren et al.[12] examined polypyrrole containing a variety of counteranions by means of X-ray diffraction and found that substituted benzenesulfonate and long aliphatic chain counteranions produced the highest order. Recently, the structure of polypyrrole containing poly(4-styrenesulfonate) was investigated by means of scanning tunneling microscopy[13] and helical chains of polypyrrole were observed. Work in this laboratory has focused on the use of transition-metal complexes as counteranions and the study of the subsequent properties.[15-17] These materials may be considered as polymer-transition metal complex com-

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Table 1. Atom Mole Ratios, Conductivities, Flotation Densities, and Preparation Conditions for Various Polypyrrole Films

polymer	applied potential (V)[a]	Q_e (C/cm^2)[b]	atom mole ratio[c]	material balance (%)	oxygen equiv[d]	conductivity (S/cm)[e]	density (g/mL)
PPyPTS	0.90	20.1	$(C_{4.00}H_{3.21}N_{0.92})(PTS)_{0.20}$	94.08	0.39	11–50	1.38–1.39[f]
PPyCoEDTA	0.80	14.0	$(C_{4.00}H_{3.31}N_{1.01})(CoEDTA)_{0.13}$	92.03	0.60	6.4–11.1	1.51–1.52
PPyCrEDTA	0.85	14.3	$(C_{4.00}H_{3.04}N_{0.98})(CrEDTA)_{0.16}$	95.51	0.35	0.056–0.160	1.46–1.47
PPyFeEDTA	0.80	20.0	$(C_{4.00}H_{3.21}N_{1.00})(FeEDTA)_{0.059}$	88.00	0.73	0.032–0.134	1.42–1.44
PPyCoCDTA	0.80	13.9	$(C_{4.00}H_{3.78}N_{0.96})(CoCDTA)_{0.13}$	85.81	1.21	2.4–5.6	1.47–1.48
PPyFeCDTA	0.85	19.6	$(C_{4.00}H_{3.68}N_{0.99})(FeCDTA)_{0.081}$	91.25	0.59	0.011–0.048	
PPyCr/CoEDTA	0.85	14.5					
PPyFe/CoEDTA	0.80	13.9					

[a] Relative to Ag/AgCl 3 M Cl^- (aq) reference electrode. [b] Electropolymerization charge density. [c] Values normalized to carbon. [d] Oxygen equivalent of missing weight. [e] Measured at room temperature after 23–26 h of air exposure. [f] In this case the density range was obtained from one preparation only.

posites, and as such, the chemistry associated with the counteranions is of equal importance to that of the polymer in determining the final properties.

In the present work, we have employed counteranions based upon ethylenediaminetetraacetate ($EDTA^{4-}$) and cyclohexanediaminetetraacetate ($CDTA^{4-}$). The polymers studied, PPyMEDTA (M = Co, Cr, and Fe) and PPyCoCDTA, were first briefly reported by Takakubo.[18,19] However, to our knowledge, the only published data consist of the room-temperature conductivities of PPyCoEDTA, PPyCoCDTA, and PPyCrEDTA. We have therefore undertaken a much more detailed investigation of these materials. In addition, PPyFeCDTA has been prepared and characterized for the first time. The coordination of $EDTA^{4-}$ within $MEDTA^-$ complexes is variable and is influenced by the nature of the chelated cation. For example, the crystal structures of FeHEDTA and RbFeEDTA have revealed quinquedentate and sexadentate coordination of the chelate, respectively.[20,21] Due to the largely amorphous nature of the polymers studied in this work, we have employed indirect techniques in an attempt to determine the coordination of the chelate within the incorporated counteranions.

The primary advantage in using metal chelates as counteranions is that the paramagnetic transition-metal ions implanted into the polymer can act as spectroscopic probes in techniques such as EPR and Mössbauer spectroscopy. This permits detailed information about the counteranion environment, and hence the structure of the material, to be obtained. The structures of the above counteranions are very different from those of the transition-metal complexes that we have previously incorporated into polypyrrole.[16,17] Thus, they facilitate investigation of the influence of the counteranion size and shape on the environmental stability of the conductivity. Our earlier work showed that very large anisotropic macrocyclic counteranions yielded conductivities which decreased rapidly upon exposure to the environment.[15,17]

In the present work the compositions of the polymers were determined by elemental analysis. The effect of the counteranion on the charge carriers within the polymer was studied using conductivity measurements and UV–visible spectroscopy. Information regarding the degree of order and structure of the polymers was obtained from TEM and X-ray diffraction. The $EDTA^{4-}$ coordination within the incorporated metal chelate, and the counteranion environment within the material, were examined using infrared, EPR, and Mössbauer spectroscopy.

Experimental Section

Reagents. Pyrrole (Aldrich) was distilled prior to use and stored at −18 °C under nitrogen in the absence of light. Water was "milli-Q" quality, and propylene carbonate was used as received. Tetrabutylammonium perchlorate (SACHEM) and sodium *p*-toluenesulfonate (BDH) were also used as received. NaMEDTA and NaMCDTA (M = Co and Fe) were synthesized using modifications of the published methods.[22,23] NaCrEDTA was prepared by the neutralization of CrHEDTA. The latter was prepared by the reaction of stoichiometric equivalents of $Cr(NO_3)_3$ (Hopkins and Williams) and H_4EDTA (Merck) in distilled water at 95–100 °C. (The reaction is exothermic and should be carried out in a well-ventilated fume cupboard.) Upon cooling, the product was precipitated by the addition of ethanol. The solid was purified by subsequent dissolution in water and precipitation with ethanol and then dried in dynamic vacuum overnight at room temperature over P_2O_5. To an aqueous solution of CrHEDTA, a NaOH solution was added until a pH of 5.0 was reached (corresponding to the first inflection point on the potentiometric curve). The solution was concentrated, and the solid precipitated by the addition of ethanol. The solid was purified and dried as above. The compositions and purities of the metal chelates prepared above were confirmed using elemental analysis, magnetic moment measurements, as well as infrared, UV-visible, and EPR spectroscopy.

Polymer Synthesis. The electrochemical cell and instrumentation used in the present study have been described previously.[17] The applied potentials and charge densities employed for the preparation of the polymers appear in Table 1. For $PPyClO_4$, the potential used during preparation was 0.96 V (Q_e = 11.3 C/cm^2) vs the Ag/AgCl 3M Cl−(aq) reference electrode. The polymerizations were all conducted in a controlled temperature bath (0–4 °C). In the present study, the thick films had thicknesses in the range 30–90 μm. From the measured thicknesses of the thick films, and the charge passed during their preparation, the average charge density required for a film thickness of 0.1 μm was 40 mC/cm^2. Using this figure, the thicknesses of the thin films studied by UV-visible and infrared spectroscopy are estimated as 0.3–0.5 μm from the amount of charge passed during their preparation. Similarly, the films used in the TEM investigation are estimated to have had thicknesses in the range 0.05–0.1 μm.

$PPyClO_4$ was prepared and handled in the manner previously described.[17] The PPyPTS, PPyMEDTA (M = Co, Cr, and Fe), and PPyMCDTA (M = Co and Fe) films were prepared using aqueous solutions containing 0.10 M pyrrole and 0.020 M of the respective sodium salt of the counteranion. PPyFe/CoEDTA was prepared from a solution containing 0.010 M NaFeEDTA and 0.010 M NaCoEDTA. PPyCr/CoEDTA was prepared using 0.006 M NaCrEDTA and 0.014 M NaCoEDTA. In each case, the electrolyte was purged with nitrogen prior to the polymerization, and this atmosphere was maintained over the solution through the course of the synthesis. The films were removed from the

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electrode and thoroughly washed in distilled water. It was found that drying PPyCoEDTA and PPyCrEDTA at 120 °C, in dynamic vacuum, caused an irreversible decrease in the conductivity. However, no significant difference in the resulting flotation densities were detected. The flotation densities shown for these films (Table 1) contain some data which were obtained from films dried in the above manner. It is emphasized that all of the remaining data presented in this paper were obtained on films that were dried exclusively at room temperature. This was performed under dynamic vacuum, over P_2O_5, for approximately 24 h. Prior to analysis, all films were washed continuously with milli-Q quality water for 24 h and then dried at room temperature as above. The polymers were subjected to an additional drying, in the above manner, immediately prior to analysis.

Physical Methods. Elemental analysis was performed by the University of Otago microanalytical service (New Zealand) and Galbraith Laboratories (Knoxville, TN). The conductivity measurements were made using the linear four-probe method and were performed at 20 ± 1 °C. A solvent blend of iodomethane and *n*-hexane was used for the determination of the flotation densities. At least three separate films (>20 μm) of each polymer listed in Table 1 were grown. It was observed that the thickness of the films on the electrode increased with increasing depth in the electrolyte solution, in agreement with the observation of Takakubo.[18] This is attributed to variations in the current density over the electrode surface. Four samples were cut from each film, corresponding to maximum and minimum depths in the solution, and two intermediate positions. The measured flotation densities and conductivities increased with increasing depth in the solution. The conductivity and density columns in Table 1 show, for each polymer, the data obtained at minimum and maximum depths averaged over the three (or more) separate films. TEM investigations were conducted on thin films suspended on copper grids using a Philips CM20 electron microscope operated at 200 keV. The electron microscope was equipped with an Oxford Instruments ultrathin window energy-dispersive spectrometer. X-ray diffraction data were collected in both reflection and transmission geometries using a SCINTAG PAD(V) diffractometer and Cu Kα radiation. Transmission infrared spectra were obtained on thin polymer films, supported on a sodium chloride plate, using a Perkin-Elmer 1600 Series spectrometer. The equipment and procedures employed in recording the UV–visible, EPR, and Mössbauer spectra have been described previously.[17] In the latter, the data fitting used a least-squares procedure employing Lorentzian line shapes, except for the unresolved magnetic structure which was approximated by a Gaussian. EPR spectra of frozen solutions of NaCrEDTA and CrHEDTA were obtained using water–methanol–dimethylformamide blends (in the volume ratios of 2:8:1 respectively) such that about 10 mg of solid was dissolved in 10 mL of solvent. The spectra were recorded at approximately 100 K using a microwave frequency of 9.11 GHz.

Results and Discussion

Elemental Analysis. From elemental analysis data, the compositions of PPyPTS, PPyMEDTA (M = Co, Cr, and Fe), and PPyMCDTA (M = Co and Fe) have been determined and are shown in Table 1. The washing procedure employed ensured that the films contained negligible concentrations of residual electrolyte. Examination of the films via electron microprobe showed that they were chloride free, indicating no contamination from the reference electrode. Nevertheless, all of the films contain an unidentified mass. This is ascribed to an oxygen species.[14,24,25] The compositions of the pyrrole moiety, in each polymer, reveal excess hydrogen when compared to the ideal C_4H_3N formula. This is attributed to a combination of residual water,[26] covalently bound hydroxyl groups,[27] and sp^3-hybridized C–H species.[28]

From Table 1, it will be seen that the extent of oxidation of the metal chelate containing polymers is in the 0.06–0.16 range. The levels of counteranion incorporated in these materials are thus comparable to those found[18] in polypyrrole containing $Cr(C_2O_3)_3^{3-}$. While it is clear that the size of the counteranion influences its level of incorporation into polypyrrole, the data do not allow any more detailed conclusions to be drawn.

Environmental Stability of the Conductivity of PPyMEDTA, PPyMCDTA, and PPyPTS. The room-temperature conductivities of PPyMEDTA (M = Co, Cr, and Fe), PPyMCDTA (M = Co and Fe) and PPyPTS are shown in Table 1. The conductivities of PPyPTS, PPyCoEDTA, and PPyCoCDTA are similar to the values previously reported.[12,18] In the early work of Takakubo,[18] the conductivities of PPyCrEDTA and PPyFeEDTA were not measured because of the poor mechanical properties of the polymers. However, in a subsequent publication the conductivity of PPyCrEDTA was reported as 5 S/cm.[19] This value is not consistent with the present work.

From Table 1 it can be seen that the conductivities of PPyFeEDTA and PPyCrEDTA are much lower than that of PPyCoEDTA. This is surprising, and a definitive explanation is not yet available. NaCrEDTA and NaFeEDTA were not electroactive under the conditions used to prepare PPyCrEDTA and PPyFeEDTA. It is plausible that chemical oxidation of electrochemically produced oligomers may have occurred during the preparation of PPyMEDTA. The redox potentials of $[M^{II/III}EDTA]^{2-/-}$ (M = Cr, Co, and Fe) are −1.23, 0.13, and −0.12 V vs SCE, respectively.[29,30] The latter two redox potentials are comparable to those reported for pyrrole oligomers.[31] However, the electrolyte solutions did not exhibit any evidence of chemical polymerization. The EPR spectrum of PPyCoEDTA (see below) revealed that Co(II) was absent. In view of the above, it is unlikely that chemical oxidation of pyrrole oligomers occurred.

The conductivity of polypyrrole has been reported to be unstable in that substantial reductions have been observed upon exposure to the atmosphere.[9,32,33] An important area of research is the study of the effect that the counteranion has on this property. In Figures 1 and 2 the normalized conductivity as a function of exposure time is shown for PPyMEDTA (M = Co, Cr, and Fe), PPyMCDTA (M = Co and Fe), and PPyPTS. The scatter in the data is attributed to fluctuations in the humidity and temperature. (The latter varied between 19.0 and 21.0 °C, and this had a more pronounced effect on the materials with lower conductivity.) The conductivity of PPyPTS rapidly decreases below the original value soon after exposure to air. Conversely, PPyCrEDTA and PPyFeEDTA show an increasing conductivity up to nearly constant values within the experimental period. This tendency to retain conductivities higher than the original value, for exposure times up to 100 days, is noteworthy and in this respect the conductivity of PPyMEDTA (M = Co, Cr, and Fe) and PPyFeCDTA is superior to that of

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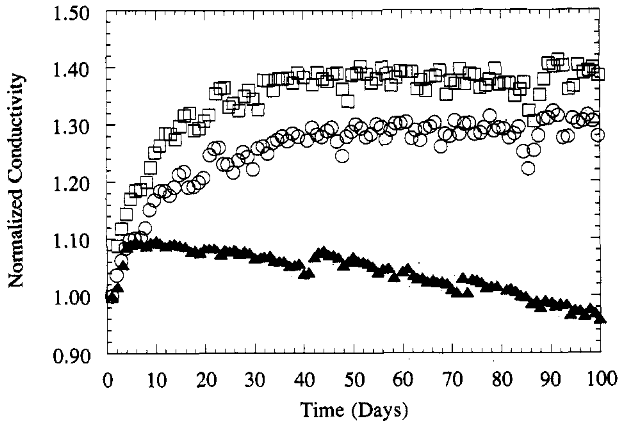

Figure 1. Normalized conductivity versus time of exposure to laboratory air for PPyCrEDTA (□), PPyFeEDTA (○), and PPyCoEDTA (▲).

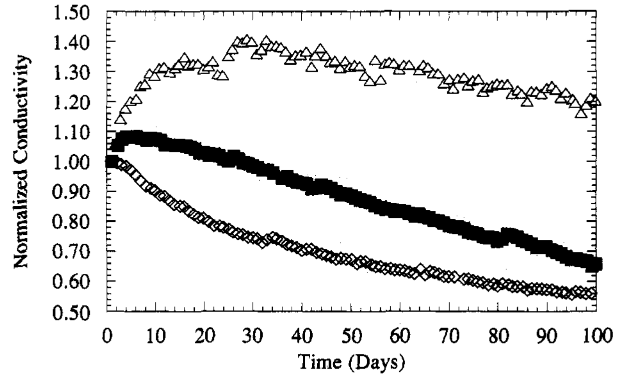

Figure 2. Normalized conductivity versus time of exposure to laboratory air for PPyFeCDTA (△), PPyCoCDTA (■), and PPyPTS (◇).

thick polypyrrole films containing other transition metal complex counteranions.[9,15-17,33]

By analogy to the mechanism proposed for polyacetylene, the initial increase in conductivity observed for the metal chelate containing polymers is attributed to the formation of a charge-transfer complex with oxygen.[34] This is consistent with the low extents of oxidation of pyrrole found in these polymers (see Table 1). Qualitatively similar behavior was observed when electrochemically reduced polypyrrole was exposed to oxygen.[35] For PPyPTS, the conductivity increase was always more rapid and less pronounced than that observed for the polymers containing the metal chelate counteranions. The subsequent conductivity decrease observed for PPyPTS, PPyCoEDTA, and PPyMCDTA (M = Co and Fe) is attributed to an irreversible oxidation resulting in the formation of covalently bound oxygen species.[36,37]

The present data suggest that the nature of the counteranion strongly affects the rate and extent of the reactions discussed above. Presumably, the size and shape of the counteranions influence the access of molecular oxygen to the polymer chains. The metal chelate counteranions are of moderate size (see below) and approximately spherical and occupy a large proportion of the total volume in these materials. In addition, the Mössbauer data for PPyFeEDTA (see below) indicate that a large proportion of the counteranions are well dispersed throughout the polypyrrole matrix. These effects could result in a restriction of oxygen access to the reactive sites of the polymer chains and lead to a slowing of the rate of the above reactions. The MEDTA (M = Co, Cr, and Fe) counteranions appear near to the optimum size in this regard since the stabilities of both PPyCoCDTA and PPyFeCDTA are lower than those observed for the PPyMEDTA (M = Co and Fe) analogs. Support for the notion of an optimum counteranion size and shape can be found from the poor stabilities observed for polypyrrole containing relatively large tetrasulfonated metallophthalocyanines.[15,17]

The crystal structures[21,38,39] of $CoEDTA^-$, $FeEDTA^-$, and $FeCDTA^-$ (and effective van der Waals radii data[40]) allow estimates of the sizes of these counteranions to be made. For each counteranion, the lengths along three axes were calculated from the atomic coordinates, and the van der Waals radii of the peripheral atoms added. The lengths of $CoEDTA^-$, $FeEDTA^-$, and $FeCDTA^-$ (averaged along the three axes) were calculated as 9.3, 10.2, and 11.1 Å, respectively. Assuming a spherical structure, the volume of $FeCDTA^-$ is then about 30% larger than that of $FeEDTA^-$. The size of $CrEDTA^-$ would be similar to that of $CoEDTA^-$, since they are isomorphous. For comparison, the van der Waals length of a tetrasulfonated metallophthalocyanine counteranion was estimated as 24–28 Å. While the data for polypyrrole containing the above counteranions indicate that the size and shape of the latter are important, it is clear that other factors also influence the conductivity stability.

Transmission Electron Microscopy. TEM studies were undertaken in an attempt to compare the morphology of thin films of PPyCoEDTA, PPyCrEDTA, and PPyPTS. The data for PPyCrEDTA were inconclusive; those for PPyCoEDTA showed that the films were largely amorphous although small crystallites were frequently observed and comprised about 1% of the surface area. Figure 3a is a micrograph of PPyCoEDTA, showing a central crystallite (dark area) surrounded by regions of decreasing structural order. It is suggested that the crystallites are the regions where the nucleation and early growth of the polymer commence; the transition to the amorphous phase occurs as the result of subsequent polymer growth. The higher magnification image of the crystallite (see Figure 3b) clearly shows parallel crystalline lattice fringes as well as the more irregular features characteristic of an amorphous phase. The average lattice fringe spacing was consistently measured to be 4.8 Å. This value is comparable to the reported spacing of side-by-side pyrrole rings[41] and could originate from aligned polypyrrole chains. However, without the use of computer-simulated images based on such a model, such an interpretation must remain tentative.

An energy-dispersive spectrum obtained from the crystallite shown in Figure 3 appears in Figure 4. The signal due to copper originates from the grid used to support the film. The spectrum shows evidence of cobalt, oxygen, and carbon; the small peak at approximately 0.4 keV is assigned

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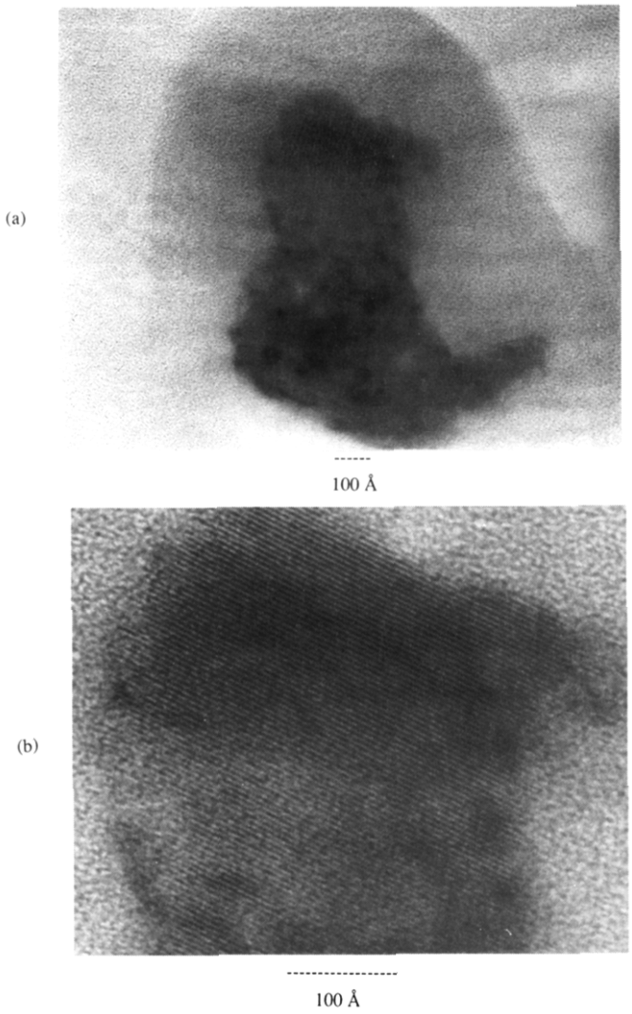

Figure 3. Transmission electron micrographs of PPyCoEDTA showing (a) a crystallite and (b) lattice fringes. The latter is a higher magnification image of part of the crystallite shown in (a).

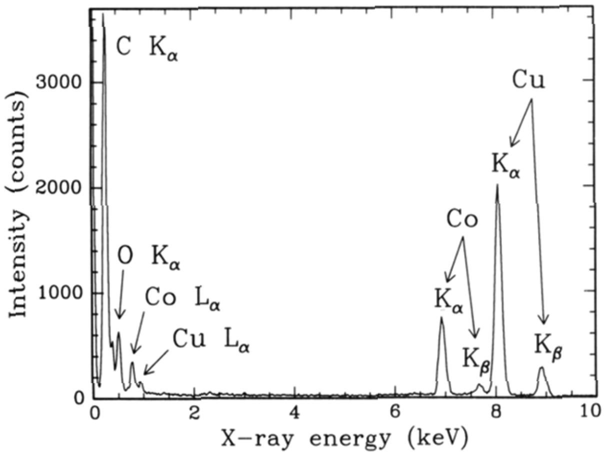

Figure 4. Energy-dispersive spectrum of the crystallite shown in Figure 3.

to nitrogen. The spectrum indicates that the crystallite contained negligible impurity concentrations.

A preliminary electron diffraction study of PPyCoEDT was undertaken which confirmed the crystallinity noted above; however, no definitive conclusions have been drawn concerning the structure. The acquisition of these data is difficult due to the small size of the crystallites and their sensitivity to the electron beam. More work is required to elucidate the structural arrangements present within PPyCoEDTA. The data presented above show that the CoEDTA counteranion has the ability to promote a highly ordered structure. This is most likely related to the choice of metal within this counteranion as well as its size and shape. In this context it should be noted that crystallites were not observed in PPyPTS films prepared under identical conditions.

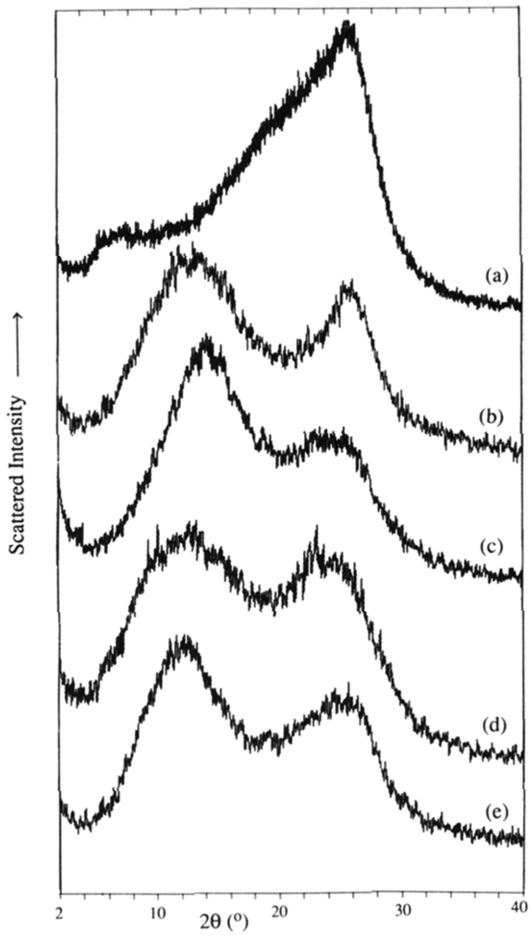

Figure 5. X-ray diffractograms of (a) PPyPTS, (b) PPyCoEDTA, (c) PPyCrEDTA, (d) PPyFeEDTA, and (e) PPyCoCDTA obtained using reflection geometry.

X-ray Diffraction and Flotation Density Measurements. X-ray diffraction was employed to obtain information about the structural arrangements within thick films of PPyMEDTA (M = Co, Cr, and Fe) and PPyCoCDTA. The diffractograms of these polymers, as well as those of PPyPTS and $PPyClO_4$, are shown in Figures 5 and 6; the tabulated data appear in Table 2. Broad scattering maxima are present in all of the diffractograms which indicate that the underlying structures are largely amorphous. From the work of Mitchell et al.[42,43] and Buckley et al.[41] it is possible to divide the scattering maxima in the high-angle region into two groups: maxima in the 2Θ = 18–22° and 24–26° regions are assigned to scattering from side-by-side pyrrole rings and face-to-face aromatic units (including pyrrole rings), respectively. The low-angle maximum observed in the diffractogram of PPyPTS (Figure 5a) is attributed to scattering from PTS counteranions.[25]

From Figure 5 it is evident that the diffractograms of PPyMEDTA (M = Co, Cr, and Fe) and PPyCoCDTA bear a strong resemblance to each other and differ considerably

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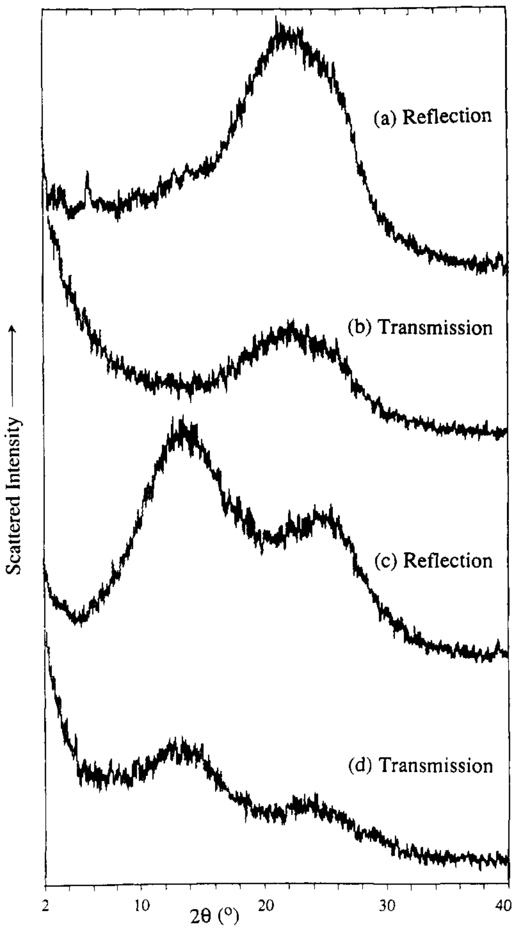

Figure 6. X-ray diffractograms of PPyClO$_4$ ((a) and (b)) and PPyCrEDTA ((c) and (d)) obtained using reflection and transmission geometries.

Table 2. X-ray Diffraction Data[a]

sample[b]	2θ (deg)	d (Å)[c]
PPyPTS	6.5 br, w; 19.0 sh, w; 25.8 s, st	13.6, 4.7, 3.5
PPyClO$_4$	22.0 br, st; 25.0 sh, m	4.0, 3.6
PPyClO$_4$[d]	22.0 br, m; 25.5 sh, w	4.0, 3.5
PPyCoEDTA	13.0 br, st; 26.0 s, st	6.8, 3.4
PPyCrEDTA	14.0 br, st; 25.0 br, m	6.3, 3.6
PPyCrEDTA[d]	13.5 br, m; 24.0 br, w	6.6, 3.7
PPyFeEDTA	12.5 br, st; 24.0 br, st	7.1, 3.7
PPyCoCDTA	12.0 br, st; 25.5 br, m	7.4, 3.5
NaCoEDTA	14.0 br, st	6.3

[a] st = strong, m = medium, w = weak, s = sharp, br = broad, and sh = shoulder. [b] Data obtained using reflection geometry unless otherwise stated. [c] Evaluated from Bragg equation. [d] Data obtained using transmission geometry.

from that of PPyPTS. This indicates that the structure of PPyPTS is quite different from those present in the metal chelate containing polymers. The diffractograms of the latter show a broad maximum in the $2\Theta = 10$–18° region and there is little, if any, evidence of scattering from side-by-side pyrrole rings. The latter observation implies that the polymer moiety is unlikely to consist of intercalated sheets containing coplanar polypyrrole chains, as is the case in PPyPTS.[43] This is not a surprising result, since, on space-filling grounds, intercalation of coplanar polypyrrole chains and spherical counteranions is not expected.[44,45] Because the metal chelates are neither aromatic or planar, the maxima in the $2\Theta = 24$–26° region are restricted to scattering from face-to-face pyrrole rings. Therefore, the relative sharpness of maxima in this region provide a qualitative guide to the degree of order present in the polypyrrole chains.[12] It can be seen from Figure 5 that the degree of order of the polypyrrole moiety is dependent on the nature of the metal chelate incorporated, being higher in PPyCoEDTA and lower in PPyCrEDTA and PPyFeEDTA.

The relatively strong maxima observed in the $2\Theta = 10$–18° region of the diffractograms of the metal chelate containing polymers are ascribed to counteranion scattering because the diffractograms of NaCoEDTA also exhibits a broad maximum in this region (see Table 2). The diffractogram of PPyCrEDTA was not significantly altered after washing in distilled water for 24 h, indicating that the counteranions responsible for the maxima are electrostatically bound to the polypyrrole cation. The relative sharpness of the maxima in the $2\Theta = 10$–18° region is indicative of the degree of counteranion order within the materials. From Figure 5, it is evident that the degree of order is higher in PPyCrEDTA and PPyCoCDTA. In the former, this is attributed to the relatively high level of counteranion incorporation (see Table 1). For PPyCoCDTA, the relatively large size of the CoCDTA counteranion would result in a higher proportion of the total volume being occupied by the metal chelate and a concomitant increase of order within this moiety. From the above arguments it is apparent that the degree of order present in both the counteranion and polymer moieties of the metal chelate containing polymers are essentially independent, i.e., a relatively high degree of counteranion order does not impart a relatively high degree of order to the polymer, and vice versa.

In Figure 6 the diffractograms for PPyClO$_4$ and PPyCrEDTA obtained using both reflection and transmission geometries are shown. For each polymer, the difference in the relative intensities of the two curves is due to the dissimilarity in the scattering volumes present in each geometry. In assessing the degree of anisotropy in each polymer, the differences in the position of the scattering maxima are the important factor. The positions of the maxima in the diffractograms of PPyClO$_4$ are the same for both geometries which indicates that the polymer has an isotropic structure, as previously reported.[45] Likewise, the diffractograms of PPyCrEDTA (Figure 6c,d) reveal that the polymer is also isotropic. Similar results were obtained for PPyCoEDTA (not shown). It is suggested that, locally, the structures of PPyMEDTA (M = Co, Cr, and Fe) and PPyMCDTA (M = Co and Fe) consist mainly of isolated stacks of polypyrrole chains which are separated by layers of aggregated counteranions. From the above data, it is evident that the local structure is randomly oriented on a global scale within the materials. This structure differs from that recently proposed for polypyrrole containing camphor sulfonate where some anisotropy was observed,[46] and this is attributed to the more spherical shape of the metal chelates.

The flotation densities of the metal chelate containing polymers (Table 1) are comparable to those usually reported for polypyrrole.[26] When the compositions of the materials shown in Table 1 are considered, it may be shown that the packing efficiency of the counteranions (as

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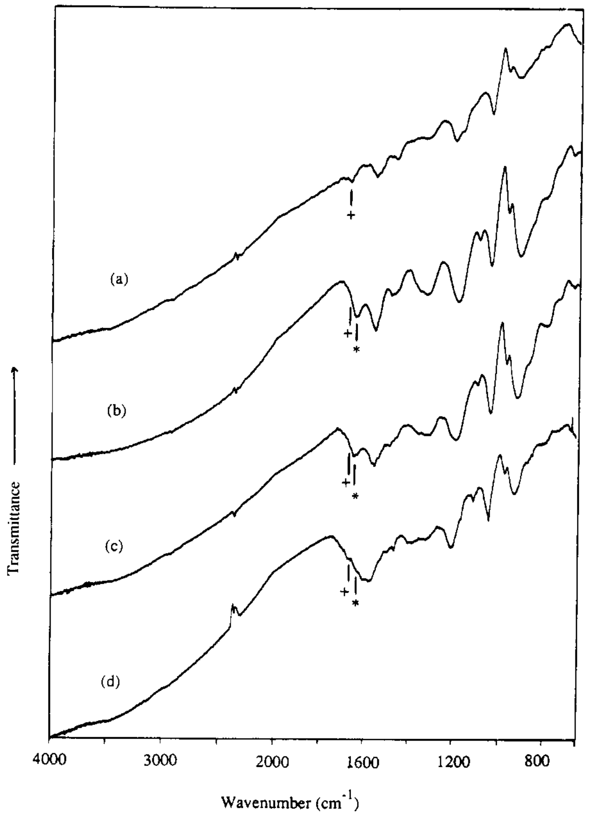

Figure 7. Infrared spectra of (a) PPyPTS, (b) PPyCoEDTA, (c) PPyCrEDTA, and (d) PPyFeEDTA. The bands originating from MEDTA$^-$ and polypyrrole are labeled (*) and (+) respectively; see text. The spectra have been smoothed.

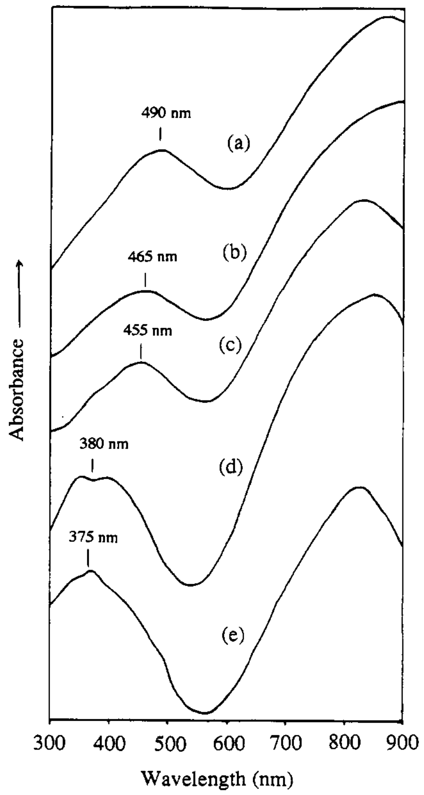

Figure 8. UV-visible spectra of (a) PPyPTS, (b) PPyCoEDTA, (c) PPyCoCDTA, (d) PPyCrEDTA, and (e) PPyFeEDTA. The spectra have been smoothed.

reflected by the number of counteranions per unit volume of material) is highest in PPyPTS.

Infrared Spectroscopy of PPyMEDTA (M = Co, Cr, and Fe) and PPyPTS. The infrared spectra of PPyPTS and PPyMEDTA (M = Co, Cr, and Fe) are shown in Figure 7. With the exception of the absorption bands in the 1600–1700-cm^{-1} region, the spectra are similar to that reported for PPyClO$_4$.[27] The vibrational modes responsible for the bands in the region below 1600 cm^{-1} have been assigned by Watanabe et al.[47] A broad absorption is present above 1800 cm^{-1} in all of the spectra, and this has been attributed to free charge carriers.[27,47] The 1600–1700-cm^{-1} region of the spectrum of PPyMEDTA (M = Co, Cr, and Fe) also exhibits absorption bands due to the antisymmetrical vibration of the carboxylate group (COO$^-$) originating from the counteranions.[48] These are observed at 1640, 1645, and 1630 cm^{-1} in the spectra of PPyCoEDTA, PPyCrEDTA, and PPyFeEDTA (as a shoulder), respectively. The positions of these bands correspond closely to those in the respective spectra of NaMEDTA (M = Co, Cr, and Fe), confirming the presence of the counteranions within each of the polymers. This also implies that the nature of the M–COO$^-$ bonding within the counteranions remains largely unchanged as a result of incorporation into polypyrrole.

A weak band is present in the spectra of PPyPTS and PPyFeEDTA at approximately 1670 cm^{-1} and probably exists in the spectra of PPyMEDTA (M = Co and Cr). This may be assigned to vibrations of carbonyl groups that are conjugated with C=C units.[49] The relative weakness of the bands indicate that the levels of carbonyl groups incorporated into the polymers are relatively low. Therefore, the majority of the excess oxygen present in these polymers (see Elemental Analysis section) must originate from residual water and covalently bound hydroxyl groups. The absorption bands of the latter would not be observed since they are only apparent in the spectra of electrochemically reduced polypyrrole.[27]

Considering the antisymmetrical vibration of the COO$^-$ group in more detail, it is evident that the sharpness of this band is greatest in the spectra of PPyCoEDTA and PPyCrEDTA. This supports the possibility of exclusive sexadentate coordination of the EDTA^{4-} chelate within the counteranions of PPyCoEDTA and PPyCrEDTA.[50] However, the existence of such species cannot be proven from infrared data alone.[48,50]

UV–Visible Spectra. The UV–visible spectra of PPyPTS, PPyMEDTA (M = Co, Cr, and Fe), and PPyCoCDTA are presented in Figure 8. Broad absorption bands are evident in the 800-nm region of each spectrum, and these are attributed to polarons and/or bipolarons.[11,51] The absorption bands in the 300–500-nm range are assigned to transitions from the valence band to the uppermost bipolaron band.[11,52] It is noteworthy that the absorption bands due to the counteranions are absent in the spectra of PPyCoEDTA and PPyCrEDTA.[53,54] Conversely, the UV–visible spectra of polypyrrole containing tetrasulfonated metallophthalocyanines were dominated by bands originating from the counteranions.[17] The

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absence of the counteranion bands in the spectra of PPyCoEDTA and PPyCrEDTA is the result of the relatively low molar extinction coefficients of these counteranions,[53,54] which are approximately 2 orders of magnitude smaller than those reported for tetrasulfonated metallophthalocyanines.[55] The main absorption bands of the FeEDTA counteranions occur outside the range of the spectrometer used in this study.[56]

A striking feature of the spectra (Figure 8) is that for PPyX, the wavelength of maximum absorption in the 300–500-nm region decreases in the order X = PTS^- > $CoEDTA^-$ > $CoCDTA^-$ > $CrEDTA^-$ > $FeEDTA^-$. A correlation between wavelength and conductivity has been established for several poly(alkylthiophenes);[57] examination of the conductivities of the above polymers (Table 1) shows a decrease in the same order as that observed for the wavelength above. The wavelength decreases observed above are ascribed to reductions in the conjugation length of the polymer. Kuwabata et al.[10] examined the UV–visible spectra of polypyrrole containing various substituted aromatic sulfonates and found that an increase in the negative charge of the counteranion caused a reduction in the wavelength. This was attributed to a narrowing of the resonant length of the bipolarons. Accordingly, in the present work the higher wavelength observed for PPyCoEDTA is indicative of a reduction in the effective negative charge (and nucleophilicity) of the incorporated counteranion. The relatively high conjugation length observed in PPyPTS is consistent with the poor nucleophilicity of the PTS counteranion.[58]

EPR Spectra. The EPR spectra of PPyCoEDTA and PPyCoCDTA consisted of sharp, Lorentzian-shaped resonances with g values of 2.003 (not shown). This value is typical of that reported for polypyrrole containing diamagnetic counteranions.[49] There was no evidence of a Co(II) signal, and it is suggested that the cobalt is present in both PPyCoEDTA and PPyCoCDTA as low-spin diamagnetic Co(III).

The EPR spectra of PPyFeEDTA and a counteranion composite, PPyFe/CoEDTA, are shown in Figure 9. In each spectrum resonances are observed with g values of 2.0, 4.2, and 9.3. The g = 2.0 resonance is attributed to radical species located on the polypyrrole chains.[35,59] The low-field signals (g = 4.2 and 9.3) typify a rhombic type spectrum and are consistent with $FeEDTA^-$ containing high-spin ferric iron.[60] The absence of a broad resonance in the g = 2.0 region shows that the FeEDTA counteranions are monomeric,[61] which is in agreement with the Mössbauer data (see below). Comparing the relative broadness of the g = 4.2 line in each spectrum, it is evident that the incorporation of diamagnetic CoEDTA counteranions leads to a reduction of the line width. This shows that spin–spin relaxation is the major cause of the line-broadening present in the spectra.

The spectra of PPyCrEDTA and PPyCr/CoEDTA are shown in Figure 10. The resonances at g = 2.0 are also ascribed to polypyrrole (see above). The remaining features are not centered around g = 2.0 and are well defined at low field, indicating Cr(III) containing a large zero-field splitting of the $^4A_{1g}$ ground state.[62] These spectra

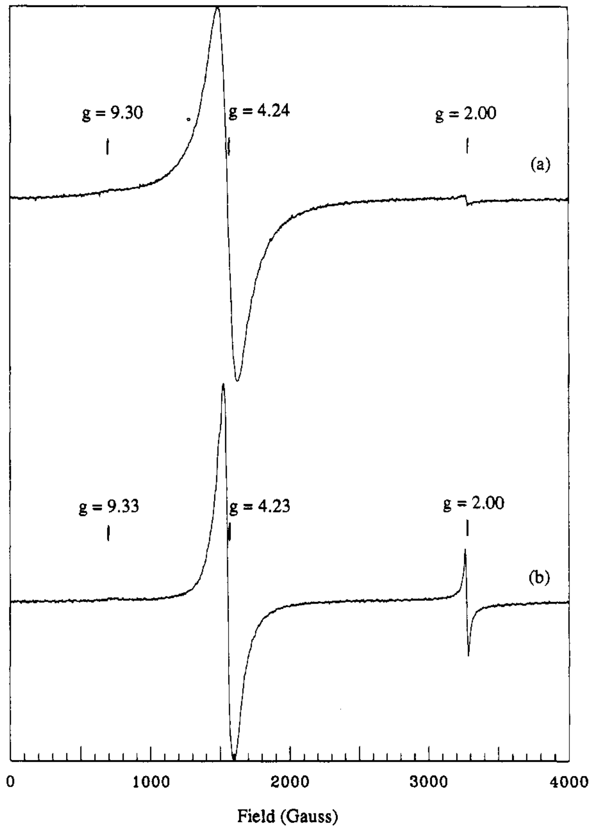

Figure 9. X-band EPR spectra of (a) PPyFeEDTA and (b) PPyFe/CoEDTA showing effective g values.

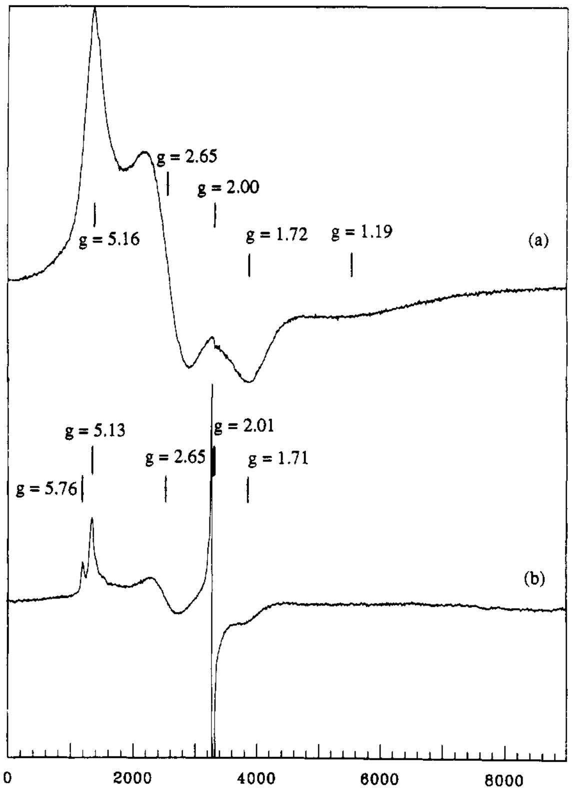

Figure 10. X-band EPR spectra of (a) PPyCrEDTA and (b) PPyCr/CoEDTA showing effective g values.

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do not exclude the presence of Cr(II) since the latter, with ^5E_g ground state, is EPR inactive. However, in view of the low redox potential of the $[Cr^{II/III}EDTA]^{2-/-}$ couple (see above), it is unlikely that Cr(II) exists within PPyCrEDTA or PPyCr/CoEDTA. Substitution of some of the CrEDTA counteranions with $CoEDTA^-$ leads to a reduction in spin–spin broadening and additional low-field features are resolved (see Figure 10b). With the exception of the line at $g = 2.0$, the spectrum bears a close resemblance to that reported for magnetically dilute NaCrEDTA,[63] and is almost identical to that obtained from a frozen water–methanol–dimethylformamide solution of NaCrEDTA (not shown). However, the equivalent frozen solution spectrum of CrHEDTA (not shown) was very different from that of PPyCr/CoEDTA, and the line positions of CrHEDTA were almost identical to those reported[64] for $Cr(bpy)_2(ox)^-$. The crystal structures of NaCrEDTA and CrHEDTA have shown sexadentate and quinquedentate coordination of the $EDTA^{4-}$ chelate, respectively.[65,66] Therefore, the correlations presented above provide strong evidence that the CrEDTA counteranions within PPyCrEDTA and PPyCr/CoEDTA contain $EDTA^{4-}$ coordinated in a sexadentate fashion. The ability to discern the coordination differences discussed above arises from the sensitivity of the EPR spectra of $CrEDTA^-$ to changes in the rhombic distortion parameter, E, and the axial zero-field parameter, D.

We recently reported evidence of a magnetic interaction in polypyrrole films containing paramagnetic counteranions.[17] This is apparent as a reduction of the signal intensity originating from the polymer radical species in the presence of counteranions containing paramagnetic metal ions. The substitution of some of the paramagnetic counteranions with a diamagnetic equivalent should result in an increase in the intensity of the signal from polypyrrole. The spectra of PPyMEDTA and PPyM/CoEDTA (M = Cr and Fe) are in accord with this since the intensity of the $g = 2.0$ signal is stronger in the latter. Similarly, Han et al. found that the introduction of $Co^{II}Cl_4^{2-}$ led to a decrease of the signal intensity originating from polypyrrole.[67] The precise nature of the magnetic interaction is not known at present.

Mössbauer Spectroscopy. Mössbauer spectroscopy has been shown[33,68,69] to be very useful for the study of the nature and the environment of the counteranion incorporated into polypyrrole, and here we have investigated PPyFeEDTA. The spectra at room temperature and 4.2 K are shown in Figure 11. Both spectra are repeatable and complex and there is no guarantee that a unique fit has been obtained for either. The parameters for the preferred fits are given in Table 3, together with the parameters for the parent salt, NaFeEDTA. The latter are similar to those reported elsewhere.[70,71] Stein et al.[71] have noted that dimeric species containing $FeEDTA^-$ possess quadrupole splitting values that are relatively large for high-spin ferric systems. From the values of the quadrupole splitting shown in Table 3, it is concluded that the counteranions are exclusively monomeric in PPyFeEDTA.

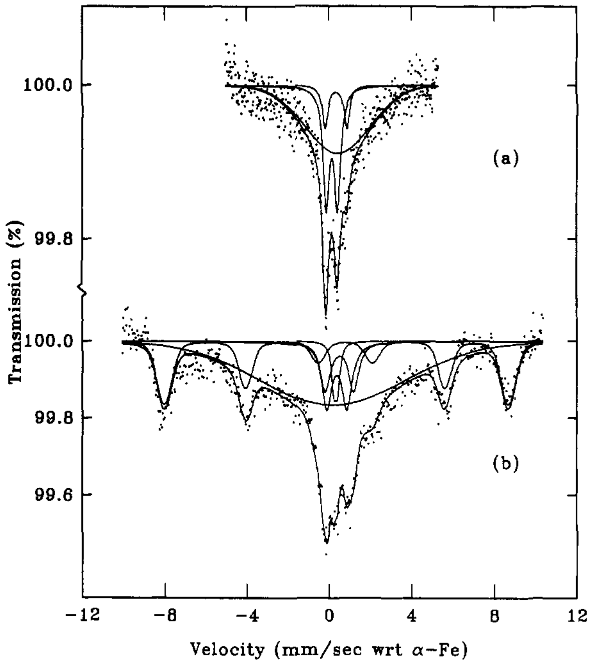

Figure 11. Mössbauer spectra of PPyFeEDTA obtained in zero applied field at (a) room temperature and (b) 4.2 K.

Table 3. Mössbauer Parameters for NaFeEDTA and PPyFeEDTA[a]

sample	T (K)	δ (mm s^{-1})[b]	ΔE_Q (mm s^{-1})	Γ (mm s^{-1})[c]	H_{int} (T)[d]	area (%)
NaFeEDTA	room	0.48 (1)	0.71 (2)[e]	0.86		100
PPyFeEDTA	room	0.13 (3)	0.54 (5)	0.36		30
		0.33 (7)	1.05 (13)	0.32		10
		0.41 (9)			Gaussian	60
PPyFeEDTA	4.2	0.2 (3)			Gaussian	53
		0.32 (5)	0.18 (5)	0.28		3
		0.37 (5)	0.98 (5)	0.58		11
		0.49 (5)	1.37 (5)	0.58		8
		0.55 (2)	−0.22 (2)[f]	0.70	52 (1)	25

[a] Values in brackets are the error (2 standard deviations) on the last digit. [b] Relative to metallic iron at room temperature. [c] Full width at half-maximum height. [d] Magnetic hyperfine field. [e] Doublet was asymmetric. [f] Value for $\epsilon \equiv {}^1/_4 e^2qQ$.

The room-temperature spectrum was fitted to the superposition of two symmetrical doublets and a Gaussian for the broad wings, although it is recognized that the restriction that the doublets be symmetrical is not always followed in these materials. The isomer shift of the Gaussian (Table 3) is indicative of high-spin Fe(III) and the species is attributed to $FeEDTA^-$ in an environment in which the spin relaxation and the Larmor precession frequencies are comparable. The doublet with the larger quadrupole splitting is attributed to a highly distorted $FeEDTA^-$ species, and the increased splitting compared to that in NaFeEDTA is most probably the result of a polymer···counteranion interaction. Similar behavior was reported[68] for polypyrrole containing $FeCl_4^-$ and attributed to the presence of hydrogen bonding between the counteranion and the polymer. Since each FeEDTA counteranion contains eight oxygen atoms, hydrogen bonding could also be present in PPyFeEDTA.

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The origin of the doublet with the smaller splitting is less clear. The isomer shift is slightly lower than that observed for high-spin Fe(III), implying that the iron nucleus has a higher s-electron density. This could result from an interaction between the $FeEDTA^-$ species and polypyrrole that involves either conduction electrons or partial electron donation from the polymer to the iron nucleus. In this context it should be noted that the transfer of electrons from polypyrrole to the incorporated counteranion has been reported[33] for polypyrrole containing $Fe(CN)_6^{4-}$.

The low-temperature spectrum (Figure 11b) shows a much more pronounced magnetic splitting with a well-defined sextet, a broad absorption due to unresolved magnetic structure which has been fitted to a Gaussian, and a central region for which several fitting combinations of doublets and a narrow Gaussian were tried. The fit shown uses three doublets, which produced the lowest misfit and appeared the best visually, but the parameters must be treated with caution.

The isomer shift of the sextet agrees well with that from the room-temperature Gaussian after allowing for the thermal shift, suggesting that part of the intensity from the Gaussian has had sufficient change in relaxation time to show resolved structure. The line width of the sextet is very broad so that the tabulated hyperfine field of 52 T is really an average over a distribution 2–3 T wide. These values are close to the reported value of 55 T for magnetically dilute FeHEDTA[72] containing $EDTA^{4-}$ coordinated in a quinquedentate manner. We are not aware of any values of H_{int} for solid $FeEDTA^-$ containing sexadentate $EDTA^{4-}$. In view of the uncertainty in the uniqueness of the parameters and the lack of literature data on the hyperfine fields, it is not possible at this point to decide whether the coordination of the $EDTA^{4-}$ to the iron is sexadentate or quinquedentate.

The observation of both magnetic relaxation and nonmagnetic contributions to the spectra at room temperature and 4.2 K indicates that the counteranions are contained in at least two physically different environments within PPyFeEDTA. It is difficult to make a simple correlation between the areas of the subspectra which are due to the same phase for each of the two spectra. The counteranions which contain the iron atoms showing magnetic structure must be well separated from each other and effectively diluted by the polymer. The remaining counteranions must be reasonably closely associated, giving an increased spin–spin relaxation rate and thus an absence of resolved magnetic structure. Combining these data with those from X-ray diffraction (see above) suggests that the closely associated counteranions must reside within aggregates. Over half the intensity is from subspectra displaying resolved or unresolved magnetic splitting at both temperatures, so that it would seem that the majority of the counteranions reside in the dilute environment.

It has been reported[73,74] that the Mössbauer lattice temperatures found in conducting polymers are quite low. In the case of polypyrrole containing $FeCl_4^-$ and $SnCl_5^-$ no resonant absorption was observed at room temperature, and this has been ascribed[73] to an extremely loose bonding between the inserted counteranions and the polymer chains. However, this is not a general observation, and the room-temperature spectra of PPyFeEDTA (Figure 11a) and polypyrrole containing iron tetrasulfonated phthalocyanine[17] show resonant absorption. In the latter polymers the iron nuclei are coordinated to relatively large chelates, which provide additional vibrational stability. This bonding then dominates over the polymer··· counteranion bonding and higher Mössbauer lattice temperatures result. Thus it is possible for the relative areas of the subspectra to change dramatically due to the temperature dependence of the recoilless fraction.

Conclusions

From the work presented above, the following conclusions may be drawn:

(1) The conductivities of PPyMEDTA (M = Co, Cr, and Fe) and PPyMCDTA (M = Co and Fe) are strongly dependent on the choice of metal ion contained within the counteranion.

(2) The environmental stability of the conductivity of polypyrrole is influenced by the size and shape of the incorporated counteranion. Spherical counteranions of moderate size (MEDTA, M = Co, Cr, and Fe) appear to be effective in retarding the rate of chemical attack of the polymer backbone by oxygen.

(3) TEM investigations of thin films of PPyCoEDTA reveal some crystallinity. The X-ray diffraction data obtained on thicker films show that, for the polymers containing metal chelates, the CoEDTA counteranion confers the highest degree of order on the polypyrrole chains. It is suggested that PPyMEDTA and PPyMCDTA consist of stacked polypyrrole chains and aggregated counteranion layers with no preferred orientation.

(4) The EPR spectra are consistent with a magnetic interaction between the unpaired electrons of the polymer and the paramagnetic metal ion centers contained in the counteranions. The coordination of the $EDTA^{4-}$ chelate within PPyCrEDTA is sexadentate as judged by the EPR line shapes.

(5) The low-temperature Mössbauer spectrum of PPyFeEDTA has shown that the FeEDTA counteranions reside in both aggregated and well-dispersed environments within the material. The incorporation of relatively large counteranions (such as $FeEDTA^-$) results in an increase in the Mössbauer lattice temperature compared to that observed[73] for polypyrrole containing $FeCl_4^-$.

(6) The metal ions contained within PPyCoEDTA and PPyCrEDTA exist in the trivalent oxidation state. For PPyFeEDTA, the presence of Fe(III) has been indicated by both the EPR and Mössbauer data. However, the latter reveal that some of the ferric species have additional s-electron density.

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