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PREPARATION AND CHARACTERIZATION OF NEUTRAL AND OXIDIZED POLYPYRROLE FILMS

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Oxidized and neutral films of polypyrrole have been prepared electrochemically in the absence of oxygen and water. The neutral films are insulating and can be readily oxidized by chemical oxidizing agents to give films of greater conductivity than can be achieved by electrochemical oxidation. Optical spectroscopy provides evidence for the similarity of the polymeric carbonium ion produced by both types of oxidation. NMR studies are consistent with the α,α' bonding in these polymers; they also show the expected downfield shifts relative to the neutral polymer on both chemical and electrochemical oxidation. ESR studies of both the electrochemically oxidized and the neutral polymer suggest the presence of highly mobile spins.

INTRODUCTION

Conducting materials derived from pyrrole by acid catalysis or anodic oxidation have been reported for several years.[1] However, there was little motivation for their characterization until Kanazawa et al.[2,3] showed that electrochemically prepared films[4] had a metal-like thermopower and were quite stable. Unfortunately, their lack of crystallinity, complete insolubility, and poorly defined stoichiometry have impeded the characterization of these materials. In an attempt to control the preparation of the films more closely, we have now carried

out the polymerization under rigorous exclusion of oxygen and water. In this paper, we present the details of this preparation and experiments to characterize both insulating neutral polypyrrole (PP°) and conducting electrochemically oxidized polypyrrole (PP^{+}).

FILM PREPARATION

Attempts to grow polypyrrole films in the dry box using the technique of Diaz et al.[4] but with no added water and very carefully dried, deoxygenated acetonitrile and carefully dried tetrabutylammonium perchlorate TBAP were not successful. In the absence of water, no film is formed unless oxygen is deliberately added to the TBAP - acetonitrile electrolyte solution. Apparently, under the Diaz et al.[4] conditions, oxygen or water is required as a reducible species for the counter-electrode reaction. This problem was resolved by using silver salts as the electrolyte, thereby providing the facile cathode reaction $Ag^{+}+e \rightarrow Ag^{\circ}$. Besides being compatible with dry box operation, this cathodic reaction is attractive because the silver plates out on the cathode and does not contaminate the film formation at the anode. In a typical film growth experiment, the cathode is a 3×1 inch microscope slide wound with silver wire and the anode is a similar microscope slide, either plated with platinum or coated with conducting tin oxide. The electrolyte is carefully dried and purified[5] $AgClO_4$ (0.1 molar) in dry deoxygenated acetonitrile. The films are grown in a one compartment cell with a constant applied voltage of 0.5V. In order to avoid contamination, no reference electrode is used during normal film growth, however, it was established that when the applied voltage is 0.5V, the working electrode was poised +0.7V relative to SCE. Under these film growth conditions, the current rapidly becomes constant at ~1 ma and 4000Å films grew in 30 minutes. Thick films are a shiny copper-bronze color; thin transparent films are grey. The room temperature electrical conductivity of the films is ~50 ohm^{-1} cm^{-1}.

Cyclic voltammetry showed that in the presence of Ag salts, the peak anodic current occurred at about 0.2 volts less positive than with TBA salts suggesting that in the presence of silver salts, the pyrrole is easier to oxidize. In fact, as described below, crystalline complexes of pyrrole can be formed with silver salts.

Chemical analysis of these films gave a composition of $C_{3.94}N_{1.0}H_{3.37}(ClO_4)_{0.33}$. The perchlorate content of the films suggests there are approximately three pyrrole rings per perchlorate anion as shown in the idealized structure in Fig. 1 where we assume only α,α' linkages. Relative to this ideal structure, the films are

hydrogen rich suggesting that some of the pyrrole rings may have been hydrogenated. Evidence for aliphatic as well as aromatic C-H in these films is obtained from IR studies. Attempts to produce films with the stoichiometry of the ideal composition shown in Fig. 1 have not been successful.

Films of neutral polypyrrole were prepared by reducing the oxidized films in dry deoxygenated acetonitrile containing 0.1M dried TBAP. The reduction was affected in a one compartment cell using a gold wire wound anode with an applied voltage of 2.3 volts. The maximum thickness of the film which could be reduced in this way was ~5000Å. These films were readily removed intact from the substrate. The absence of ClO_4^- in these neutral film was confirmed by energy dispersive x-ray analysis (EDX) and also by electron spectroscopy (XPS). The neutral films are insulating with conductivities $<10^{-5}$ ohm^{-1} cm^{-1} depending on previous history.

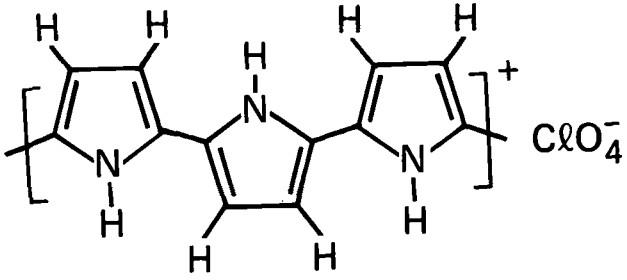

FIGURE 1 Ideal stoichiometry of pyrrole perchlorate.

PYRROLE-SILVER ION COMPLEX FORMATION

White polycrystalline complexes are precipitated when pyrrole is added to toluene solutions of silver perchlorate or tetrafluoroborate. Thermal analysis is consistent with two pyrroles per silver ion and chemical analysis confirms this composition. X-ray analysis shows that both complexes are isostructural. IR spectra of KBr pellets of both complexes are dominated by the anion bands and the pyrrole moiety bands are weak, though the NH bands can be readily seen. These spectra contrast sharply with those described later for PP^+ films where the pyrrole moiety bands dominate the spectra. ^1H NMR of the pyrrole-Ag salt solution in CD_3CN shows that the complex is largely dissociated in solution. However, evidence that the presence of Ag ions

in the environs of the working electrode is important in the electrochemical oxidation of the pyrrole was obtained from cyclic voltametry in a two-compartment electrochemical cell. If TBAP was used as the electrolyte salt in both halves of the cell, the peak anodic current occurred at +1.32V (versus SCE). Similar results were obtained if the TBAP in the counter-electrode compartment were replaced by $AgClO_4$. However, if the TBAP in the working electrode compartment is replaced by $AgClO_4$, the peak anodic current occurred at +0.96 volts under corresponding conditions. These results suggest the silver is not only providing a convenient cathode reaction, but is also involved in the film formation reaction at the anode, however, no silver is found in the resulting films either by chemical analysis or EDX.

These pyrrole silver complexes are of interest in another respect because conducting polypyrrole films form on the walls of flasks containing the precipitated complex and toluene. These films can be large in area, though they are not of good quality. X-ray analysis shows that the films contain free silver. These films are conducting and show an order of magnitude decrease in conductivity on exposure to NH_3 vapor. This behavior[2] is characteristic of electrochemically prepared polypyrrole films and we assume they are similar. The mechanism of their formation is not obvious, however, if the complexes are assumed to decompose to form neutral polypyrrole films, then as we shall discuss later, Ag^+ solutions would oxidize these neutral polypyrrole films to give conducting films. The reaction is analogous to the oxidation of neutral $(CH)_x$ by silver tetrafluoroborate solutions in toluene.[6] Neutral polypyrrole is, however, even more readily oxidized than $(CH)_x$, as would be expected from their measured oxidation potentials.[7]

REACTION OF NEUTRAL AND ELECTROCHEMICALLY OXIDIZED POLYPYRROLE FILMS WITH OXYGEN

UV-Visible Spectra

Thick films of electrochemically oxidized polypyrrole perchlorate prepared in the dry box using $AgClO_4$ as the electrolyte are shiny copper-bronze when viewed in reflection. On standing in air over a period of about two weeks, the films slowly darken. The weight of the films does not significantly change during this process nor does the conductivity. However, over periods of several months, the conductivity does begin to decrease. The yellow/green films of the neutral polymer are much more sensitive to air and oxygen. They

become quite black in a period of 15 minutes. The oxygen uptake determined by weighing is 0.07 moles/mole of pyrrole after exposure to dry oxygen for ~12 hrs.

The influence of oxygen on the optical properties of both forms of the polymer is shown in Fig. 2 and 3. These data were obtained for pyrrole film samples electrochemically deposited on nesa glass microscope slides. The upper half of the microscope slide was removed from the electrochemical cell while the lower half of the film, still immersed in the cell, was reduced using the conditions described earlier. Thus, the upper half of the slide was a grey-colored transparent film of the oxidized polymer, whereas the lower half of the slide was a transparent yellow/green film of the reduced neutral polymer. The absorption data for the polypyrrole perchlorate film before exposure to

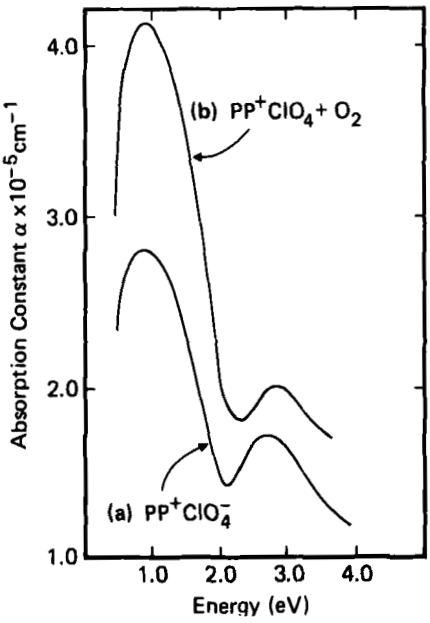

FIGURE 2 Optical absorption curves of polypyrrole (a) before and (b) after exposure to oxygen.

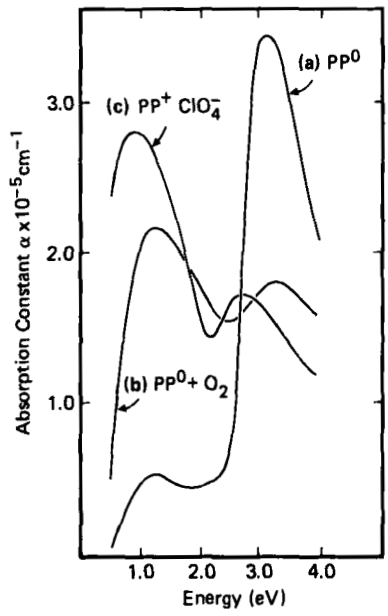

FIGURE 3 Optical absorption curves for (a) neutral polypyrrole after exposure to oxygen; (b) neutral polypyrrole after exposure to oxygen; (c) polypyrrole perchlorate.

oxygen is shown in Fig. 2(a). These absorption data for the oxidized film are similar to those reported previously by Kanazawa et al.[3] These authors interpreted the broad band peak near 1.0 eV as due to the conduction electrons. The peak near 3.0 eV was associated with an interband transition perhaps derived from the π-π^* transition of the pyrrole moiety which occurs at ~6 eV in pyrrole monomer.[8] On exposing the grey film of oxidized pyrrole to half atmosphere of dry oxygen, the intensity of the ~1.0 eV "free carrier" peak increases significantly Fig. 2(b). After pumping for several hours at 10^{-6} Torr, the ~1.0 eV peak decreased to α~3.5 cm^{-1}.

The absorption spectrum of the yellow/green neutral pyrrole before exposure to oxygen, Fig. 3(a), shows two peaks. The major one at ~3.2 eV and a smaller peak near 1.3 eV. The yellow/green film of neutral pyrrole rapidly becomes black on exposure to oxygen and the ~3.2 eV peak height decreases by a factor of two; the low energy 1.3 eV peak increases until it becomes the dominant peak. The general appearance of the spectra of this film is very similar to that of electrochemically oxidized pyrrole (Fig. 2(c)) though there are some small shifts in the energy of the two peaks. It is interesting to note that for both PP^+ and PP° reaction with oxygen leads to an increase in the intensities of peaks in the 1 eV region, which have been associated with the free carriers. This increase in intensity is accompanied by an increase in the conductivity of the neutral polymer from $<10^{-5}$ ohm^{-1} cm^{-1} to 10^{-2} ohm^{-1} cm^{-1}, however, the conductivity of the PP^+ does not increase. This suggests that the ~1.0 eV peak is not directly associated with free carriers. This peak is probably not intrinsic to the neutral polymer but reflects partial oxidation of the neutral polymer.

Infrared Spectra

Figure 4(a) shows the IR transmission spectrum of a thin, free standing film of polypyrrole perchlorate. The region below 1800 cm^{-1} contains bands consistent with the pyrrole moiety; the perchlorate anion bands are not visible but are apparently obscured by the pyrrole bands. Similarly, the NH and CH bands expected around 3400 cm^{-1} and 3100 cm^{-1} are not visible. However, on electrochemical reduction of the polypyrrole perchlorate film the NH and CH band at 3400 cm^{-1} and 3100 cm^{-1} are visible in the resulting neutral film, Fig. (4(b)), together with bands between 2870 and 2960 cm^{-1} probably arising from aliphatic C-H stretches (consistent with the ~10% excess hydrogen in the chemical analysis). In the region below 1800 cm^{-1}, the spectra of both the electrochemically oxidized and the neutral film are similar but not identical. Figure 4(c) shows the data for the same

neutral film used in Fig. 4(b) after exposure to 1/2 atmosphere of dry oxygen for ~1 hour. The NH and CH vibrations are no longer visible as in Fig. 4(a) and the region below 1800 cm^{-1} is now almost identical to that in Fig. 4(a). Thus, the IR data and the optical absorption data both suggest that the chemical oxidation of neutral polypyrrole with oxygen produces a similar polymerication to that present in the original electrochemically oxidized material.

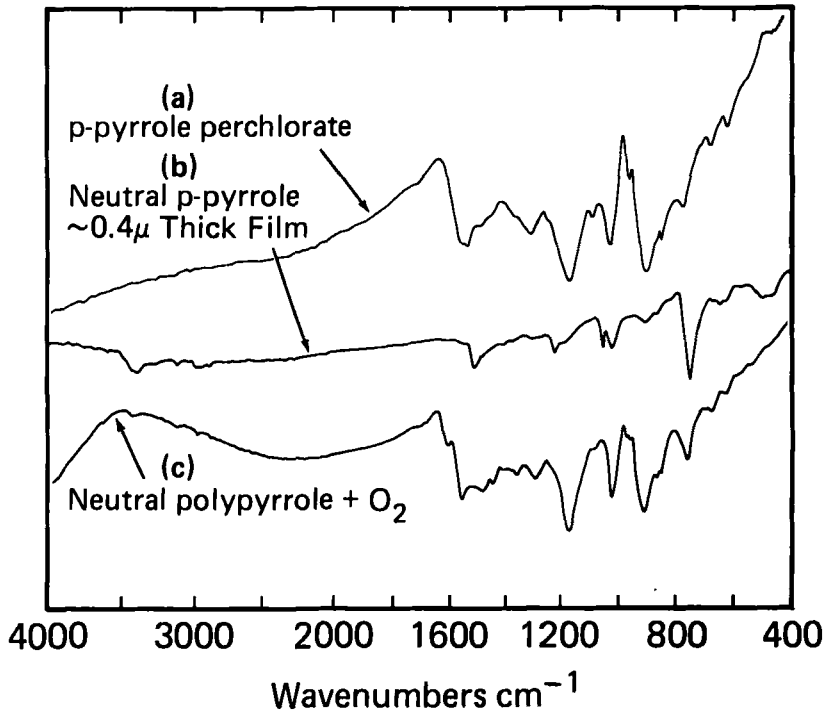

FIGURE 4 (a) IR transmission spectrum of polypyrrole perchlorate; (b) IR transmission spectrum of neutral polypyrrole; (c) IR transmission spectrum of neutral polypyrrole exposed to oxygen.

The reasons for the low intensity of the NH and CH bands in the electrochemically oxidized polymer relative to the neutral polymer and the absence of bands due to the anion in the electrochemically oxidized polymer are uncertain at this time. However, these effects may be

explained in terms of a vibronic enhancement mechanism similar to that proposed to explain the changes in the IR spectrum of $(CH)_x$ on oxidation.[9]

Chemical Oxidation of Neutral Polypyrrole

The low oxidation potential of neutral polypyrrole suggests that these films should be oxidized by a variety of oxidizing agents as is the case for polyacetylene.[6] We have shown that neutral polypyrrole films can be oxidized by various metal salt solutions including Ag^+, Cu^{2+}, and Fe^{3+}. The resulting oxidized films are more conducting than oxygen treated films, but less conducting than the electrochemically oxidized films. Bromine and iodine vapors also readily oxidize the neutral films to give highly conducting material. In the case of iodine, the conductivity exceeds that of the electrochemically oxidized films reaching values of at least 600 ohm^{-1} cm^{-1}. The nonoxidizing proton acid, HF vapor, also reacts with neutral polypyrrole to give conductivities ~40 ohm^{-1} cm^{-1}.

Thus, the chemistry of doping of neutral polypyrrole seems closely analogous to polyacetylene. This is particularly remarkable in view of the absence in polypyrrole of the energy degenerate bonding schemes which are presumed to play a dominant role in the soliton mechanism of conductivity in trans-polyacetylene.[10] However, it should be pointed out that the loss of aromaticity resulting from switching of the double bonds and the single bonds in the cis-$(CH)_x$-like portion of the polypyrrole chain shown in Fig. 1 involves only about 10 kcals per pyrrole molecule.[8]

^{13}C NMR of Polypyrrole

X-ray diffraction studies of the polypyrrole perchlorate prepared in the dry box have shown it to be as highly disordered as previously prepared material.[3] Electron diffraction shows the same haloes characteristic of graphite present in earlier material.[3] Currently, this graphitic structure is under investigation to establish whether it is characteristic of polypyrrole or whether it represents an impurity. The evidence for the structure in Fig. 1 is based largely on chemical degradation studies.[1] However, we have now obtained ^{13}C NMR data for electrochemically prepared pyrrole polymers which are consistent with the predominantly α,α' bonding shown in Fig. 1. These data also confirm the presence of the pyrrole moiety and are consistent with the IR studies. The ^{13}C NMR data shown in Fig. 5 were obtained using cross polarization and magic angle spinning techniques. Figure 5(a) shows the spectrum

of a 17 mg sample of neutral polypyrrole film which was packed into a rotor. All sample handling and loading of the rotors was carried out in the dry box. In this spectrum, three peaks can be distinguished. The major peaks are shifted ~123 and ~105 ppm downfield from TMS. These peaks correspond well with the α and β carbons of the pyrrole monomer which occur at 117 and 108 ppm downfield relative to TMS.[8] The two peaks confirm the presence of the pyrrole moiety in the polymer, and the downfield shift of the α carbons relative to monomeric pyrrole is consistent with α,α' linkages.[8] The third peak at ~135 ppm probably indicates the presence of some non α,α' linkages, e.g., α-β linkages though it could also be due to carbons in chain terminating groups. Figure 5(b) shows the spectrum of a sample of the electrochemically oxidized polypyrrole perchlorate. This conducting sample was dispersed by grinding with glass powder and loaded into the rotor in the dry box.

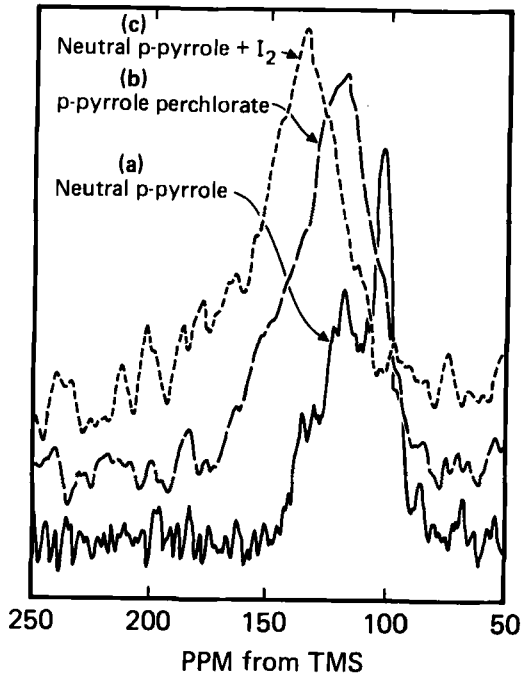

FIGURE 5 ^{13}C NMR spectra of (a) neutral polypyrrole; (b) polypyrrole perchlorate; (c) neutral polypyrrole reached with iodine.

The spectrum shows a very broad asymmetric peak shifted downfield relative to the neutral polypyrrole and consistent with the removal of the π electrons, and the formation of a polymeric pyrrole carbonium ion. Figure 5(c) shows the spectrum of a sample of neutral polypyrrole after oxidization with iodine vapor to give a highly conducting film. This sample contained 0.9 I/pyrrole ring and was also dispersed by grinding in the dry box using glass powder. The downfield shift relative to neutral polypyrrole was greater than that of the electrochemically oxidized polypyrrole perchlorate, indicating a higher degree of oxidation consistent with the higher conductivities observed for the iodine treated samples. Although these downfield shifts for the oxidized samples are consistent with oxidation to form carbonium ions, there may also be a contribution from a Knight shift.

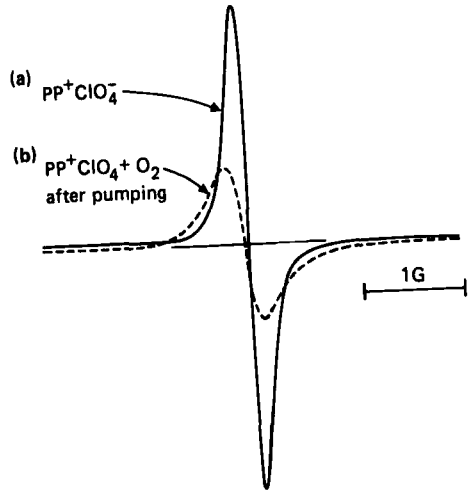

FIGURE 6 ESR spectra of polypyrrole perchlorate (a) before exposure to oxygen, and (b) after exposure to oxygen and pumping.

ESR of Polypyrrole

The ESR spectrum of dry box prepared polypyrrole perchlorate is shown in Fig. 6(a). The line width is remarkably narrow 0.2-0.3 Gauss. This can be compared with 0.7G for trans-polyacetylene where the carriers are presumed to be highly mobile solitons.[10] This narrow line width implies highly mobile spins in polypyrrole perchlorate.

Exposure to oxygen broadens the line dramatically to ~30G and it is lost in the base line of Fig. 6. It should be recalled that such short term exposure to oxygen does not significantly effect the conductivity of p-pyrrole perchlorate though it does effect the optical spectra (see Fig. 2). On pumping, the original line begins to grow back though it remains broadened (Fig. 6(b)). This partial reversibility of the reaction with oxygen was also observed in the optical spectra. The ESR spectrum of the neutral polymer is very similar to that shown for the conducting polypyrrole perchlorate suggesting that similar highly mobile spins are present in the insulating polymer where they are presumably confined to the chains. The concentration of the spins in the neutral polymer is ~1 spin/3000 pyrrole rings. Comparison of the results from transport measurements with the optical and ESR data strongly suggest that the spins seen in ESR are not involved in the transport process.

CONCLUSIONS

Electrochemically prepared films of polypyrrole prepared in the absence of air or water are reactive to oxygen. In the case of the conducting electrochemically oxidized films, the oxygen has no immediate effect on the conductivity of the film, though it may play a role in the slow deterioration of the conductivity over a period of several months. Reaction of the neutral films with oxygen causes changes in the IR spectrum, consistent with the formation of an oxidized polymeric carbonium ion structure similar to the electrochemically oxidized material. These findings are also confirmed by spectra in the UV-visible region. NMR studies are consistent with the presence of the pyrrole moiety bonded together by primarily α,α' linkages though, there are probably a number of α,β linkages. On oxidation of the neutral polymer to the conducting state, either electrochemically or chemically, the NMR spectrum reveals the anticipated carbonium ion shifts. The ESR spectra of both electrochemically oxidized and neutral polypyrrole have very narrow lines indicative of highly mobile spins.

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