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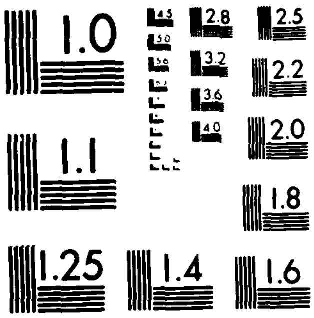

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The Chemical and Physical Properties of Pyrrole-Based Conducting Polymers: The Oxidation of Neutral Polypyrrole

by

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Research Report

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THE OXIDATION OF NEUTRAL POLYPYRROLE

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ABSTRACT: A series of experiments on the physics and chemistry of polymers derived from pyrroles, show that the oxidation of neutral insulating polypyrrole (PP°) to its conducting counterpart (PP^{+}) is a multistep process. In particular, the conductivity of the polymers increases only in the early stages of oxidation whereas significant changes in the optical and EPR properties occur in later stages of the oxidation when no further changes in the conductivity take place. The early stages of oxidation lead to an ionic (PP^{+} anion^{-}) polymer and the later stages of oxidation result in chemistry at the nitrogen atoms of the pyrrole rings. Similar behavior is observed for all the oxidized pyrrole polymers independent of the method of oxidation.

INTRODUCTION

Of the polymeric materials which can be made conducting by doping,[1] the polypyrroles are are amongst the most interesting.[2] Polypyrrole is readily obtained in its conducting form (PP^+) (Fig. 1) by electrochemical oxidation of pyrrole.[3] Recently, free standing films of insulating neutral polypyrrole (PP°) have become available by electrochemical reduction of PP^+[4] under drybox conditions. This neutral PP° has proven to be of great importance for the characterization of the whole family of polypyrroles, and is of interest here because it can be redoped by gas-phase, solution and electrochemical reactions.

We have used these doping reactions to study the changes in the physics and chemistry of polypyrrole as doping of the PP° to PP^+ proceeds. An article on the preparation and characterization of neutral and oxidized polypyrrole films has been published previously[4] and contains comparisons of optical absorption, infrared transmission and ^{13}C NMR spectra in neutral and fully-oxidized as-grown polypyrrole. Preliminary electron paramagnetic resonance (EPR)[5] and X-ray photoelectron spectroscopy (XPS)[6] data on polypyrrole films have also been reported recently. In the present paper, spectroscopic, conductivity and weight uptake data will be used to characterize the nature of the conversion of PP° to PP^+. The changes in the properties of polypyrrole on oxidation do not occur monotonically but in what will be described as three discrete stages. However it should be mentioned that these stages are to some extent overlapping. It has generally been assumed that the oxidation of PP° occurs by homogeneous charge extraction from the π-system of the otherwise unaffected polypyrrole. This idea will be discussed further and evidence will be presented which shows that although this concept is essentially correct for the first of three stages in the oxidation of PP°, later stages involve more severe changes in the chemistry of the pyrrole rings.

OPTICAL ABSORPTION IN O_2 and I_2 DOPED FILMS

Optical absorption data obtained for polypyrrole films, has been reported previously.[4,7,8] The buildup of the absorption peak in the 1 eV region with oxidation was originally thought to be related to free carriers.[7] However, this idea was later questioned because the 1 eV structure in polypyrrole perchlorate ($PP^+ClO_4^-$) can be increased by exposing the films to O_2 without causing a further rise in the electrical conductivity.[4] Features at ~0.03 eV have also been interpreted in terms of free carriers but these features could be related to the contribution of molecular vibrations to the optical absorption and to the polarizability of the films.[8] In this section the optical evidence for free carriers in polypyrrole will be examined.

In gas-phase doping experiments of PP° with O_2, the evolution of the absorption spectra has now been followed carefully. The peak appearing at 1.4 eV photon energy does not shift in energy as a function of dopant concentration although its intensity increases. This is in contrast to a free carrier absorption for which $\omega_p \sim \sqrt{n}$, where n is the free carrier concentration. Therefore if this 1.4 eV peak were the free carrier absorption it would be expected to shift as a function of the degree of oxidation. We have also investigated the changes of the optical absorption and the electrical conductivity of PP° on doping with I_2 at 0°C, which corresponds to an iodine vapor pressure of 31.10^{-3} torr. Figure 2 shows that, after 2 minutes doping, the electrical conductivity σ_{el} of the films increases by more than 6 orders of magnitude, whereas the main part of the growth of the absorption peak at 0.9 eV becomes apparent only after the films have reached within an order of magnitude of their final conductivity. This absorption peak, which causes the color of PP° to change from transparent yellow/green to the black opaque color of PP^+ is therefore not simply related to the electrical conductivity of the films. It should be pointed out that conductivity measurements are much more sensitive to changes in the degree of oxidation than the optical properties. Nevertheless the fact that the optical peak, which was previously thought to be associated with the free carriers, continues to increase long after the conductivity has saturated is strong evidence that it is, in fact, not the free carrier absorption. The fact that the changes in the optical absorption and the conductivity do not cease simultaneously indicates what will become even more obvious in the following sections, namely that the oxidation of PP° to PP^+ is a process including more than one stage and that only the first of these stages leads to, an increase in the conductivity.

SIMULTANEOUS EPR, CONDUCTIVITY AND WEIGHT UPTAKE MEASUREMENTS

The doping of PP° by O_2 gas has been monitored by simultaneous conductivity, EPR and weight uptake measurements. Three pieces of the same PP° film were mounted in the helium atmosphere of a dry box into three different glass apparatuses, the first was equipped for four-probe conductivity measurements, the second was an EPR sample tube, and the third contained a quartz oscillator to measure the weight uptake. All three parts were attached to the same vacuum system and pumped to 2.10^{-7} torr. Ultrahigh purity oxygen (99.9999%) was then leaked into the system at constant pressures, starting as low as 10^{-4} torr. After the system had stabilized at a given O_2 pressure, the conductivity, the EPR signal and the weight uptake were recorded. The maximum O_2 concentration in the films was obtained after several hours at 600 torr and the weight uptake curve showed no evidence of staging. After reaction with oxygen some films were exposed to vacuum and it was shown that the oxygen takeup was irreversible.

It was observed that the conductivity of the doped films rapidly rises by several orders of magnitude, and reaches saturation slightly below 10^{-2} $(\Omega \cdot cm)^{-1}$ at typically 1% weight uptake. After this point, σ_{el} remains constant within a factor of 2, independent of the O_2 pressure (10^{-4}-600 torr) to which the films are subjected despite the fact that a further large irreversible weight uptake is observed with increasing O_2 pressures and reaction time. As was observed in the I_2 doping experiments, the increase in conductivity on exposure to oxygen was achieved at low O_2 pressures ($<10^{-2}$ torr) without any visibly detectable change in the optical properties of the polypyrrole films. In contrast to I_2 doping, the O_2 doped films reached their maximum conductivity after their first oxidation step, whereas the I_2 doped films went through a second rise in σ_{el} after the initial step. This second step is associated with an increase of approximately another order of magnitude in conductivity.

PP° exhibits two distinct EPR lines at room temperature. The first line is narrow with a width of ~0.3 gauss and an intensity of 10^{19} spins/g which corresponds to ~1 spin/1000 pyrrole rings. The second line is considerably broader with a width of 2-3 gauss and an intensity of 10^{20} spins/g corresponding to ~1 spin/100 pyrrole rings. In spite of its smaller integrated intensity, the narrow component dominates the observed signal in the derivative spectrum and it is convenient to follow its evolution as PP° is doped with O_2. At first the intensity of the EPR signal increases along with σ_{el}. At ~1% weight uptake, when the electrical conductivity saturates, the EPR signal intensity goes through a maximum and subsequently drops back to its initial value (Fig. 3, points 1-14). In contrast, the EPR linewidth is practically constant while the conductivity and the EPR intensity are increasing. Only after σ_{el} has saturated does the linewidth begin to increase, reflecting the diminution of the narrow component and the growing importance of the broad line which lies under it. A second apparent increase of the intensity is associated with this growing linewidth (Fig. 3, points 15 and 16). Finally, considerable irreversible oxygen uptake occurs which is not accompanied by any change in σ_{el}, the EPR linewidth or the EPR intensity. Some insight into the origin and the detailed behavior of the observed narrow (~0.3G) and broad (~4G) EPR lines has been gained from extensive studies of their temperature dependence. These details, and the details of the optical absorption curves shown in Fig. 2, will be addressed in separate publications on the chemical and physical properties of polypyrroles.[9] In summary we should note that on doping PP° with O_2 gas, several regimes are observed. First, the conductivity and the intensity of a 0.3 Gauss wide EPR line increase, before any changes in the optical properties become apparent (Fig. 3, points 1-7). After the maximum in the conductivity is reached the intensity of the EPR line decreases, while σ_{el} remains constant, and the EPR linewidth increases only slightly as optical changes start to become visible (Fig. 3, points 8-14). In the next step, EPR linewidth and intensity increase rapidly, along with a further darkening of the film (Fig. 3, points 15-16). Finally, no more EPR, optical or conductivity changes occur but the films take up significant amounts of O_2 irreversibly. By pumping these heavily oxidized films, the narrow EPR line can be restored as shown in Fig. 3, by the remaining black dots.

SLOW DOPING OF PP° WITH $FeCl_3$

The conductivity and weight uptake of PP° films exposed to $FeCl_3$ vapor has also been measured. The reactions and all measurements were carried out in the helium atmosphere of a dry box. Since the vapor pressure of $FeCl_3$ at room temperature is very low, the reaction was slow taking weeks to go to completion. Such a slow doping process might be expected to result in particularly homogeneous samples and to resolve different oxidation steps, if they are present. Figure 4 shows that this was indeed the case. First, within minutes, a conductivity plateau was reached which is associated with a small weight uptake of the order of 1%, as in the case of O_2 doping. At this stage the conductivity had reached ~0.2 $(\Omega\cdot cm)^{-1}$, which is approximately 30 times higher than for O_2 doping and as in the O_2 and I_2 cases, the optical properties of the films had not changed significantly. The films were still green and transparent and their color did not start to darken until the first plateau region (Fig. 4), where significant amounts of reactant were incorporated into the polypyrrole without further increase in σ_{el}. After a second step which raised the conductivity to ~5 $(\Omega\cdot cm)^{-1}$, the films had the black opaque color characteristic of electrochemically grown PP^+ films. As in the case of oxygen doping, a weight uptake associated with a plateau in the conductivity, concludes the oxidation process. Recall that a second conductivity step was also observed for I_2 doped films, but not for their O_2 doped analogs. In spite of the apparent absence of a second rise in σ_{el} for the oxygen doped films, there is a possibility that such an oxidation step exists and may be associated with the onset of the 4 Gauss EPR line before the final weight uptake plateau.

X-RAY PHOTOELECTRON STUDIES OF THE OXIDIZED FILMS

An attempt has been made to characterize the different stages of oxidation by X-ray photoemission studies (XPS, ESCA). The experimental techniques pertinent to our XPS investigations of polyheterocyclic films in general (instrumentation, sample handling and calibration techniques) are described in detail in a previous paper.[10] In the present paper the striking differences found in the nitrogen spectra (and only in the nitrogen spectra) between PP^+ films after the different oxidation steps will be discussed. Figure 5 shows the N1s region for green conducting films obtained from PP° by chemical (Fig. 5a) oxidation to the first stage of oxidation, compared to films which have been taken past this first stage by further oxidation using electrochemical (Figs. 5b,e) or chemical (Fig. 5c,d) methods. It should be emphasized that none of the PP^+ films discussed in this work is an as-grown film, but that they were all first reduced to PP° which was then subjected to various schemes of reoxidation. As indicated in Fig. 5, three classes of N1s spectra are observed. (As-grown films are discussed in Ref. 11 and form a further category.) The curves shown here have been selected to exemplify the prominent XPS structures of each class. A representative of both electrochemically and chemically doped films is included to show that the main features of each class are independent of the method of preparation. With the exception of Figs. 5a and 5d, the spectra were not taken on the same films. Therefore it is not surprising that the strength, sharpness and position of the N1s features vary somewhat from spectrum to spectrum. However all films investigated clearly fit in either one of the three categories shown.

Before discussing the different features of these classes in detail, an important result will be anticipated which is true for all electrochemically cycled PP$^+$ films and which will be discussed extensively in a future publication. The only element besides C and N found in PP$^+$ films after repeated cycling is O regardless of the anion (ClO_4^-, BF_4^-, PF_6^-) present in the electrolyte solution and originally present in the as-grown PP$^+$ films (hydrogen is obviously also present in the films, but is the only element not detectable by XPS). As the films are electrochemically cycled, the concentration of original anions decreases and they are believed to be replaced by some presently unidentified oxygen based anion. The source of this oxygen is unclear as considerable care was taken to purify, dry and degas all the reagents under dry-box conditions. The chemical nature of this oxygen based anion is not readily apparent because the IR bands of the anionic species are completely masked by the bands of the polymeric cation in the conducting PP$^+$ materials.[4] One should be aware, however, that all the changes seen in the N1s spectra and described in the following sections are associated with the presence of oxygen (with or without hydrogen).

N1s Spectra After The First Oxidation Step

Only samples which have not been oxidized beyond the first stage have the simple, narrow and symmetric N1s line centered close to 400 eV, shown in Fig. 5a, which one expects from the idealized structure of polypyrrole perchlorate shown in Fig. 1. Indeed, only for these samples is the N1s lineshape and position consistent with the presence of a single kind of pyrrole-type nitrogen atom, resulting from uniform charge compensation of the negative charge on the counterion species by the extended positive charge of the pyrrole rings.[3,4,7,8,11]

N1s Spectra At Intermediate Oxidation Levels

Completely different N1s lineshapes are obtained from films for which oxidation has proceeded beyond the first stage. The pyrrole N1s peak at ~400 eV becomes asymmetric on its high binding energy side, due to the appearance of at least two shoulders, the intensity, width and position of which, depend on the sample history (Figs. 5b,c). This phenomenon is very general in the sense that it is observed in any dark PP+ film investigated, including the as-grown films. These features are believed to arise from an inhomogeneous charge distribution among the nitrogen atoms of the pyrrole rings. The higher binding energy components are due to more positively charged nitrogens having a stronger electrostatic interaction with the new anion species incorporated into the switched film in the course of this additional oxidation step. The same argument has been proposed to account for a higher binding energy component of the C1s main peak in Br_3^- doped polyacetylene.[12] Note that the shoulders in PP+ films appear ~0.5-2.5 eV above the main peak, which is well below the energies typical for shake-up satellites in organic aromatic systems.[13] The N1s core level is known to shift by ~5.8 eV per unit charge in the 401 eV binding energy region.[14] According to this number, extra charges of the order +0.1-+0.4 are induced on selected nitrogen atoms by the anions. On the low binding energy side of the pyrrole-type N1s main peak, a side peak appears at ~397.8 eV, a position at which, for example, the N1s line of cyanides appears.[15] One might therefore be led to suspect the CH_3CN solvent, used for the electrochemistry of the polypyrroles investigated here, was the source of CN groups incorporated into the polymers. This explanation, however, can effectively be ruled out, because first stage oxidation films of the type shown in Figs. 5a, which do not have any structure in the 397.8 eV area can be converted into more oxidized forms exhibiting this structure in the absence of CH_3CN by exposure to O_2 or air. The nitrogen atoms of amino groups also give rise to an XPS peak in the binding energy range in question (Table I, compounds 1-4, 9). However, amino-type nitrogen atoms are not very likely to produce the 397.8 eV structure in polypyrroles because this would require breaking and rearrangement of the pyrrole rings. No indication for such chemistry is found in the C1s spectra which, as indicated earlier, do not undergo any changes with increasing degree of oxidation. Furthermore, in the course of electrochemical cycling, oxidized polypyrrole films with N1s spectra similar to those shown in Fig. 5b-e can be converted to neutral PP°, films which then show the simple symmetric N1s line similar to those in Fig. 5a. In other words, the changes of the N1s XPS spectrum upon oxidation are fully reversible electrochemically which would not appear feasible if the breakup of the pyrrole rings were involved. Instead, we can speculate that, this second oxidation step involves stripping the hydrogen off the nitrogen of some of the pyrrole rings, with the N atoms then forming three bonds within the aromatic ring. This type of nitrogen is known to give rise to XPS peaks in the 397.8 eV region in the case of pyridine, adenine and quinoline as shown in Table I, compounds 4,6,7. At the present moment, we believe that removal of some of the hydrogen from the nitrogen with subsequent rearrangement of the double bonds in the polypyrrole ring could provide an explanation of the structure at the low binding energy side of the main pyrrole peak. It should not be forgotten that, during the process of electrochemical cycling some oxygen based anion gradually replaces the anion originally incorporated into the film from the electrolyte solution. It is certainly conceivable that this new anion is OH^-. Whatever the nature of this anion it is assumed that it is incorporated into the pyrrole chain structure such as to cause a nonuniform distribution of charge between the surrounding nitrogens, and that this, rather than any chemistry, gives rise to the high binding energy shoulders discussed earlier. In contrast to these shoulders, the 397.8 eV structure is not observed in regular as-grown films.[10]

N1s Spectra of Fully-Oxidized Films

The features of the N1s spectra (Figs. 5b, 5c), associated with the second stage of oxidation, were discussed in the previous section. In this section the structure in the N1s spectra appearing at 405-406.5 eV in strongly oxidized polypyrrole samples (Figs. 5d, 5e) is discussed. This structure is all that distinguishes this third stage in the oxidation from the previous two. The separation of this peak from the main peak is characteristic of shake-up phenomena in aromatic systems. As shake-up peaks were absent in the earlier stages of oxidation it is difficult to imagine why it should suddenly appear so strongly with increasing degree of oxidation. On the contrary, Salaneck et al.[19] claim that the N1s shake-up peak they observed in condensed pyrrole is considerably weakened in PP+. Therefore the structure in the 406 eV area of highly oxidized PP+ is not attributed to shake-up phenomena, but instead to strongly oxidized forms of nitrogen. A comparison with known model compounds, (Table I)[15] shows that only NO_2 or NO_3 compounds are found in this binding energy region. Again, for the same reason stated earlier, it is unlikely that NO_2 or NO_3 groups are produced because this would involve breaking the pyrrole rings. It seems more likely that oxygen is attached, in some presently unknown form, to nitrogens of intact pyrrole rings. Unfortunately, the pyrrole monomer does not provide very valuable information on the oxidation processes in polypyrrole because oxidation of polypyrrole takes place at the nitrogen site, while in pyrrole monomers oxidation proceeds exclusively in the α positions, or in side chains if the α positions are blocked.[20] It is important to emphasize that despite the chemistry which occurs at the nitrogen atoms of some pyrrole rings, the original structure centered at ~400 eV, characteristic of the idealized form of oxidized polypyrrole, Fig. 1, remains the main peak of the N1s spectra (Fig. 5) independent of the stage of the oxidation. In other words most of the pyrrole rings (~2/3) do not undergo chemistry. However, the O:N ratio is found close to 1:1 in the heavily oxidized PP+ films. In these films therefore more than one oxygen atom must be attached to the (~1/3)of the nitrogen atoms which have reacted. This conclusion is in agreement with the chemical shifts observed here and in the compounds 9-12 of Table I.

It is remarkable that the severe modification of (~1/3) of the nitrogen sites occurs without any significant change in the conductivity. This is particularly surprising since polymers derived from N-substituted pyrroles have conductivities on the order of $10^{-3}(\Omega\cdot cm)^{-1}$, 4-5 orders of magnitude lower than the most conducting polypyrroles.[21] We conclude that the conjugated carbon backbone is responsible for the HOMOs or, equivalently, for the Fermi surface properties within one type of polypyrrole. On the other hand, steric effects and the amount of crystallographic disorder seem to be the key features in determining the differences in conductivity between various pyrrole polymers and also between various types of heterocyclic conducting polymers.[10]

CONCLUSION

It has been shown that the PP°/PP^+ system is much more complicated than originally assumed and that many of the simple concepts previously put forward for polypyrrole in the past have to be reconsidered. Changes in the optical properties continue after the conductivity saturates, ruling out free carrier processes as the origin of the 1 eV optical absorption structure. Several steps occur during the oxidation of polypyrroles, which can be seen in EPR, in slow doping weight uptake measurements and in conductivity experiments. These steps have been characterized to some extent by XPS studies. The electrochemical oxidation of PP° does not necessarily lead to inclusion of the anion incorporated originally into the initially grown PP^+ film from the electrolyte solution. Instead these films seem to preferentially incorporate some presently unidentified oxygen based counterion derived from residual oxygen or water in the electrolyte solution. This same counterion seems to be formed during the gas-phase oxidation of PP° by O_2 or air. In these XPS experiments the effects of oxidation are seen only at the nitrogen and not at the carbon atoms which indicates that no chemistry is taking place at the carbons. This is not surprising as polymerization blocks the α positions, which are the readily oxidized carbons. The oxidation of the nitrogen should also effect the positions of the carbon 1s lines but these shifts appear to be obscured by the already broad signal characteristic of the superposition of the α and β carbons with some non-α,α' bonded carbons present in the polymer. The XPS data of the films oxidized to the first stage of oxidation are fully consistent with the idealized structure of Fig. 1. The two subsequent stages of oxidation are characterized by chemical changes at as many as 30% of the nitrogen sites. The conductivity of the films is not affected by this chemistry taking place at the nitrogens during the second and third stages of oxidation, which are completely reversible on electrochemical reduction. The second oxidation step, is associated with the change in color of the PP^+ films from yellow/green to black and the XPS data shows that a number of nitrogens are now in a different oxidation state. Some of the approximately 70% of the nitrogen which do not change their oxidation state become electrostatically inequivalent, due presumably to differences in their proximity to the anions. In addition to these effects, the XPS of the third highly oxidized stage shows the presence of very strongly oxidized nitrogens where more than one oxygen atom appears to be attached to about 30% of the nitrogens. Finally, it is remarkable that these effects were all observed on compounds prepared by different methods, thus allowing us to identify them all according to their N1s XPS spectra.

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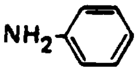
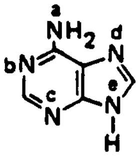
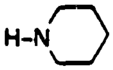
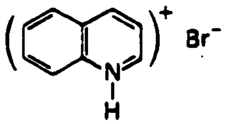
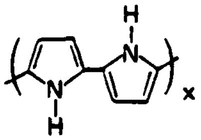
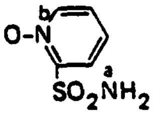
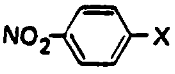
TABLE I

Nitrogen 1s Core Level Binding Energies in Selected Compounds

Compound #	Chemical Structure	Name	N 1s Binding Energy (eV)	Ref.
1	$(NH_2\text{-}CH_2\text{-}COO)^{-}Na^{+}$	sodium glycinate	397.3	[15]
2	$NH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$	n-butylamine	398.1	[15]
3		aniline	398.6	[15]
4		adenine	a 398.6 b 397.6 c 398.1 d 398.5 e 399.9*	[16]
5		piperidine	397.8	[15]
6		pyridine	398.0	[15]
7		quinolinium hydrobromide	398.5	[17]
8		polypyrrole polycation	399.7–400.2**	this work
9		2-pyridine-1-oxide sulfonamide	a 398.7 b 402.2	[15]
10		nitrobenzene 4-hydroxinitrobenzene	X=H 405.1 X=OH 405.3	[15]
11	$NaNO_2$	sodium nitrite	404.1	[18]
12	$NaNO_3$	sodium nitrate	407.4	[18]

*binding energy scale determined by setting the pyrrole-like nitrogen to 399.9 eV

**depending on the anion and the degree of oxidation

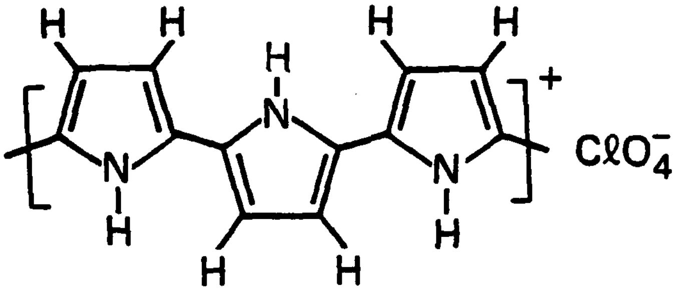


Figure 1. Idealized chemical structure of electrochemically grown polypyrrole perchlorate $PP^+(ClO_4^-)$.

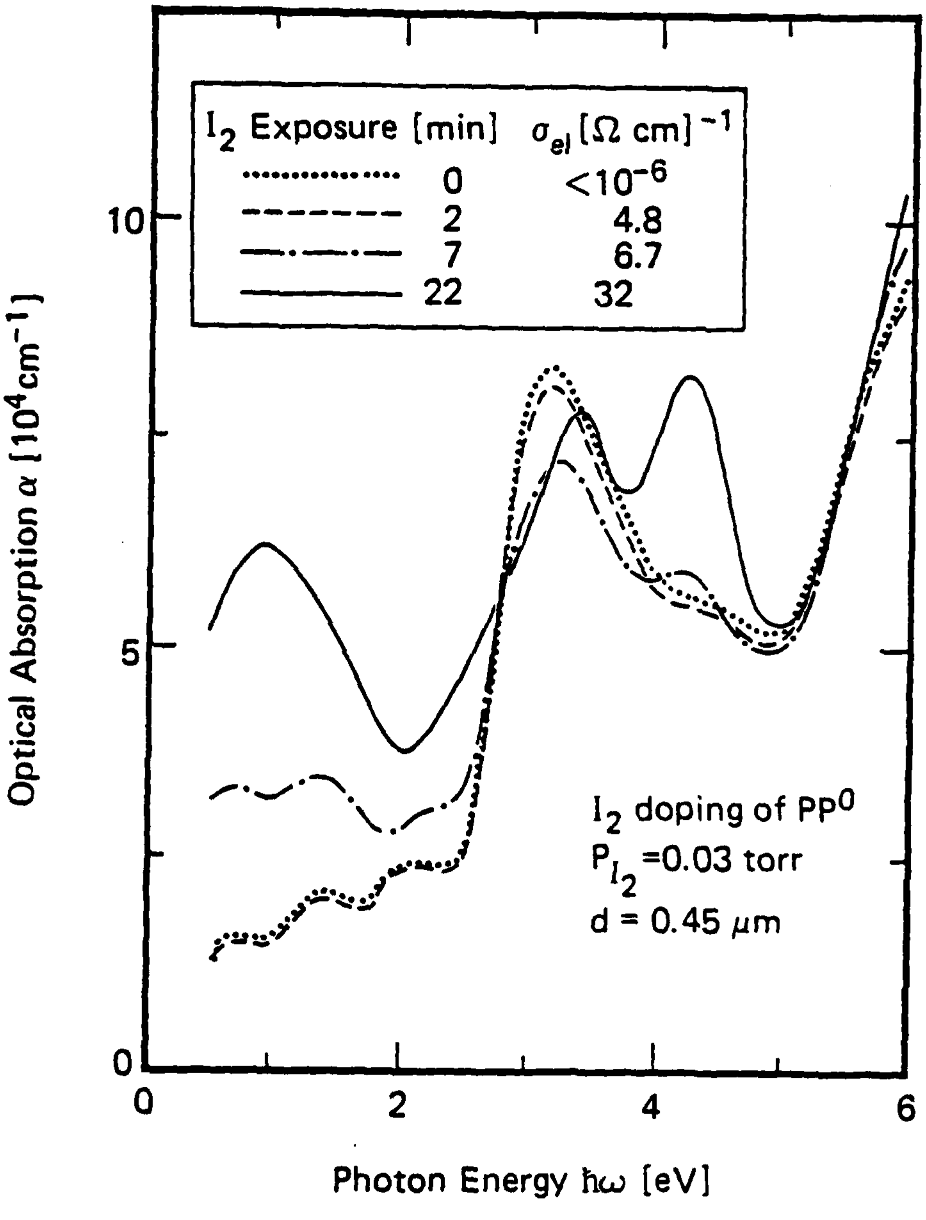


Figure 2. Room temperature optical absorption spectra of neutral polypyrrole films (PP°) doped with I_2 to various levels. The 3 structures seen on the low-energy side of the unexposed, 2 and 7 minutes exposed films are possibly artifacts due to interference effects in the 0.45 μm thick films.

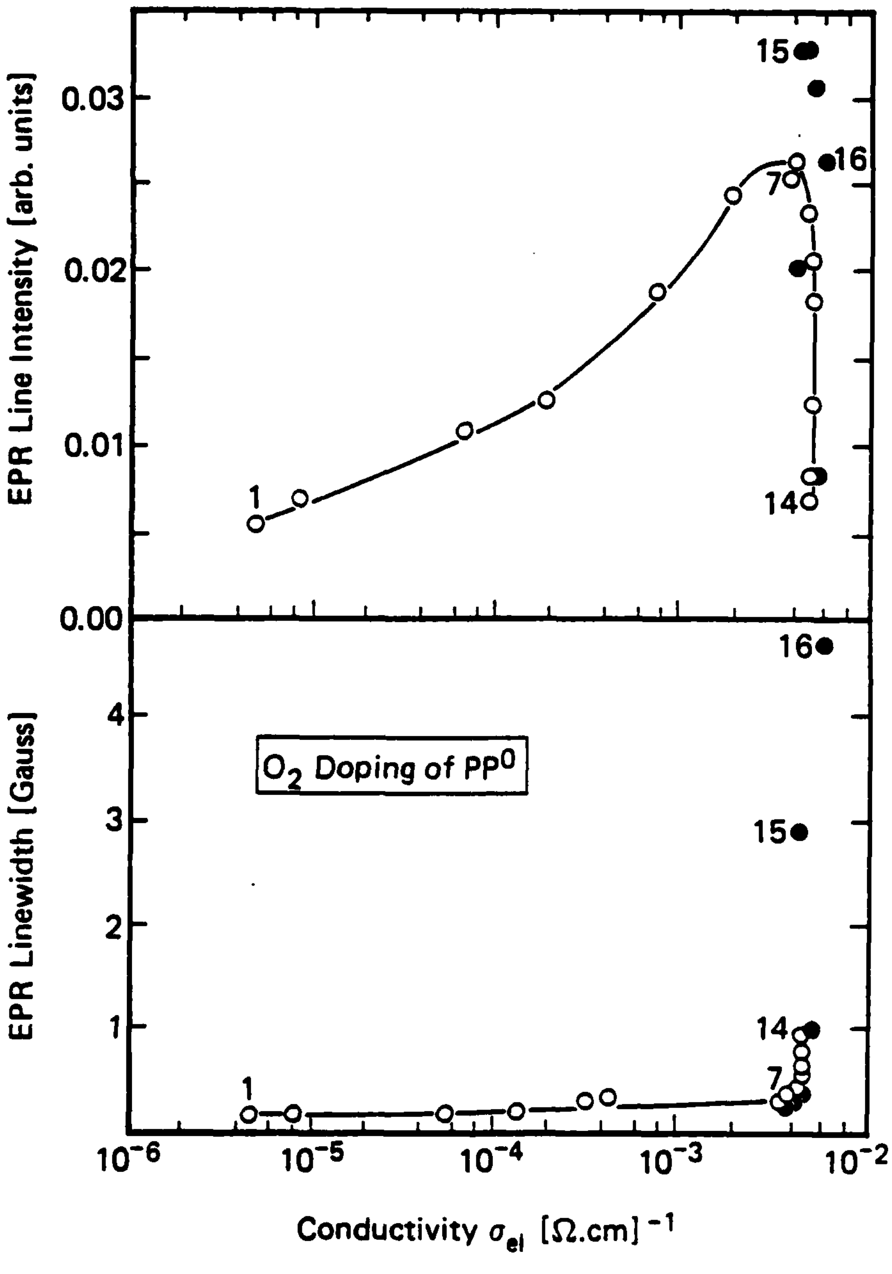


Figure 3. Width and integrated intensity of the EPR line in neutral polypyrrole films (PP^0) doped with O_2 to various levels versus electrical conductivity of the corresponding films. The numbers indicated the order in which the data points were obtained; oxidation proceeded gradually from 1 to 16.

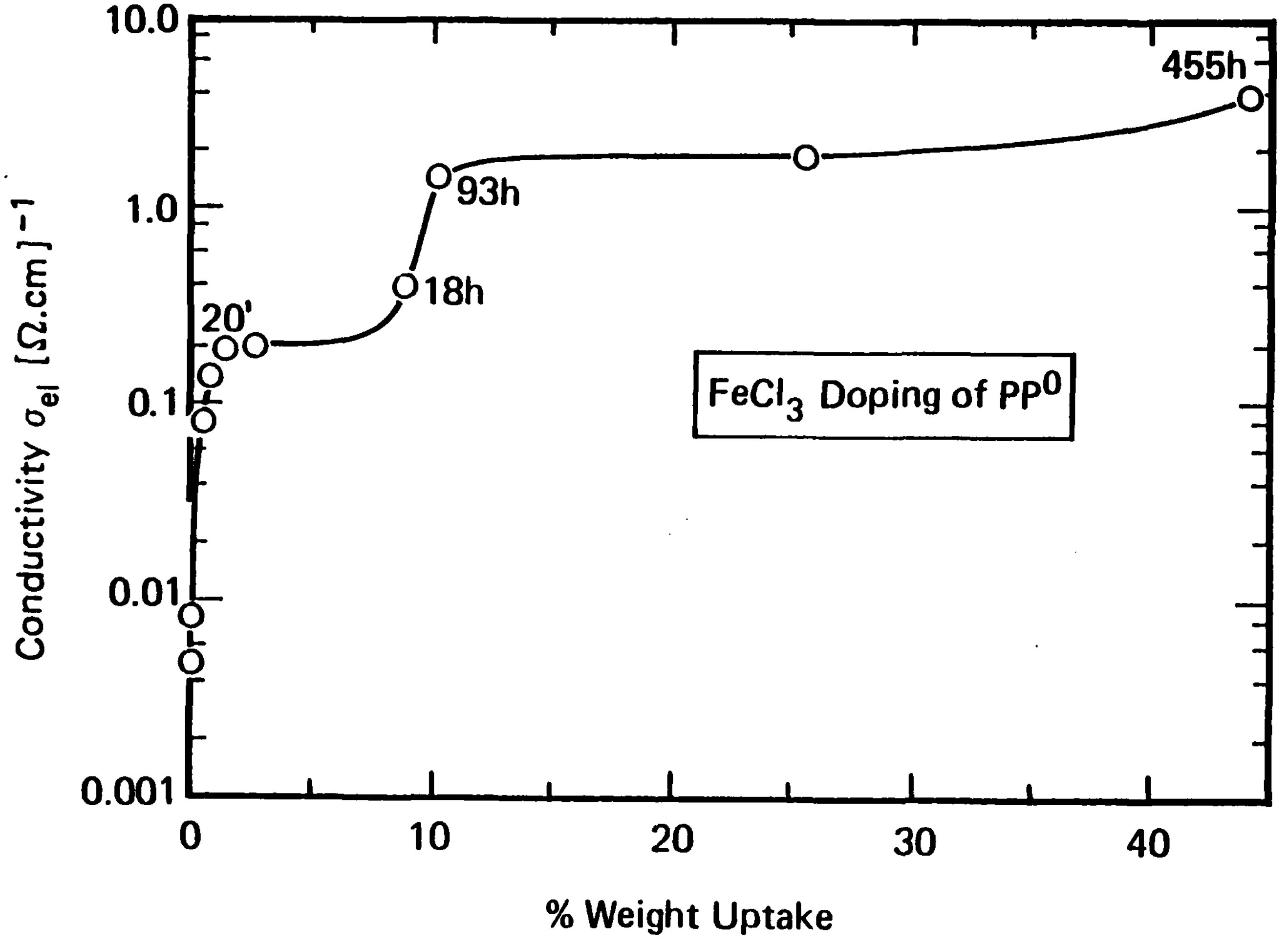


Figure 4. Electrical conductivity versus weight uptake of neutral polypyrrole films (PP°) exposed to FeCl$_3$ vapor. Typical reaction times are given at some points along the curve. The initial conductivity of the PP° films was of the order 10^{-6} $(\Omega \cdot cm)^{-1}$.

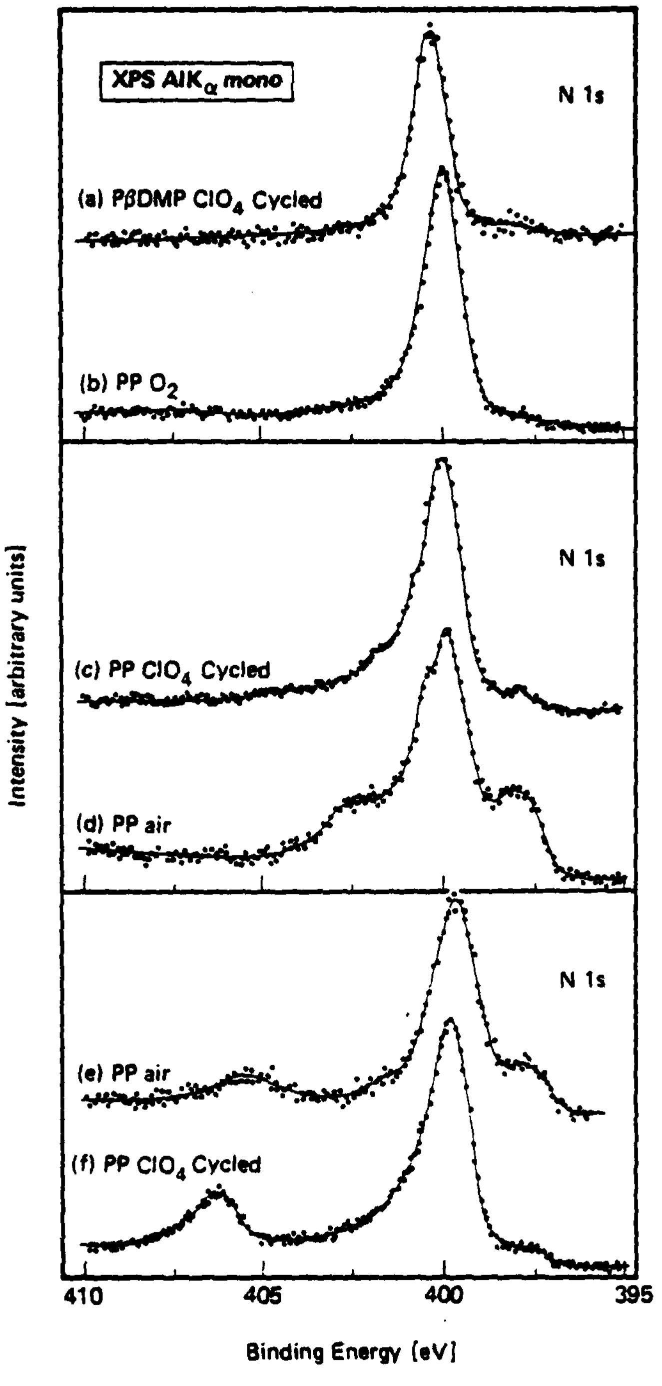


Figure 5. Nitrogen 1s core level spectra of various oxidized polypyrrole films, obtained from X-ray (monochromatic AlK$_\alpha$ radiation) excited photoelectrons. All films were obtained from PP° starting material. The degree of oxidation increases from group to group towards the bottom of the figure. Several techniques were used to oxidize the films; all spectra were obtained from different films, except spectrum (e), which was generated from (b) by further oxidation.

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