

Investigations of the Chemical Interactions between Molecular Oxygen and Pristine (Undoped) Polypyrrole

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Polypyrrole is unique among the heterocyclic conductive polymers in that the undoped (i.e., pristine) form of the polymer is oxidized by molecular oxygen. Because of the O₂ reactivity of pristine polypyrrole, it has been difficult to prepare and characterize the pristine material. We have recently solved this problem through the use of a rigorously airtight infrared spectroelectrochemical cell. This new spectroelectrochemical cell has provided an opportunity to explore the fundamental chemistry of the interaction between molecular oxygen and pristine polypyrrole. We have found that pristine polypyrrole interacts with O₂ via three primary pathways. The first entails partial electron transfer to O₂ to form a molecular association complex. Such complexes have been observed for monomeric pyrroles. The second process is analogous to oxidative doping and involves complete electron transfer to form the polycationic version of the polymer with the superoxide anion as the counterion. Finally, after long times (i.e., hours) the superoxide anion deprotonates the polymer to yield an imine form of polypyrrole.

Introduction

Polypyrrole is one of the most intensely investigated of the electronically conductive polymers.¹⁻¹⁰ Polypyrrole is unique among the heterocyclic conductive polymers in that the undoped (i.e., pristine)^{4,5} form of the polymer is oxidized by molecular oxygen. The other common heterocyclic conductive polymers (e.g., polythiophene, poly(*N*-methylpyrrole)) have redox potentials that are sufficiently positive that the pristine forms are not oxidizable by O₂. Because of the O₂ reactivity of pristine polypyrrole, it has been difficult to prepare and characterize the pristine material.^{4,5,8} We have recently solved this problem through the use of a rigorously airtight infrared spectroelectrochemical cell.^{4,5}

This new spectroelectrochemical cell has provided an opportunity to explore the fundamental chemistry of the interaction between molecular oxygen and pristine polypyrrole.^{1-3,10} We have found that pristine polypyrrole interacts with O₂ via three primary pathways. The first entails partial electron transfer to O₂ to form a molecular association complex. Such complexes have been observed for monomeric pyrroles.¹¹⁻¹³ The second

process is analogous to oxidative doping and involves complete electron transfer to form the polycationic version of the polymer with the superoxide anion as the counterion.^{3,10} Finally, after long times (i.e., hours) the superoxide anion deprotonates the polymer to yield an imine form of polypyrrole. The results of these investigations are described in this paper.

Experimental Section

Materials. Pyrrole monomer (Aldrich) was purified by fractional distillation and stored under nitrogen. Lithium perchlorate and tetrabutylammonium perchlorate (Fisher Scientific Company and Aldrich) were twice recrystallized from ethanol and dried in vacuo prior to use. The solvent for all electrochemical experiments was rigorously-dried^{4,5} acetonitrile. Unless otherwise noted LiClO₄ was used as the supporting electrolyte for the electrochemical experiments. Polypyrrole films were synthesized electrochemically as described in our previous papers;^{4,5} 400-nm-thick films were used in these studies.

Equipment and Protocol. The spectroelectrochemical cell employs an infrared-transparent working electrode that also serves as the window for the cell.^{4,5} The diameter of this working electrode/window is 16 mm.⁴ The counter electrode is a Pt wire. The reference is an aqueous SCE; all potentials are quoted relative to this reference. The cell is mounted inside the sample chamber of a Mattson Galaxy 4021 FTIR spectrometer.

The general protocol for obtaining FTIR spectroelectrochemical data with this cell is as follows:^{4,5} (1) Electrochemically synthesize the film in the cell using a solution of the electrolyte plus monomer. This yields the ClO₄⁻-doped form of the polypyrrole. (2) Drain the cell and then rinse and dry⁴ the doped film. (3) Fill the cell with the electrolyte solution. (4) Reduce the doped form of the polymer at -0.8 V to generate the pristine polymer.^{4,5} (5) Disconnect the potentiostat and drain the cell. (6) Rinse and dry the film. (7) Expose the pristine polymer to O₂ by admitting 1 atm of pure O₂ into the cell. (8) Obtain the desired FTIR data. (9) Add electrolyte again and do other desired electrochemistry on the O₂-exposed film.

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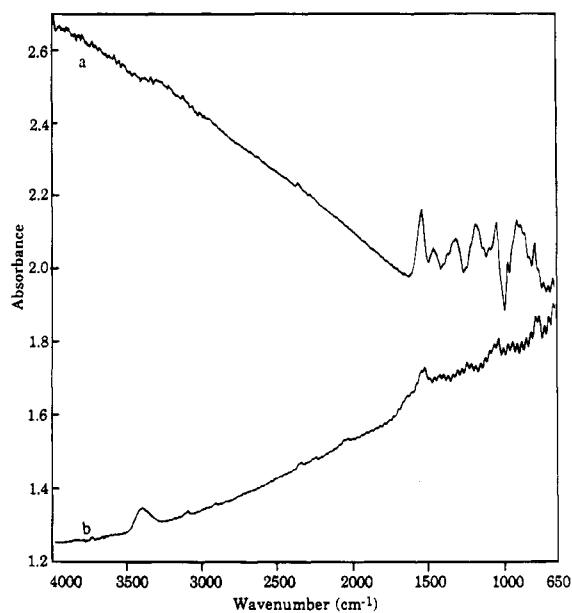


Figure 1. FTIR spectra for as-synthesized (fully ClO_4^- -doped) polypyrrole (curve a) and for the same film after reduction at -0.8 V (i.e., for a pristine film, curve b).

Note that the electrolyte is removed from the cell when the infrared data are obtained.^{4,5} This is essential because the infrared absorbance by the solvent and electrolyte would overwhelm the signal due to the thin polymer film. One might worry that drying the O_2 -exposed film (which is done by exposure to a stream of Ar)⁴ might cause loss of O_2 from the film. Scott et al. have shown, however, that an O_2 -exposed film can be evacuated (10^{-6} Torr) for prolonged periods of time and only negligibly-small amounts of O_2 (less than 0.2%) are lost from the film.³ Hence, the O present in the O_2 -exposed film is strongly bound.

X-ray photoelectron spectroscopy (XPS) was used to determine the O content of the polypyrrole films, to explore how oxygen affects the chemistry of the ring nitrogen and to determine the doping level of the as-synthesized (ClO_4^- -doped) polymer. We have made extensive use of such XPS measurements in our prior studies.^{6,7} XPS data were obtained with a Hewlett Packard 5950 spectrometer. The doping level of the as-synthesized polymer was found to be 28%. Finally, Li^+ analyses (see below) were obtained using a Varian AA-175 atomic absorption spectrophotometer.

Results and Discussion

Investigations of this type were conducted several years ago by Street et al.,¹⁻³ who correlated measurements of O_2 uptake by pristine polypyrrole with electron paramagnetic resonance and conductivity data. These investigations provided evidence for the concept of polarons and bipolarons in polypyrrole.^{2,3} However, the nature of the molecular-level interaction between O_2 and the pristine polymer was not elucidated.

FTIR Spectra of Polypyrrole before Exposure to O_2 . A typical infrared spectrum for an as-synthesized ClO_4^- -doped polypyrrole film is shown as curve a in Figure 1. This spectrum shows a featureless absorption tail at energies above 1600 cm^{-1} and a series of bands below 1600 cm^{-1} .⁴ The featureless tail is due to free-carrier absorption and is a unique signature of the conductive state.⁴ We and others have discussed the origins of the various bands observed below 1600 cm^{-1} ,^{4,8,9} as we shall see, these are also characteristic of the doped, electronically conductive, form of the polymer.

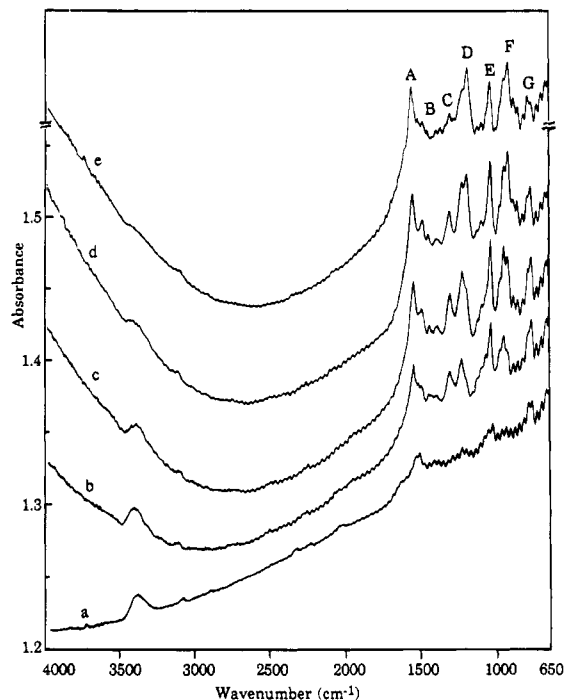


Figure 2. FTIR spectra for a pristine film after various times of exposure to 1 atm of O_2 . Exposure times were (a) 0 s, (b) 15 s, (c) 30 s, (d) 60 s, (e) 30 min.

A typical FTIR spectrum for a pristine (i.e., electrochemically undoped⁴) polypyrrole film is shown as curve b in Figure 1. Note that the free carrier absorption is not present in the pristine polymer. This proves that an electronically insulating material has been obtained.^{4,5} Furthermore, the low-energy bands are dramatically diminished in intensity.^{4,5} The spectra shown in Figure 1 serve as convenient references by which to evaluate the spectral features of polypyrrole that has been exposed to O_2 .

Exposure to O_2 Results in Oxidative Doping of Pristine Polypyrrole. After the spectrum for the pristine material was recorded (Figure 1, curve b), the spectroelectrochemical cell was filled with 1 atm of O_2 . Infrared spectra were obtained at 15 s intervals after admitting the O_2 into the cell. Typical spectra are shown in Figure 2. Note that both the free-carrier absorption and the series of bands below 1600 cm^{-1} reemerge upon exposure to O_2 . The bands labeled D and F in Figure 2 are of particular importance in this regard. These bands have been called the "doping-induced" bands and have been attributed to lowering of the symmetry of the polymer upon oxidative doping.⁹ The reemergence of these spectral features indicate that exposure to O_2 results in oxidative doping of the polymer.^{3,10}

That exposure to O_2 results in doping of the pristine polymer is also supported by visual observations. Pristine polypyrrole has a green-yellow color. In contrast, doped polypyrrole is brown to black, depending on the doping level. Upon exposure to O_2 , our pristine films go from green-yellow to brown. Finally, electrical conductivity data obtained by Scott et al. also show that exposure to O_2 results in doping of pristine polypyrrole.³ Scott et al. have shown that, in analogy to chemical or electrochemical doping, exposure to O_2 causes a dramatic increase in the conductivity of pristine polypyrrole.³ It is of interest to note, however, that a maximum

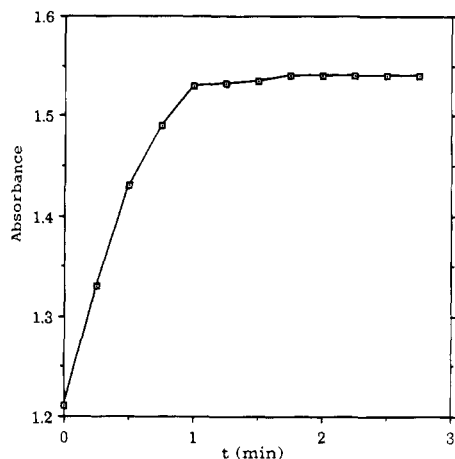
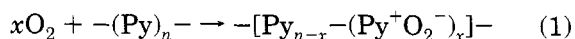


Figure 3. FTIR absorbance at 4000 cm^{-1} as a function of time after admitting 1 atm of O_2 to the cell.

conductivity of only 10^{-2} S cm^{-1} was obtained for the O_2 -exposed polymer. This is ca. 2 orders of magnitude lower than the conductivity of the fully doped material.

The simplest chemical reaction that can be written to explain the O_2 -induced doping of pristine polypyrrole is as follows:



Py in eq 1 represents a neutral (i.e., unoxidized) pyrrole monomer unit along the polypyrrole chain. Py^+ represents an oxidized monomer unit obtained after electron transfer to O_2 . O_2^- is the superoxide anion which serves as the counterion for the oxidized polymer unit. We will present independent evidence for the existence of O_2^- in the oxygen-doped films later in this paper. Suffice it to say for now that if H_2O were present in these films, the O_2^- generated (eq 1) would not survive. Water is, however, rigorously removed from the solvent and electrolyte and rigorously excluded from the spectroelectrochemical cell.⁴

Extent of Doping by O_2 . Figure 3 shows a plot of absorbance at 4000 cm^{-1} (free carrier region) vs time of exposure of the film to O_2 . Note that the free-carrier absorption reaches a plateau after 1 min of exposure. This indicates that for this film thickness (400 nm) and this pressure of O_2 (1 atm), the O_2 -doping process (eq 1) is complete in ca. 1 min. This conclusion is also supported by an analysis of the position of the doping-induced bands.⁹ Rabolt et al. have shown that the doping-induced bands in polypyrrole redshift, relative to their positions in the pristine polymer, as the polymer is doped.^{14,15} Figure 4 shows a plot of redshift of the doping-induced bands vs time of exposure of the film to O_2 . Note that in complete agreement with the free-carrier absorption data (Figure 3), the doping-induced bands redshift during the first minute of exposure to O_2 , after which no further change in position (or intensity) is observed. Figures 3 and 4 show that after 1 min of exposure to O_2 , a maximally O_2^- -doped film is obtained. We will hereafter refer to this maximally O_2^- -doped polymer as " O_2^- -doped polypyrrole".

A wealth of evidence indicates that the doping level in O_2^- -doped polypyrrole is significantly lower than the maximum achievable by electrochemical doping (28% for the films prepared here). For example, Rabolt et al. have shown that the magnitude of the redshift

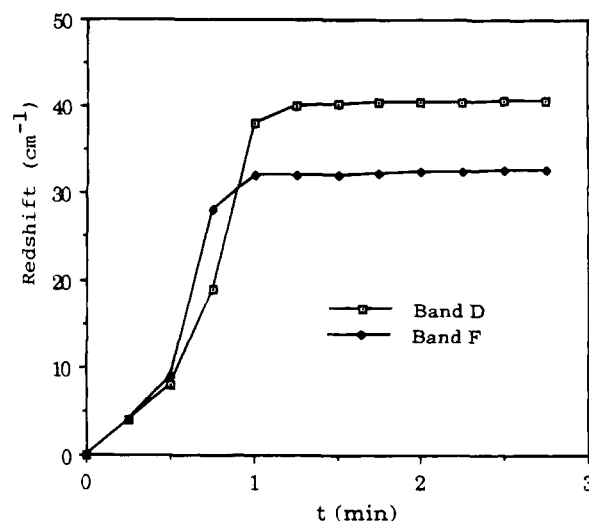


Figure 4. Redshift of the D and F bands (see text) relative to their positions in the pristine polymer as a function of time after admitting 1 atm of O_2 to the cell.

(relative to the pristine material) in the D and F bands (Figure 4) can be used as a qualitative measure of the doping level.^{14,15} Note that the maximum redshifts observed for the D and F bands in the O_2^- -doped polymer are 44 and 37 cm^{-1} , respectively (Figure 4). In contrast, the D and F bands in the fully electrochemically doped polymer (Figure 1, curve a) show redshifts of 56 and 55 cm^{-1} , respectively. The smaller redshifts observed for the O_2^- -doped polymer, relative to the fully doped material, indicate that the doping level is lower in O_2^- -doped polypyrrole. This conclusion is also supported by the conductivity data because the conductivity of O_2^- -doped polypyrrole is ca. 2 orders of magnitude lower than the conductivity of the fully doped material.³ Finally, the dramatically lower absorbance in the free-carrier region (compare Figure 1, curve a and Figure 2, curve d) also indicates that the doping level is lower in the O_2^- -doped material.⁴

In principle, a quantitative evaluation of the doping level for the O_2^- -doped polymer could be obtained by assaying the film for the dopant, O_2^- . We have used XPS to conduct such assays for other dopant anions (e.g. ClO_4^-) in polypyrrole.^{6,7} Unfortunately, an analysis for dopant anion is more difficult in O_2^- -doped polypyrrole because, as we will see, O_2^- is not the only form of O_2 in the polymer. A combination of FTIR and electrochemical data can, however, provide an estimate of the doping level.

In our previous studies we obtained a library of spectra for polypyrrole at various doping levels between the fully doped and pristine forms.⁴ This was accomplished by equilibrating a polypyrrole film-coated electrode with various values of applied electrode potential and then taking the spectrum of the film.⁴ We have compared the spectrum for the O_2^- -doped polymer with the spectra in this library of partially doped polypyrrole films and attempted to obtain the best match. Criteria used to judge the best match included magnitude of absorbance in the free-carrier region, position, and intensity of the D and F bands, and

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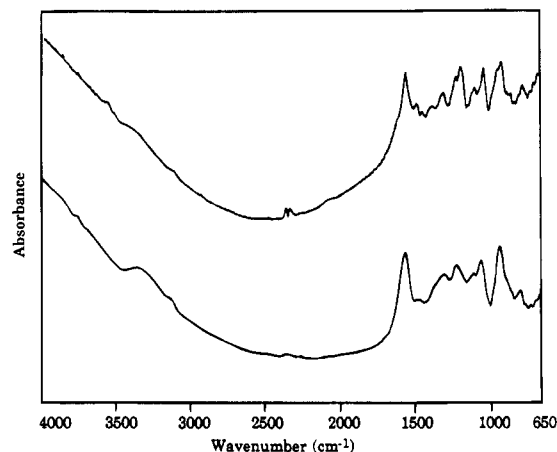


Figure 5. Comparison of the FTIR spectrum for an O_2^- -doped film (upper) with the spectrum for a film that had been equilibrated at an electrode potential of 0 V (see text). The spectra have been arbitrarily offset along the absorbance axis.

definition of the spectral features in the region below 1600 cm^{-1} .

Figure 5 compares the spectrum of the O_2^- -doped polymer with the spectrum for the partially doped polymer⁴ judged to be the best match. This best-match spectrum was obtained (see ref 4) by equilibrating a polypyrrole film at an applied electrode potential of 0.0 V. A simple analysis (see Appendix A) shows that this corresponds to a doping level of approximately 6%. This analysis is based on prior work from this lab which related applied potential to doping level.¹⁶ Hence, to a first approximation, the doping level in O_2^- -doped polypyrrole is ca. 6%. As expected, this is significantly lower than the 28% maximal doping level obtained for the as-synthesized ClO_4^- -doped polymer.

O_2^- Is Not the Only Form of Oxygen in the O_2^- -Doped Polymer. If O_2^- were the only form of oxygen incorporated after exposure of the pristine polymer to O_2 , then the doping level data presented above would suggest that the O content of the film would increase by approximately 0.06 mol of O/mol of pyrrole monomer units. We have shown that XPS provides a convenient route for assaying polypyrrole films for O and other species.^{6,7} Such XPS analyses show that the O content of the film after exposure to O_2 increases by 0.35 mol of O/mol of pyrrole monomer units. Diaz et al. obtained an increase of 0.48 mol of O/mol of monomer upon exposing a pristine polypyrrole film to air.¹⁰ These data clearly show that O_2^- is not the only oxygen-containing species introduced upon exposure of pristine polypyrrole to O_2 . We have used a series of FTIR and electrochemical experiments to obtain the chemical identity of the other form of O introduced.

Exposure of Pristine Polypyrrole to O_2 Does Not Introduce Carbonyl or Hydroxide into the Polymer Film. Diaz et al. have suggested that in addition to oxidative doping (i.e., eq 1), exposure of pristine polypyrrole to O_2 results in the formation of carbonyl groups along the polymer chain.¹⁰ If true, this would explain why there is significantly more oxygen in the film than the amount engaged in oxidative doping. Since carbonyl would show a characteristic signature in the infrared (as would the tautomeric⁵ hydroxy substituent), this premise can be tested using our spectroelectrochemical cell. Indeed, we have recently

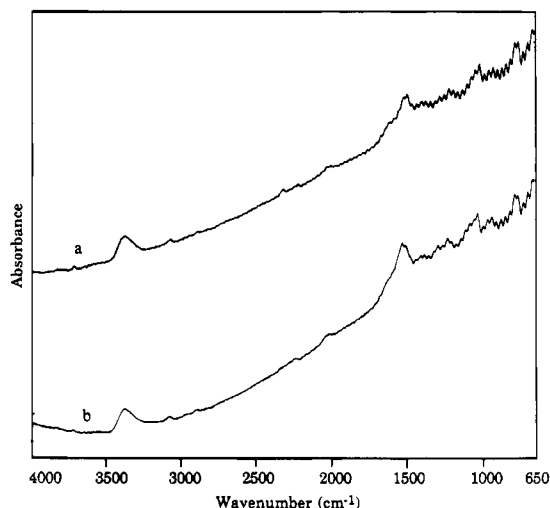


Figure 6. Comparison of the FTIR spectra for a pristine film before exposure to O_2 (curve a) with the same film after 30 min exposure to O_2 followed by electrochemical reduction at -0.8 V . The spectra have been arbitrarily offset along the absorbance axis.

conducted FTIR investigations of pristine and doped polypyrrole looking for just such chemical functionalities.⁵

A freshly synthesized polypyrrole film was reduced at -0.8 V to generate the pristine polymer, and an infrared spectrum of the pristine film was obtained. The pristine film was then exposed to 1 atm of O_2 for 30 min to generate the O_2^- -doped form of the polymer. The O_2^- -doped film was then reduced again at -0.8 V , and a second infrared spectrum was obtained. Figure 6 shows the FTIR spectra for the pristine film before and after exposure to O_2 . These spectra are identical. Furthermore, we have shown that when $-OH$ is present in the pristine polymer, the $O-H$ stretch and the $C-O$ stretch can be seen at 3558 and 1115 cm^{-1} , respectively.⁵ Furthermore, if $C=O$ were present one would expect a band in the region $1870-1540\text{ cm}^{-1}$.¹⁷ None of these bands are observed in the spectra in Figure 6. Hence, the excess oxygen observed in the O_2^- -doped films is not attributable to carbonyl, hydroxide, or other covalently attached forms of O.

Electrochemistry of O_2^- -Doped Polypyrrole. Because the FTIR spectra before and after exposing the pristine film to O_2 are the same (Figure 6), FTIR cannot be used to ascertain the chemical identity of the other form of O present in the O_2^- -doped film. In contrast, cyclic voltammograms for the film before and after exposure to O_2 are quite different, and these differences provide important clues as to the chemical identity of the excess O. A freshly synthesized polypyrrole film was reduced at -0.8 V to generate the pristine polymer, and a cyclic voltammogram of the pristine film was obtained. The pristine film was then exposed to 1 atm of O_2 for 30 min to generate the O_2^- -doped form of the polymer. The O_2^- -doped film was then reduced again at -0.8 V , and a second cyclic voltammogram was obtained. Note that this experimental protocol is identical to that used to obtain the infrared spectra shown in Figure 6.

The voltammogram before exposure to O_2 (Figure 7A) shows the characteristic¹⁶ polypyrrole oxidation wave

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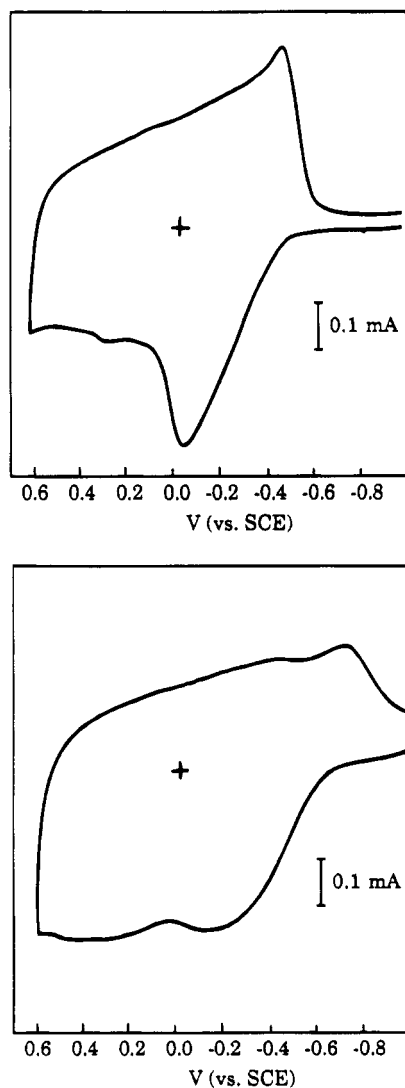


Figure 7. Cyclic voltammograms for polypyrrole films. (A, top) Before exposure to O_2 . (B, bottom) After reduction at -0.8 V and then exposure to O_2 . Scan rate = 5 mV s^{-1} .

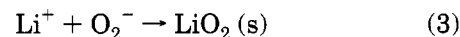
on the positive-going (forward) scan and the characteristic reduction wave on the reverse scan. These waves correspond to the oxidation of the pristine polymer to yield doped polypyrrole (forward scan) and the subsequent rereduction of the doped polymer to regenerate the pristine material (reverse scan). The voltammogram for the film after exposure to O_2 (Figure 7B) is more complicated. It is clear from the appearance of the current plateau¹⁶ at the most positive potentials that the polymer redox wave is still present; however, this wave is convoluted with the electrochemistry of a second, more easily oxidized, redox species. This is evidenced by the fact that anodic currents are observed at more negative potentials (relative to Figure 7A) on the forward scan and that cathodic currents (and a cathodic peak) are observed at more negative potentials on the reverse scan.

Proposed Molecular Association Complex between O_2 and Pristine Polypyrrole. Cooney et al. investigated the interaction of monomeric alkyl pyrroles with O_2 .^{11,12} Using 2,5-dimethylpyrrole (DMP) as a

model compound, they showed that molecular oxygen can interact with DMP via three distinct chemical processes. The first, and simplest, is via a "molecular association complex", which can be viewed as resulting from a partial electron transfer from the electron-rich DMP to O_2 . Evans has shown that the formation of such complexes is common for electron-rich aromatics such as pyrrole.¹³ The second chemical process, which is slower, is electron transfer to yield the DMP^+ and O_2^- .¹¹ This reaction is analogous to our doping process (eq 1). Finally, at long times, oxidation products analogous to those proposed by Diaz et al. are observed for the monomeric pyrroles.

Pristine polypyrrole is also an electron-rich aromatic system. We propose, therefore, that in analogy to DMP, pristine polypyrrole interacts with O_2 via both electron transfer (eq 1) and formation of a molecular association complex. This molecular association complex is the second form of O (see above) in the O_2^- -doped polymer. Indeed, because the doping process accounts for only ca. 0.06 O's per monomer unit, and XPS shows that 0.34 O's are introduced, the majority of O in the O_2^- -doped polymer is present as the molecular association complex. This molecular association complex hypothesis is consistent with both the infrared data in Figures 2 and 6 and the electrochemical data in Figure 7. Furthermore, this hypothesis leads to chemical predictions that can be tested experimentally.

Turning first to the electrochemical data, recall that after exposing the pristine polymer to O_2 , the film is reduced by holding the potential of the electrode at -0.8 V. What would be the fate of the O_2 present in the proposed molecular association complex at such negative potentials? It is known that when Li^+ is present as the cation of the supporting electrolyte, O_2 can be reduced in acetonitrile to form an insoluble Li^+ salt.^{18,19} These processes can be represented as follows:



The -0.8 V used to reduce the O_2^- -doped film is sufficiently negative to drive the reduction of O_2 (eq 2) in the presence of Li^+ .¹⁹ Hence, we propose that the O_2 that is present in the film as the molecular association complex gets reduced to O_2^- . This O_2^- then precipitates out in the film as LiO_2 . Again, it is clear that this electrogenerated O_2^- would not survive if water were present in the cell. However, as discussed in detail in our prior papers,^{4,5} we go to great lengths to eliminate trace H_2O .

This electrogenerated O_2^- accounts for the set of redox waves, observed at potentials negative of the polypyrrole waves, in the O_2^- -doped film (Figure 7B). The oxidation wave (forward scan) seen at more negative potentials (relative to Figure 7A) is due to the reoxidation of the O_2^- , and the corresponding reduction wave (reverse scan) is due to the rereduction of the O_2 generated during the forward scan. Hence, the proposed molecular association complex can be used to explain the electrochemical data obtained for the O_2^- -doped polymer. The molecular association complex theory also explains why

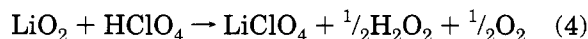
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it is impossible to observe the excess O in the O_2^- -doped polymer via FTIR. This is because the oxygen in the molecular association complex is present as O_2 , and O_2 is not IR active.

It is important to point out, however, that charge-transfer complexes of this type typically show a characteristic absorption in the visible or near-IR region. Unfortunately, the doped form of polypyrrole (including the O_2 -doped form) absorbs strongly in these regions. Furthermore, the partial transfer of electron density from pristine polypyrrole to O_2 should perturb the polymer chain in a fashion analogous to oxidative doping. Hence, the charge-transfer band should have characteristics similar to the absorbance of the doped form. For these reasons, it is probably impossible to see the charge-transfer band for this proposed complex. As a result, we chose to obtain electrochemical evidence for this proposed molecular association complex.

Testing the Molecular Association Complex Hypothesis. If the model proposed above is correct, a film that has been exposed to O_2 and then reduced at -0.8 V should contain the electrogenerated LiO_2 (eq 3). This is an experimentally testable prediction. A pristine polypyrrole film was exposed to O_2 , electrochemically reduced as described above, and then rinsed thoroughly with acetonitrile. The film was then removed from the spectroelectrochemical cell and immersed into 25 mL of aqueous 0.2 M $HClO_4$; this resulted in the following reaction:¹⁸



The film was immersed in the $HClO_4$ solution for 10 h to allow the $LiClO_4$ produced to extract into the aqueous phase. An identical film that was exposed to O_2 and $LiClO_4$ but not reduced electrochemically served as the control.

The control film was found to contain 8.9×10^{-8} mol of Li^+ ; this Li^+ is present because of partitioning of $LiClO_4$ from the electrolyte into the film.¹⁶ In contrast, the film that had been exposed to O_2 and then electrochemically reduced contained 2.7×10^{-7} mol of Li^+ . When corrected for the background Li^+ from the control film, this corresponds to 0.13 moles of LiO_2 (or 0.26 mol of O)/mol of pyrrole monomer units. This agrees reasonably well with the 0.34 mol of O obtained from the XPS method. These data support our contention that the excess O present in the O_2^- -doped film is present as a molecular association complex and that this molecular association complex can be reduced at -0.8 V to form the salt LiO_2 ^{18,19}(eqs 2 and 3) in the film.

The molecular association complex model was tested in a second way. The reduction potential of O_2 is shifted to less negative potential in the presence of Li^+ due to the formation of the LiO_2 salt (eq 3). If Bu_4N^+ is used as the cation of the supporting electrolyte, O_2 cannot be reduced at the -0.8 V used in these studies. Hence, if Bu_4N^+ is used, reduction of the O_2^- -doped film (at -0.8 V) will not cause concomitant reduction of the O_2 present in the film as the molecular association complex. This means that as soon as the film is unpotentiostated, a fraction of the O_2 present in the molecular association complex should be available to reoxidize the film. Hence, if an IR spectrum is obtained after reduction at -0.8 V in Bu_4NClO_4 , the spectrum will not be that of the pristine polymer (as was the case when Li^+ was the

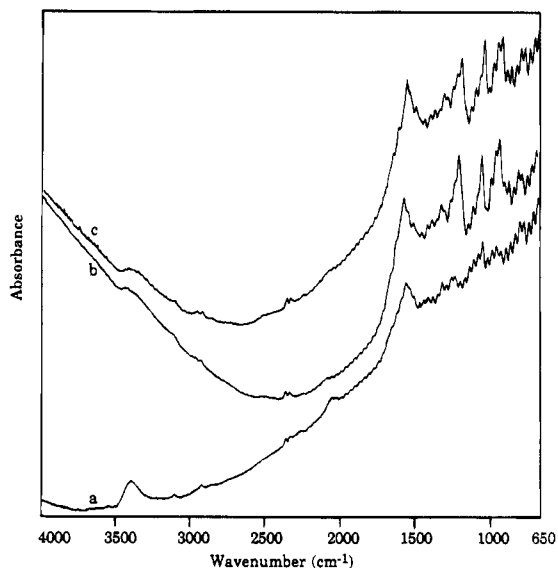


Figure 8. FTIR spectra for a pristine film (curve a), the same film after exposure to O_2 for 30 min (curve b), and after exposure to O_2 and then reduction at -0.8 V in CH_3CN containing 0.1 M Bu_4NClO_4 electrolyte (curve c).

electrolyte, Figure 6b). Rather the spectrum should be that of the O_2^- -doped polymer.

Figure 8 shows that this is indeed the case. A pristine film was generated by reduction of a freshly synthesized film at -0.8 V in 0.1 M Bu_4NClO_4 in acetonitrile. The infrared spectrum for this pristine film (Figure 8, curve a) is identical to that for the analogous film generated in $LiClO_4$ (Figure 6, curve a). The film was then exposed to O_2 and a second IR spectrum was obtained (Figure 8, curve b). Note that the characteristic features of the O_2^- -doped polymer are observed. Finally, the film was rereduced at -0.8 V in 0.1 M Bu_4NClO_4 in acetonitrile, and a third FTIR spectrum was obtained (Figure 8, curve c). Note that in complete agreement with the above prediction, the spectrum is that of the O_2^- -doped polymer rather than that of the reduced polymer. These results lend further support to the molecular association complex model.

Prolonged Exposure of the Pristine Polymer to O_2 Causes Deprotonation of the Pyrrole Nitrogen.

In all of the previous experiments, the pristine polymer was exposed to O_2 for only brief periods of time (30 min or less). Only reversible chemistry (formation of the molecular association complex and electron transfer to yield O_2^-) occurs during such brief exposures to O_2 . In contrast, prolonged exposure of the pristine polymer to O_2 produces irreversible chemistry. Figure 9 compares FTIR spectra for a pristine film that was not exposed to O_2 (curve a), a pristine film that was exposed to O_2 for 3.5 h and then reduced (curve b), and a pristine film that was exposed to O_2 for 20 h and then reduced (curve c). The N-H stretching mode (3400 cm^{-1}) is clearly seen in the film that was not exposed to O_2 . This band becomes progressively weaker upon prolonged (hours) exposure to O_2 . These data suggest that the pyrrole N becomes deprotonated upon prolonged exposure.

This conclusion is supported by the XPS data. Figure 10 compares XPS spectra for an as-synthesized polypyrrole film (curve a) with that for a pristine film that had been exposed to air for 20 h (curve b). Note that the air-exposed film shows a shoulder which can be

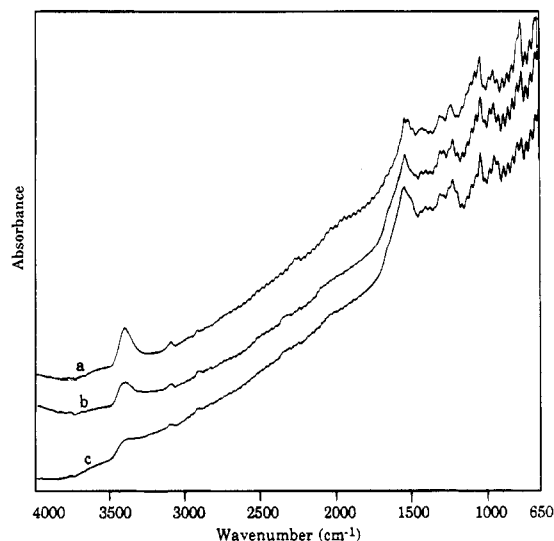


Figure 9. FTIR spectra for a pristine film that had been exposed to O_2 for various lengths of time and then rereduced at -0.8 V in CH_3CN containing 0.1 M $LiClO_4$. Exposure times were 0 min (curve a), 3.5 h (Curve b), 20 h (curve c).

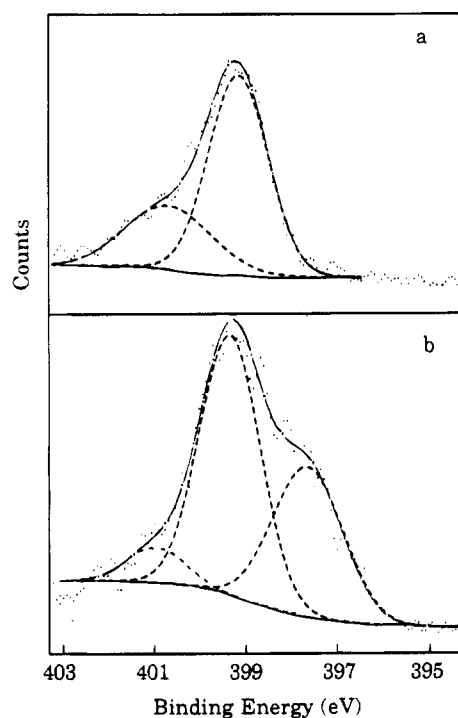


Figure 10. N(1s) XPS core level spectra for an as-synthesized film (a) and a film that had been reduced and exposed to air for 20 h (b).

deconvoluted^{6,7} to reveal a peak centered at 397.5 eV. Analogous results were obtained by Pfluger et al. who

have suggested that this peak is due to imine.² (A peak at about this energy is observed in pyridine,²⁰ adenine,²¹ and quinoline.²²) Hence, the XPS and FTIR data tell a consistent story about the fate of the pristine polymer upon prolonged exposure to O_2 .

Conclusions

We have shown that pristine polypyrrole can interact with O_2 via three distinct chemistries—formation of a molecular association complex (partial electron transfer), electron transfer to form an O_2^- -doped form of the polymer, and (at long times) deprotonation to form an imine-form of the polymer. We have found that the O_2^- -doping level is low (ca. 6%), and this accounts for the low conductivity of O_2^- -doped polypyrrole.³ In contrast a large amount of oxygen (ca. 0.28 mol of O/mol of monomer units) is associated via the molecular association complex. The electrochemistry of this oxygen can be observed when $LiClO_4$ is used as the supporting electrolyte and CH_3CN is used as the solvent.

Appendix A. Determination of an Approximate Value for the Doping Level of O_2^- -Doped Polypyrrole

We have shown¹⁶ that at low doping levels, the concentration of oxidized pyrrole units [Py^+] in polypyrrole is related to the applied potential via

$$E = 0.21 \log [Py^+] + 0.6 \quad (A1)$$

[Py^+] can in turn be related to the doping level X via

$$[Py^+] = Xd/(MW_{Py}) \quad (A2)$$

where d is the density of the polymer (1.48 g cm^{-3} (ref 23) and MW_{Py} is the molecular weight of pyrrole. By combination of eqs A1 and A2, the relationship between applied E and doping level X is defined. Our prior investigations yielded a library of FTIR spectra for polypyrrole at various values of applied E .⁴ As discussed above we matched the IR spectrum for the O_2^- -doped polymer with spectra from this library to obtain a best fit spectrum. The known E value (0.0 V, see above) for this spectrum was then used to calculate the doping level using eqs A1 and A2.

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