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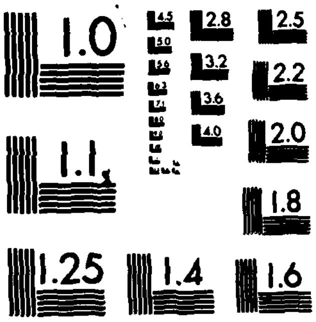

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Technical Report No. 15

The Chemical and Physical Properties of Pyrrole-Based Conducting Polymers: The Characterization of As-Grown Films by X-Ray Photoemission Spectroscopy

by

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Prepared for Publication

in the

The Journal of Chemical Physics

IBM Research Laboratory
5600 Cottle Rd.
San Jose, CA 95193

April 7, 1983

RJ 3840 (43807) 3/30/83
• Chemistry

Research Report

THE CHEMICAL AND PHYSICAL PROPERTIES OF PYRROLE-BASED CONDUCTING POLYMERS: THE CHARACTERIZATION OF AS-GROWN FILMS BY X-RAY PHOTOEMISSION SPECTROSCOPY

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RJ 3840 (43807) 3/30/83
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THE CHEMICAL AND PHYSICAL PROPERTIES OF PYRROLE-BASED CONDUCTING POLYMERS: THE CHARACTERIZATION OF AS-GROWN FILMS BY X-RAY PHOTOEMISSION SPECTROSCOPY

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ABSTRACT: XPS techniques have been used to characterize electrically conducting films of polypyrrole and polybithiophenes grown electrochemically. These techniques have yielded information not only on the nature of the polymeric cation and its counter anion but also on the structural disorder in these polymers. In particular the N1s spectra have revealed a non-uniformity in the distribution of the anions relative to the nitrogen atoms and the C1s spectra clearly show that $\sim 1/3$ of the pyrrole rings are different from the rest. Significant improvement in the structural order is achieved by blocking the β sites on the pyrrole ring with methyl groups to ensure a completely α,α' bonded polymer. Similar experiments on polybithiophene polymers show that this polymer is considerably more ordered than polypyrrole.

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I. INTRODUCTION

Electrically conducting polymers have attracted a great deal attention in the past ten years because of their unusual electronic properties which have lead to a number of potential device applications based on these materials.[1-4] Polythiazyl, $(SN)_x$, became widely known after it was recognized that this material was the first polymeric superconductor.[5] Polyacetylene, $(CH)_x$, has been the subject of the most extensive experimental and theoretical investigations because in this particular polymer bond-alternation defects[6] may lead to quasiparticles, often referred to as solitons,[7,8] which have very unusual electronic and magnetic properties.[9,10] Polypyrrole (PP), was first prepared electrochemically by Dall'Olio *et al.* in 1968[11] and as free standing films by Diaz *et al.* in 1978.[12] This polymer is attractive partly because of the ease with which PP films can be grown in their oxidized, PP^+, electrically conducting form by electrochemical polymerization of pyrrole monomer, partly because they show good environmental stability[13] and partly because of the variety of pyrrole monomers which can be polymerized. Very recently the mechanism of conductivity in pyrrole polymers has become of particular interest because it has been suggested that bipolarons may be involved.[14]

In a previous article on the chemical and physical properties of pyrrole-based conducting polymers[15] it was shown that free standing films of polypyrrole can also be obtained in their neutral form (PP^o) by electrochemical reduction of the oxidized PP^+. However, the neutral form of the polymer is highly air sensitive and the present application-oriented efforts of several research groups are centered around the use of the more stable oxidized conducting form of polypyrrole as organic electrodes.[16,17] It has been demonstrated that PP^+ films are useful for protecting semiconductor photoanodes (n-Si, n-GaAs, n-CdS) from photocorrosion in photoelectrochemical cells for solar energy conversion.[18-20] All of the potential applications use the PP^+ films directly as grown. Unfortunately present knowledge of the properties of polypyrrole, in particular their chemical and electronic structure, is far from complete. PP films are very difficult to characterize because they are *insoluble* and *much less crystalline* than other conducting polymers. Lack of structural data has impeded accurate band structure calculations and complicated the interpretation of the available data. Discrepancies between the chemical analyses of these films and their idealized formula were also confusing.[12,13,21,22] A series of X-ray photoemission spectroscopy (XPS) experiments was therefore undertaken to characterize the polypyrrole in greater detail.

Photoelectron spectroscopy has been used extensively to study of nonconducting solid polymeric materials[23,24] and also to probe the chemical and electronic structures of amorphous metals [25] and amorphous semiconductors.[26] Indeed, long-range order does not impact very heavily on the main photoemission spectral features, while short-range effects are crucial. In view of this, photoemission spectroscopy (PES) seems to be an appealing tool to study poorly ordered conducting polymers. Although doped $(CH)_x$ has been studied by this technique[27-29] and another PES study on polypyrrole systems is underway,[30] these techniques have not yet become established in the field of conducting polymers. In this paper the results of XPS core and valence level studies on as-grown conducting i.e. oxidized, PP^+ films are presented. It should be stressed that PP^+ films obtained by oxidizing neutral polypyrrole (PP^o) either chemically or electrochemically are different from the as-grown films as discussed in a previous paper.[31] Although the main emphasis of this paper is on as-grown polypyrrole perchlorate ($PP^+C\ell O_4^-$), similar films with BF_4^- and PF_6^- counterions have also been examined along with films of poly-β-dimethylpyrrole perchlorate ($P\beta DMP^+C\ell O_4^-$), in which the hydrogen on both of the β-carbons of the pyrrole ring is replaced by methyl groups.[32] Also included are some preliminary results obtained for oxidized polybithiophenes, (PBT^+), where sulfur is the hetero-atom of the aromatic ring instead of nitrogen. It is important to appreciate that the notation PC^+A^-, (polymeric-cation anion) used throughout this paper for these compounds is derived from the heterocyclic monomer and the anion of the electrolyte salt assuming that no additional chemistry takes place during the electrochemical polymerization process. Though this assumption is convenient it is in fact not always valid and both the monomer and the anion can be chemically modified. Determination of the precise nature of the final form of the polymeric cation and the anion is a primary object of this paper as well as a determination of their relative concentrations.

II. EXPERIMENTAL

(a) Samples

All PP^+ films were grown electrochemically on Pt substrates in a He-atmosphere dry box using CH_3CN solutions containing either $AgC\ell O_4$, $AgBF_4$ or $AgPF_6$ salts.[15] Considerable care was taken to purify and dry the electrolyte salts and the solvent which was also deoxygenated using freeze-thaw cycles under a vacuum of 10^{-5} torr. A similar method was used to grow $P\beta DMP^+C\ell O_4^-$ and $PBT^+C\ell O_4^-$ films. Films of $PBT^+SO_4^-$ were grown from an aqueous H_2SO_4 electrolyte in the laboratory atmosphere. A total of 42 different samples were investigated, with film thicknesses ranging from ~500Å to 15 μm. In the case of $PP^+C\ell O_4^-$, severe deviations from the stoichiometry of the anion were found for very thin films (d<1000Å). These films will be discussed in a future publication. In this paper only the results for regular films with typical thicknesses of 1-5 μm will be reported. The results described below for $PP^+BF_4^-$ and $PP^+PF_6^-$, however, are independent of thickness, since no abnormal behavior in thin films of these types was observed. The films were transferred in sealed vials from the drybox, to the spectrometer, where they were mounted onto the sample holder inside a glove bag continuously flushed with UHP argon for the 1h prior to and during the operation. Although the electrical properties of PP^+ films are rather stable in atmosphere,[13] the films do react to some extent with oxygen.[2,31,33] The precautions taken in transferring the samples were therefore necessary to maintain the pristine state of the as-grown films as completely as possible.

The question of whether the XPS results are dominated by surface effects and contamination effects rather than the bulk characteristics of the films was addressed by applying various *in situ* cleaning procedures (gentle heating and sputtering in UHV). Although surface contamination appeared to be only a minor problem, the cleaning techniques tended to alter the films. Hence, it seemed reasonable to measure samples after rare gas transfer but without further *in situ* cleaning operations, particularly in view of the fact that polymer systems have relatively high escape depths and adsorbates on polymers have low sticking coefficients. The validity of this approach has been confirmed using the even more surface sensitive UV-PES to examine polypyrrole.[34] In these experiments no difference was found between samples inserted into the spectrometer as described above and samples for which the surface was cleaned *in situ* by mechanical abrasion.

(b) XPS Techniques

For the XPS measurements a Hewlett-Packard 5950B spectrometer with monochromatized AlK_α radiation and an energy resolution of ~0.7 eV was used. The pressure during the measurements was always maintained in the low 10^{-9} torr range by ion pumps. The energy calibration of the system was checked with Au and Pt standards using either the $4f_{7/2}$ line or the Fermi edge. In all cases, the polymeric films were sufficiently conducting to prevent electrostatic charging of the samples. In several cases, clusters of gold, electrodeposited directly on the polypyrrole films were used to check the binding energy scale and the Au Fermi edge always appeared at $E_B=0$ eV. For quantitative chemical analysis of the films, the N1s, O1s, Cℓ2p, Cℓ2s, P2p, B1s and F1s signal intensities were calibrated by measuring the corresponding peaks in the following model salts of well known composition, $(Bu)_4NC\ell O_4$, $(Bu)_4NPF_6$, $(Et)_4NBF_4$, $AgPF_6$ and $NOBF_4$. All these salts were purified, dried, mounted on double-sided scotch tape in the drybox and transferred into the spectrometer under rare gas as described above. Electrostatic charging was observed for all these insulating salts and their correct binding energies had to be established by a calibration procedure using thin Au or Pt layers evaporated onto double-sided scotch tape. The C1s signals originating from the tape were measured with respect to the Au and Pt fermi edges. The most intense signal was found at 285.1 eV; another peak was located at 289.1 eV. The absolute binding energy scale of the salts was then obtained by setting the main scotch tape C1s peak to 285.1 eV. When this signal was masked by carbon signals from the salt, i.e., in $(Bu)_4NC\ell O_4$, the second scotch tape peak was adjusted to 289.1 eV. In all of these outlined procedures there was no differential charging between the tape and the salt or metal mounted on it. This was demonstrated by flooding the samples with thermal electrons and ensuring that variations of the flooding current resulted in uniform binding energy shifts of all signals. Table I summarizes the experimentally determined binding energies and atomic sensitivity factors. Since the surfaces of samples examined by XPS are most often contaminated by oxygen, particular care was taken to determine the O1s cross section in $(Bu)_4NC\ell O_4$. For this material a contaminant oxygen contribution to the O1s signal, estimated from that measured for the otherwise oxygen free $(Et)_4NBF_4$ and $(Bu)_4NPF_6$ salts, was subtracted from the integrated intensity of the O1s peak.

III. THE $PP^+ClO_4^-$ MODEL COMPOUND

(a) C1s Lineshape

Since the difference between the α and β carbons leads to an energy splitting of 0.9 eV in the C1s signal of pyrrole monomer,[36] a similar splitting would also be expected in the C1s peak of polypyrroles. Although the C1s main peaks of the polymer do not show the clear splitting of the monomer, the peak envelope obviously does not originate from a single line. Careful lineshape analysis, reveals that the C1s main peak is composed of three lines (Fig. 1). The line at lowest binding energy due to the pyrrole β carbons, is centered at 283.6 eV and has a linewidth of 1.2 eV, while the line characteristic of the α carbons, is located at 284.5 eV and has linewidth of 1.4 eV. It is remarkable that the 0.9 eV energy splitting of the monomer is exactly preserved in the polymers. On the other hand, in all samples investigated the α carbons have a consistently larger linewidth than the β carbons. This is consistent with the fact that polypyrrole is mainly α-α' linked and perhaps reflects deviations from the ideal planar conjugated chain though it should it may also result from the presence of hydrocarbon impurities which affect the α peak more than the β peak as will be discussed shortly.

It can also be seen in Fig. 1 that the C1s line is not symmetric. Further structure lies on the high binding energy side of the peak. For reasons which will become clear in the following sections fermi surface excitations, which lead to skewed XPS peaks in metals,[37] are not believed to be the source of this asymmetry. In view of the poor crystallinity of $PP^+ClO_4^-$, and the fact that ^{13}C NMR also shows other types of carbon besides the α and β species of the aromatic ring,[33,38] the asymmetry on the higher binding energy side of the C1s peak is assigned to cross-linked, chain-terminating or non-α-α' bonded carbons as well as carbons in partially saturated rings.[15] These carbons will subsequently be referred to as the disorder type carbons. The corresponding XPS line is centered at 285.4 eV and has a line width of 2.4eV, much larger than that of the α and β carbons. Such a large linewidth is not surprising for a peak due to static disorder effects. Finally, the lineshape analysis shows that a further XPS structure, located at 287.8 eV, contributes significantly to the high energy side asymmetry of the C1s peak in $PP^+ClO_4^-$. This feature will be discussed below in the section dealing with shake-up satellites.

Turning now to the relative intensities of the XPS peaks found in the complex C1s signal, it seems likely that the intensities of the α and the disorder-type carbon peaks are increased relative to the β carbon peak because of the hydrocarbon contamination present in almost any XPS spectrum at ~284.5-285 eV. This probably explains the difference in intensity between the β and α lines in Fig. 1. However, even after reducing the α and disorder peaks by an appropriate factor in order to equalize the number of α and β carbons, the resulting intensity of the disorder peak implies that 1/3 of the pyrrole rings are still found to be affected by structural disorder. In fact, 1/3 of all pyrrole rings appear to be either cross-linked, chain terminating or non-α-α' bonded. This number seems to be high but chemical analysis of $PP^+ClO_4^-$ films[15] has shown the presence of as much as 10% excess hydrogen. Even though the numbers given here from the XPS analysis are rather crude, they still give an impressive idea about the degree of disorder in polypyrrole films.

(b) N1s Lineshape

A typical N1s core level spectrum of as-grown $PP^+ClO_4^-$ can be seen in Fig. 2. As in the case of the C1s level, the peak is asymmetric on the high binding energy side. In many samples, two shoulders appear more or less well-resolved in the high binding energy wing of the main pyrrole peak at 399.6 eV. Again fermi level effects are not considered to cause the asymmetry of the N1s peak, nor is structural disorder believed to be the cause of the shoulders of the N1s peak. In fact, polymerization defects are likely to affect the carbon spectrum much more than the nitrogen spectrum. Instead, the three nitrogen features are assigned to three electrostatically inequivalent groups of nitrogen atoms. It should be kept in mind that $PP^+C\ell O_4^-$ is an oxidized material containing, as will be seen in the next section, perchlorate anions bearing one localized charge. Since these ions are located in between polypyrrole chains, they will produce electric fields at the nitrogen sites, making the atoms in their proximity look more positive than others. The exact position of the counterions with respect to the polypyrrole chains is not known at present, however it appears from the N1s lineshape that three inequivalent N sites are created. The exact positions of the shoulders, as determined by a lineshape analysis, are 400.6 eV and 402.8 eV. Since an empirical relation of ~5.8 eV binding energy shift per unit charge holds for the N1s core level in the neighborhood of 401 eV,[39] these shifts indicate that charges of ~+1/6 and ~+1/2 are induced on the nitrogen atoms of the shoulder structures compared to the pyrrole nitrogen atoms of the main peak. Justification for the assignment of features on the high binding energy side of the C1s spectrum to static disorder effects, but to electrostatic effects in the case of the N1s spectrum will be given in the section of this paper dealing with $P\beta DMP^+C\ell O_4^-$.

It is worthwhile to compare the integrated intensities of the shoulders to that of the 399.6 eV peak which appears to dominate the spectrum. This comparison shows that the ratio of what is presumably the counterions' nearest nitrogen neighbors, next nearest nitrogen neighbors and least affected nitrogen neighbors is very close to 1:2:2. The proposed interpretation of the N1s spectrum is also consistent with the linewidths of the different components. Indeed, the structure at 399.6 eV which is believed to be the least influenced by the presence of the anions is rather sharp (1.15 eV), but the linewidth of the next nearest neighbor nitrogen atoms is doubled to 2.4 eV and the linewidth of the nearest neighbor nitrogens is even larger. Certainly, the counterions cannot be expected to sit in perfect crystallographic sites when the polypyrrole matrix is so highly disordered, the nitrogen spectra influenced by these counterions are therefore expected to be inhomogeneously broadened, as observed.

(c) Anion Core Levels

The $C\ell 2s$ level appears at 278.0 eV, some 8 eV above chemically unshifted chlorine. The observed large chemical shifts are typical for chlorine in the +7 oxidation state of the $C\ell O_4^-$ anion. The corresponding O1s line is located at 532.1 eV. Comparison of the Cℓ to O integrated and corrected line intensities gives a ratio of 1:4.4. Considering the oxygen contamination present in virtually every XPS spectrum, this ratio is consistent with the $C\ell O_4^-$ stoichiometry. Chemical analysis gives a composition of $C_{3.94}N_{1.0}H_{3.37}(C\ell O_4)_{0.33}$[15] for films grown from $AgC\ell O_4$ solutions. The XPS data indicate 0.35 perchlorate ions per nitrogen averaged over 8 samples. The highest and lowest values of the ratio were 0.42 and 0.28; the rest of the samples gave ratios in the range 0.32-0.37. Thus XPS can be a reliable quantitative analytical tool for these systems provided appropriate care is taken.

(d) Valence Band Spectra

A typical valence band spectrum of $PP^+C\ell O_4^-$ has been reported previously.[40] The XPS valence band spectrum of $PP^+C\ell O_4^-$ can be understood in terms of the known valence band spectra of pyrrole monomer[36] and the perchlorate anion.[41] Primarily, valence band spectroscopy therefore confirms the core level results by identifying the existence of both, pyrrole rings and perchlorate anions. It should be mentioned, however, that no significant density of states can be seen by XPS at, or close to the fermi energy, a situation similar to that encountered for other polymeric π metals.[15] In contrast, states in the vicinity of the fermi level are clearly seen by XPS in classical metals and also in an organic metal like TTF-TCNQ.[42] In $PP^+ClO_4^-$, the uppermost, clearly observable XPS feature is a peak at ~4 eV binding energy, to which pyrrole and perchlorate orbitals both contribute. Above ~2 eV binding energy, only background can be seen. Thus the $PP^+ClO_4^-$ valence band does not look like that of a metal.

(e) C1s Satellites

Figure 3 shows the series of satellites which have been observed on the high binding energy side of the C1s peak of $PP^+ClO_4^-$. It has been shown in some detail for polymeric systems[23-24] that such structures can arise from simultaneous core electron photoionization and valence electron excitation ("shake up") or ionization ("shake off"). While structures on the high energy side of the direct photoionization peak could also arise from characteristic energy losses (i.e., plasmons), it is known that shake-up structure is most prominent in polymer systems where either the backbone or some pendant groups are unsaturated. Particularly, in systems containing aromatic rings, the shake-up satellites are believed to be due to π-π^* transitions involving the two highest occupied valence levels of the neutral molecule and the lowest unoccupied level of the corresponding core ionized species.[23-24] For a series of simple nonsaturated polymer systems, the shake-up satellites are observed 6-8 eV above the main peak.[43]

In $PP^+ClO_4^-$, up to three satellites can be seen. Since they are separated from the main photoionization peak and from each other by multiples of 3.5 eV, and since their intensity decreases with increasing distance from the main peak, they are all assigned to the same shake-up transition, involving one, two or three valence electrons, respectively. The observation of these structures is consistent with an unsaturated polymeric system. It has been proposed that the peak at ~2.7eV in the absorption spectrum of PP^+ was a π-π^*

transition derived from the π-π^* of pyrrole monomer which occurs at ~6eV. The observation of the shake-up energy of 3.5 eV, confirms the previous assignment of the optical peak.

IV. OTHER PP^+ SYSTEMS

(a) $PP^+BF_4^-$

In general the results found for $PP^+C\ell O_4^-$ can be extended to polypyrrole films prepared from $AgBF_4$ solutions. Although the center of gravity of the C1s signal, which was located at 284.2 eV in $PP^+C\ell O_4^-$, is shifted to somewhat higher binding energy (284.8 eV) in the $PP^+BF_4^-$ films, the C1s linewidth (2.2 eV FWHM), is the same as in the perchlorate compound, as is the overall lineshape. Thus, all the conclusions drawn for the carbon atoms in $PP^+C\ell O_4^-$ also apply to $PP^+BF_4^-$. Similar comments can be made concerning the N1s spectrum which is also the same as that of $PP^+C\ell O_4^-$, including the two shoulders at the high binding energy side. As in the case of the C1s, the whole N1s spectrum is slightly shifted to higher binding energies, making the main N1s feature appear at 400.0 instead of 399.6 eV. The B1s and F1s peaks are found at 194.0 and 686.1 eV, which is exactly the same energy separation as in the $NOBF_4$ and $(Et)_4NBF_4$ standard compounds. There is no doubt, therefore, that tetrafluoroborate ions are incorporated into the films. The XPS data indicate a B to F ratio of 1:3.6 as an average over 4 films. Confirmation of the nature of the final state of the BF_4^- is important because chemical analysis always shows a departure from the ideal 1:4 stoichiometry with a significant fluorine deficiency.[12,13,21,22] While the anion to pyrrole ring ratio was very close to 1:3 in $PP^+C\ell O_4^-$, XPS indicates one tetrafluoroborate anion for 4 pyrrole rings in $PP^+BF_4^-$. More precisely, 0.26 boron atoms were found on an average over 4 samples per nitrogen.

A marked difference is found in valence level spectroscopy of the polypyrrole perchlorate and tetrafluoroborate films. While perchlorate orbitals contribute strongly to the

$PP^+ClO_4^-$ valence band [40], pyrrole-type states dominate the uppermost 27 eV of the $PP^+BF_4^-$ valence band (Fig. 4). This assignment is fairly straightforward, since the 5 features at ~3.7, 8.1, 12.7, 18.1 and 24.5 eV binding energies have already been observed and identified by Gelius *et al.*[36] in an XPS study of the pyrrole monomer. The peak seen at 30.6 eV is due to F2s states of the BF_4^- species. It is not particularly surprising to find no boron 2s or 2p contributions, since the corresponding electrons are presumably predominantly located on the fluorines. However it is unexpected to see the F2p contribution buried under the pyrrole peaks while O2p derived states dominate the valence band of the perchlorate polymers, particularly in the 10-15 eV region. The number of anions per pyrrole ring is somewhat larger in $PP^+ClO_4^-$ (0.35) than in $PP^+BF_4^-$ (0.26), but this cannot account for the observed difference because the cross section of the F2p levels is ~2.5 times *higher* than that of the O2p levels, which should result in a stronger signal associated with the anion in $PP^+BF_4^-$ than in $PP^+ClO_4^-$. This point obviously needs further investigation.

(c) $PP^+PF_6^-$

The C1s and N1s signals found in polypyrrole films grown from $AgPF_6$ solution are undistinguishable in shape and width from those found in $PP^+ClO_4^-$ and $PP^+BF_4^-$. The center of gravity of the C1s spectrum is located at 284.8 eV, as in the tetrafluoroborate films, and the N1s main peak is at 399.9 eV, very close to the 400.0 eV of the $PP^+BF_4^-$ and the 399.6 eV of the $PP^+ClO_4^-$ films. In striking contrast to the films discussed so far, the anion present in solution, PF_6^-, is *not* incorporated into the polypyrrole films without undergoing chemical changes. This becomes obvious from the positions of the F1s peak at 687.7 eV, the P2p peak at 134.6 eV and the P2s peak at 192.1 eV. The binding energy separations characteristic for the fluorophosphate anions in the PP^+ films are therefore

553.1 eV in the case of the F1s/P2p lines and 495.6 eV in the case of the F1s/P2s lines. These numbers are clearly not the signature for PF_6^- ions, for which the corresponding F/P separations are 550.3 and 493.0 eV (Table I). Furthermore the P/F ratio measured for the films is not 1:6. These results illustrate the danger of assuming that the anions from the electrolyte are necessarily inert. The precise nature of the anionic species incorporated during growth of polypyrrole from these solutions is presently under investigation. Whatever the nature of the phosphorus anionic species in the films, there are 0.32 P atoms per nitrogen in the films, *i.e.*, one anion for 3 pyrrole rings, as observed for $PP^+ClO_4^-$.

V. A SUBSTITUTED POLYPYRROLE: POLY-β-DIMETHYL-PYRROLE PERCHLORATE

Substituting the β-hydrogens of the pyrrole ring by methyl groups ensures that the pyrrole rings are exclusively bonded via the α,α' carbons. This would be expected to increase the degree of order relative to the parent polymer and electron diffraction studies have shown that this is indeed the case.[44] Enhanced order is also clearly shown in the XPS data by the linewidths of both the C1s signal of the polymer backbone and the Cl2p signal from the perchlorate films. Both these linewidths are significantly reduced relative to unsubstituted polypyrrole films. Despite the fact that the methyl carbons are now included in the spectrum at ~285.0 eV (Fig. 5), the overall C1s FWHM linewidth actually decreases from 2.2 eV in $PP^+ClO_4^-$ to 1.7 eV in $P\beta DMP^+ClO_4^-$. In addition, the asymmetry on the high binding energy side of the C1s spectrum is reduced compared to the unsubstituted pyrrole polymer. In the case of $PP^+ClO_4^-$ this asymmetry on the high binding energy side of the C1s spectrum (Fig. 1) was assigned to the disorder-type carbons associated in part to non-α,α' carbon linkages and giving rise to a broad shoulder at ~285.4 eV. The reduction of this contribution in $P\beta DMP^+ClO_4^-$, is consistent with the absence of such linkages due to the presence of the blocking methyl groups. The anionic sites also seem to be better defined, as shown by the reduction in the linewidth of the $C\ell 2p_{3/2}$ from typically 1.3 eV in the unsubstituted polymer to 1.0 eV in the substituted polymer. This result is consistent with electron diffraction studies which show that the pyrrole chains are crystallographically more aligned for the substituted polymer. This in turn leads to a more ordered anion sublattice.[44]

In contrast the N1s linewidths and lineshapes are very similar in both the substituted and the unsubstituted polymer. This strongly supports the assignment of the broadening of the polypyrrole N1s and C1s spectral features to different origins; electrostatic screening of the counterions in the case of the nitrogen line as opposed to disorder effects and departures from the idealized structure in the case of the carbon line. The observed core level positions and intensities do not indicate any fundamental difference in chemical structure between the substituted and the unsubstituted polymer films. In $P\beta DMP^+C\ell O_4^-$, the C1s line peaks at ~284.7 eV, some 0.5 eV above the corresponding line in $PP^+C\ell O_4^-$. This is expected since the methyl carbons give rise to a signal at ~285.0 eV, which shifts the envelope of the whole C1s spectrum towards higher binding energy. The N1s main peak is found at 399.8 eV. As in the case of $PP^+C\ell O_4^-$, the $C\ell$:O ratio is slightly low and one perchlorate is found for three pyrrole rings. Again, the agreement between the quantitative XPS data and the chemical analysis of the $P\beta DMP^+C\ell O_4^-$ films[32] is excellent.

The shake-up satellite spectrum in the substituted films, also seen in Fig. 5, is similar to the corresponding spectrum in unsubstituted films (Fig. 3). The valence band structures of $P\beta DMP^+C\ell O_4^-$ are sharper than in $PP^+C\ell O_4^-$, again due to the higher crystallinity observed in the electron microscopy studies.[44] Figure 6 shows such a spectrum, in which the uppermost pyrrole-like peak (cf Fig. 4) is detectable as the shoulder (a) at ~2.7 eV binding energy. This structure was smeared out and therefore not observable in $PP^+C\ell O_4^-$. Otherwise, the comparison with Fig. 4 immediately shows which features of the

PβDMP$^+$CℓO$_4^-$ valence band are anion-derived and which are pyrrole-derived. For the sake of completeness, the assignments of the different valence band peaks to the pyrrole and perchlorate molecular orbitals[36,40,41] are repeated here. Structures (b) and (c) arise from three nonbonding, essentially oxygen 2pπ-type orbitals, while the structures (d) and (f) are generated from a mixture of chlorine 3s and 3p with oxygen 2p and 2pσ orbitals. The structure (i) at ~18 eV is pyrrole-derived. The shoulder (e) is not an artifact, it can be observed more clearly in PP$^+$CℓO$_4^-$, and is very likely due to the ~12 eV pyrrole peak. The perchlorate-derived feature (c) is broadened by the underlying 8 eV pyrrole group. Finally, peak (j) is not observed in perchlorate, pyrrole monomer or polypyrrole valence band spectra and therefore it is assigned to states derived from the methyl substituents.

VI. POLYMERIC FILMS FROM OTHER FIVE-MEMBERED HETEROCYLIC RINGS: POLYBITHIOPHENES

Oxidized polybithiophene films, grown electrochemically from solutions containing bithiophene and a perchlorate electrolyte, have a C1s linewidth of 1.6 eV, similar to PβDMP$^+$ films. The reason for the reduced linewidth compared to polypyrrole, however, cannot be *a priori* attributed to an increased degree of crystallinity. The energy splitting between the α and β carbons of thiophene rings is only 0.35 eV, much smaller than the 0.9 eV of pyrrole.[35] A narrower C1s envelope is therefore expected, but since the high binding energy side asymmetry is also weaker than in PP$^+$CℓO$_4^-$, the PBT$^+$CℓO$_4^-$ material might well be more ordered than its pyrrole counterpart. The PBT$^+$ films grown from a sulfuric acid, acetonitrile solution are even more ordered as shown by the C1s line which becomes fully symmetric and the linewidth which is further reduced to 1.3 eV. This suggests that asymmetric C1s spectra are not an inherent property of five-membered heterocyclic polymers in general.

Despite the changes in the C1s line shape associated with increasing order on going from $PBT^+C\ell O_4^-$ to $PBT^+SO_4^{2-}$, the S2s and S2p lines of the thiophene remain unchanged just as the N1s line in the pyrrole based polymers remained unchanged when the C1s line was narrowed due to increased crystalline order. Thus the interpretation of the carbon and heteroatom lineshapes discussed for the pyrroles also appears to valid for the bithiophene films.

The anionic species incorporated in the PBT^+ films grown from sulfuric acid was unambiguously established to be SO_4^{2-}, not HSO_4^- by comparison of the results with model compounds and unpublished SCF calculations of the O1s binding energies in HSO_4^-.[45] According to these calculations, the influence of the proton on the SO_4^{2-} tetrahedron produces a binding energy shift of the order ~4 eV on the 1s level of the neighboring oxygen atom with respect to the other three oxygens. No trace of such a peak in a 1:3 intensity ratio is found experimentally, and all the oxygens appear to be equivalent, consistent with the presence of SO_4^{2-} rather than HSO_4^- ions.

Fewer counterions are incorporated into polybithiophene films than into the corresponding pyrrole polymers. The anion to ring ratios were 1:3 in $PP^+C\ell O_4^-$ and 1:4 in $PP^+BF_4^-$, while this ratio is 1:7 in $PBT^+C\ell O_4^-$. The polybithiophene sulfate films provide a very accurate quantitative determination of this ratio, because the sulfur 2s and 2p intensities of the thiophene and the sulfate ions can be directly compared without any correction for cross section, kinetic energy dependencies, etc. Figure 7 shows the well-separated sulfur doublets with the thiophene $S2p_{3/2}$ signal at 163.5 eV and the sulfate $S2p_{3/2}$ signal at 168.4 eV from which it was determined that there is one sulfate ion for every 7 thiophene rings. Since the sulfate counterion is doubly charged the degree of oxidation of the PBT^+ films, is about the same as that found in pyrrole polymers. Thus a difference in the degree of oxidation cannot be used to explain the lower conductivities of the thiophene films which are in the range 10^{-1} to 10^{-2} $\text{ohms}^{-1}\text{cm}^{-1}$, some 3-4 orders of magnitude less than the polypyrrole films. This difference may indicate that the conductivity of the polythiophenes is more sensitive to non-α,α' bonding than is the case for the polypyrroles.[32]

VII. SUMMARY

The XPS studies of as-grown films have confirmed several ideas previously put forward about polypyrrole. More specifically, the C1s lineshape and the valence band spectra definitely show the presence of the pyrrole moiety in the polymer. The fact that the polypyrrole chain is indeed oxidized is confirmed by the presence of counterions such as $C\ell O_4^-$ or BF_4^- and their effects on the heteroatom. Quantitatively, XPS confirmed the 1:4 and 1:3 anion to ring ratios originally obtained by chemical analysis for $PP^+BF_4^-$ and $PP^+C\ell O_4^-$.[13,15]

There are some serious discrepancies between the idealized picture of polypyrrole as a linear metallic chain compound and our XPS data. Three points will be examined more closely. First, three electrostatically inequivalent nitrogen sites are detected. This means that the charge is fairly localized at the N sites and that the charge fluctuations apparently are not compensated by free holes, as would be expected for a one-dimensional metallic chain. Secondly, in some samples every third pyrrole ring seems to be a non- ideal one. With a number of defects of the order 5.10^{21} cm^{-3}, a linear chain model becomes fairly unrealistic. Thirdly, the pyrrole-derived valence bands are so similar in the solid-state polymer and in the gas-phase monomer that the question arises whether solid state effects and interactions between the rings are significant. The implications of these conclusions will be discussed in a broader framework in a later publication. However, the XPS data are certainly more consistent with a molecular solid model than with a one-dimensional metal.

Besides these very general remarks, some surprises in the details of the chemical structure in various films were found. For example, the PF_6^- ion is not inert when incorporated into polypyrrole, but undergoes electrochemically-initiated chemical transformations. Also, the valence band spectra of $C\ell O_4^-$ and BF_4^- doped films are surprisingly different in their general appearance. The bithiophene-based polymers incorporated only about half as many anions as the corresponding pyrrole polymer. From the XPS linewidths, it can clearly be established that $PBT^+SO_4^{2-}$ is more ordered than $PBT^+C\ell O_4^-$ and that β-substituted polypyrrole is far more ordered than regular polypyrrole. Although these results are themselves not unexpected *per se*, it was unexpected to find such clear evidence for this increased structural order by the XPS technique.

Finally, some comments on the position of the fermi level in these materials should be made. In an often used solid-state picture of one-dimensional organic and two-dimensional graphitic systems, the doping process is regarded as a uniform charge extraction from the semiconducting or semimetallic matrix. Since the π-band density of states near the fermi energy E_f is either zero or low in these materials, acceptor doping results in a large movement of E_f into the valence band and it is usually assumed that the rigid band model applies and that the valence band density of states does not change with doping. These ideas have to be used with caution for the polypyrrole family of materials. The optical absorption spectra of polypyrrole for instance show that the assumption of rigid π-bands upon doping may not be justified.[15] Also, a very high number of defect states is present in polypyrrole, which must be considered if E_f is to be shifted. With many of these states in the vicinity of the fermi level, it might not be possible to move E_f significantly. Thus these concepts, discussed extensively, for example, in doped polyacetylenes and in intercalated graphite, should be considered with severe reservations in the case of polypyrrole.

In conclusion, the potential of the XPS method in the investigation of materials such as polypyrrole has been demonstrated. Using this technique a great deal of qualitative understanding can be gained and even quantitative analysis seems to be fairly accurate if carried out with proper care.

ACKNOWLEDGMENTS

The authors wish to thank J. C. Scott, G. Weiser, T. C. Clarke, I. P. Batra for many fruitful discussions and V. Y. Lee and M. Krounbi for their technical assistance. The authors are indebted to P. S. Bagus and C. Nelin for their help in identifying the anionic species in $PBT^+SO_4^{2-}$. In addition, they want to thank U. M. Gubler and J. Krieg for providing them with helpful supplemental UPS and EELS information prior to publication and F. Greuter for critically reading the manuscript. This work was partially supported by a grant from the Office of Naval Research.

The first author gratefully acknowledges the financial support of the Swiss National Science Foundation.

TABLE I

Binding energies in eV and experimental atomic sensitivity factors of the anion and nitrogen atoms in salt standards used for the present study.

	F1s	O1s	N1s	Cℓ2s	Cℓ2p*	P2s	B1s	P2p
$(Et)_4NBF_4$	685.9/4.85		402.2/1.80**				193.9/0.61	
$NOBF_4$	687.1/4.85†						195.0/0.61	
$(Bu)_4NPF_6$	686.8/4.57		402.6/1.80**			193.8/1.18		136.5/1.51
$AgPF_6$	687.1							136.7
$(Bu)_4NC\ell O_4$		532.5/2.94	402.2/1.80**	278.1/1.35	207.4/3.19			

*Position of the $2p_{3/2}$ line, sensitivity factor for the total 2p doublet

**All experimental sensitivity factors normalized to 1.80 for N1s except experimental B1s sensitivity factor† which is normalized to 4.85 for F1s in $NOBF_4$

TABLE II

XPS binding energies and intensities in polyheterocyclic films. The binding energies are given in eV, while the intensities found in parentheses under these numbers are normalized to 1.00 for the heteroatom (N or S) intensity. The energies given for the C1s and N1s levels are the maxima of the envelopes, taken from the spectra before deconvolution of the peaks.

	C1s	N1s	$C\ell 2p_{3/2}$	$C\ell 2s$	O1s	B1s	F1s	P2p	P2s	$S2p_{3/2}$	S2s
$PP^+C\ell O_4^-$	284.2	399.6 (1.00)	207.1 (0.35)	278.0	532.1 (1.64)						
$PP^+BF_4^-$	284.8	400.0 (1.00)				194.0 (0.26)	686.1 (0.93)				
$PP^+PF_6^-$	284.8	399.9 (1.00)			531.8 (0.83)		687.7 (0.54)	134.6 (0.32)	192.1		
$P\beta DMP^+C\ell O_4^-$	284.7	399.8 (1.00)	207.1 (0.32)	278.2	532.2 (1.49)						
$PBT^+C\ell O_4^-$	284.6		207.5 (0.125)		532.2 (0.85)					163.6 (1.00)	228.0
$PBT^+SO_4^{2-}$	284.4				531.9					163.5 (1.00)	227.9[a)]
										168.4 (0.14)	232.2[b)]

[a)] ring heretoatom

[b)] sulfate atom

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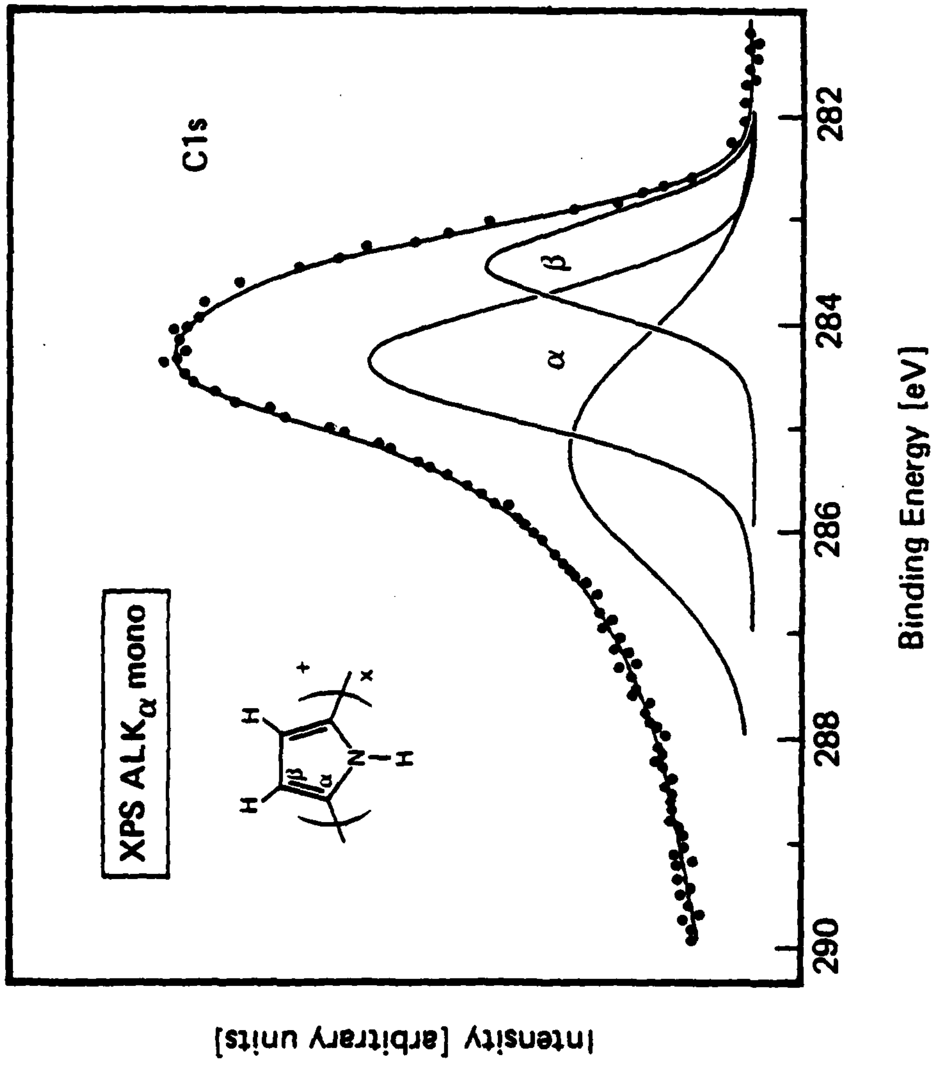


Figure 1. C1s XPS core level spectrum of polypyrrole perchlorate. The line through the data points represents the best fit obtained from a superposition of Gaussian peaks and a linear background. The lower lines show the contributions from β, α and disorder-type carbon atoms (see text).

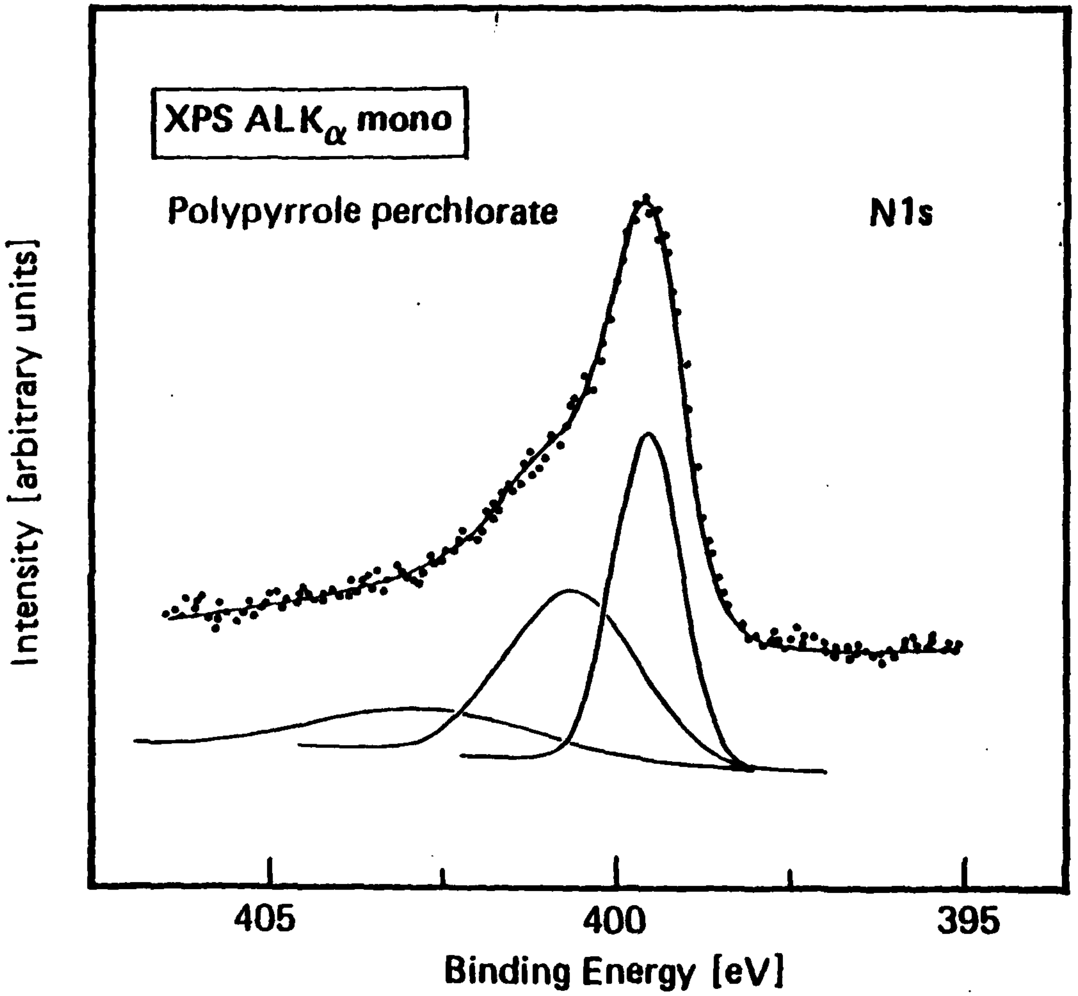


Figure 2. N1s XPS core level of polypyrrole perchlorate. The line through the points represents the best fit obtained from a superposition of Gaussian peaks and a linear background. The lower lines show the contributions from three inequivalent nitrogen sites.

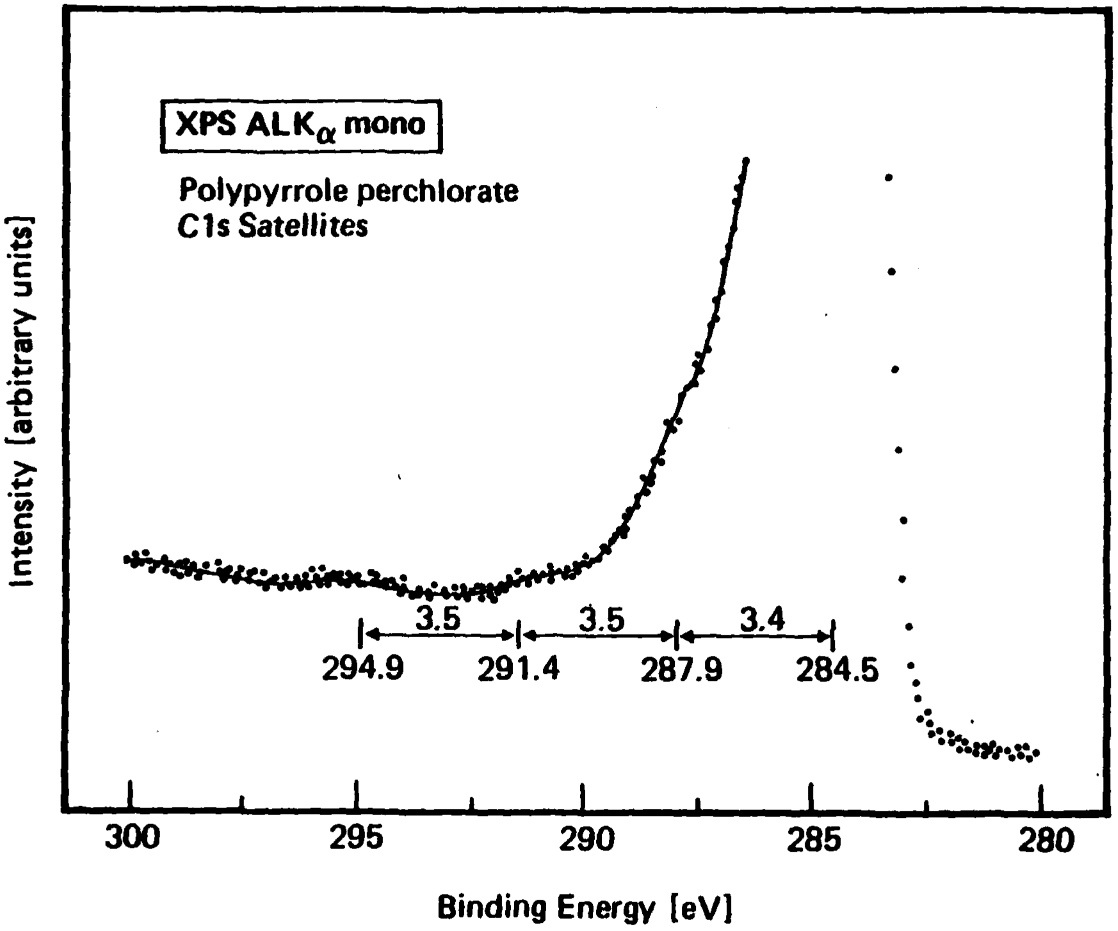


Figure 3. C1s shake-up satellites in polypyrrole perchlorate. The line through the data points is a guide to the eye.

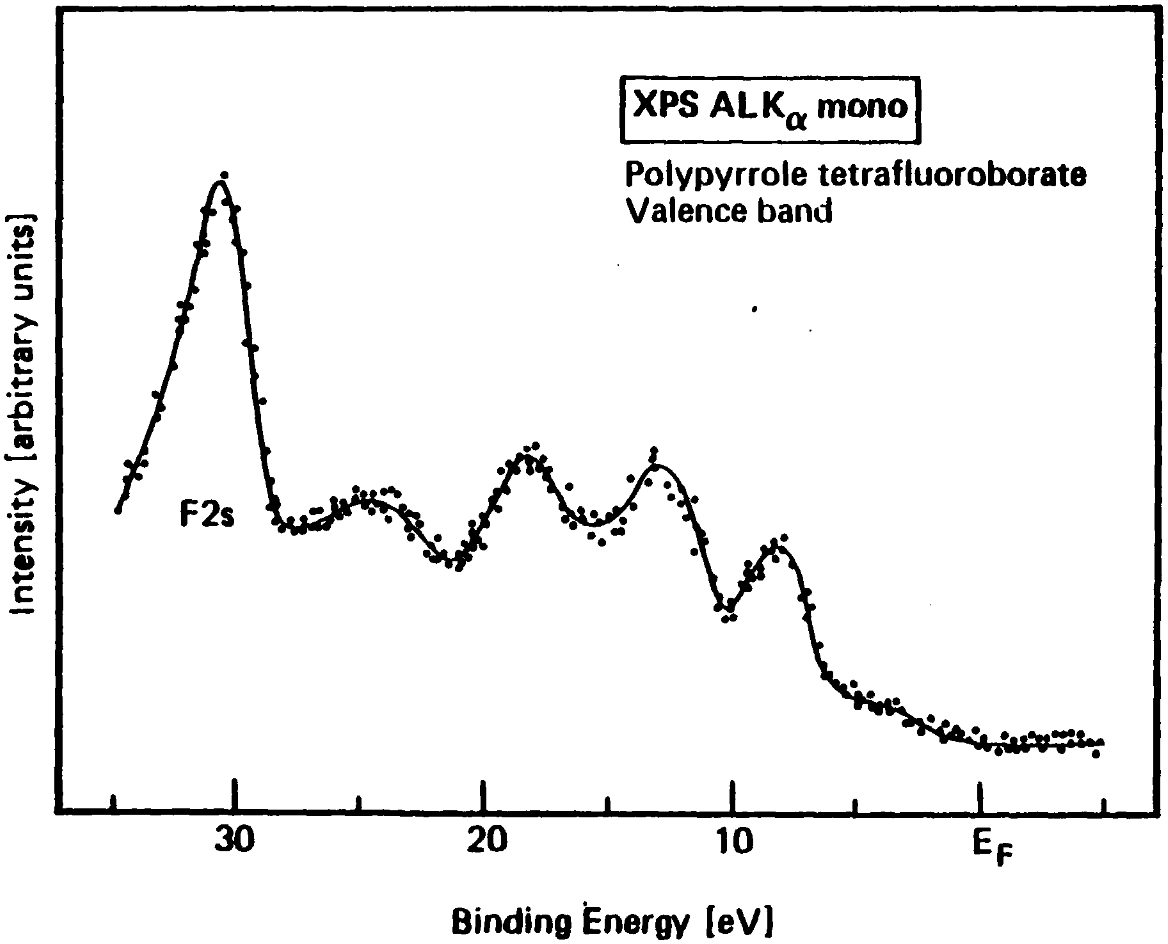


Figure 4. Valence band spectrum of polypyrrole tetrafluoroborate. The line through the data points is a guide to the eye.

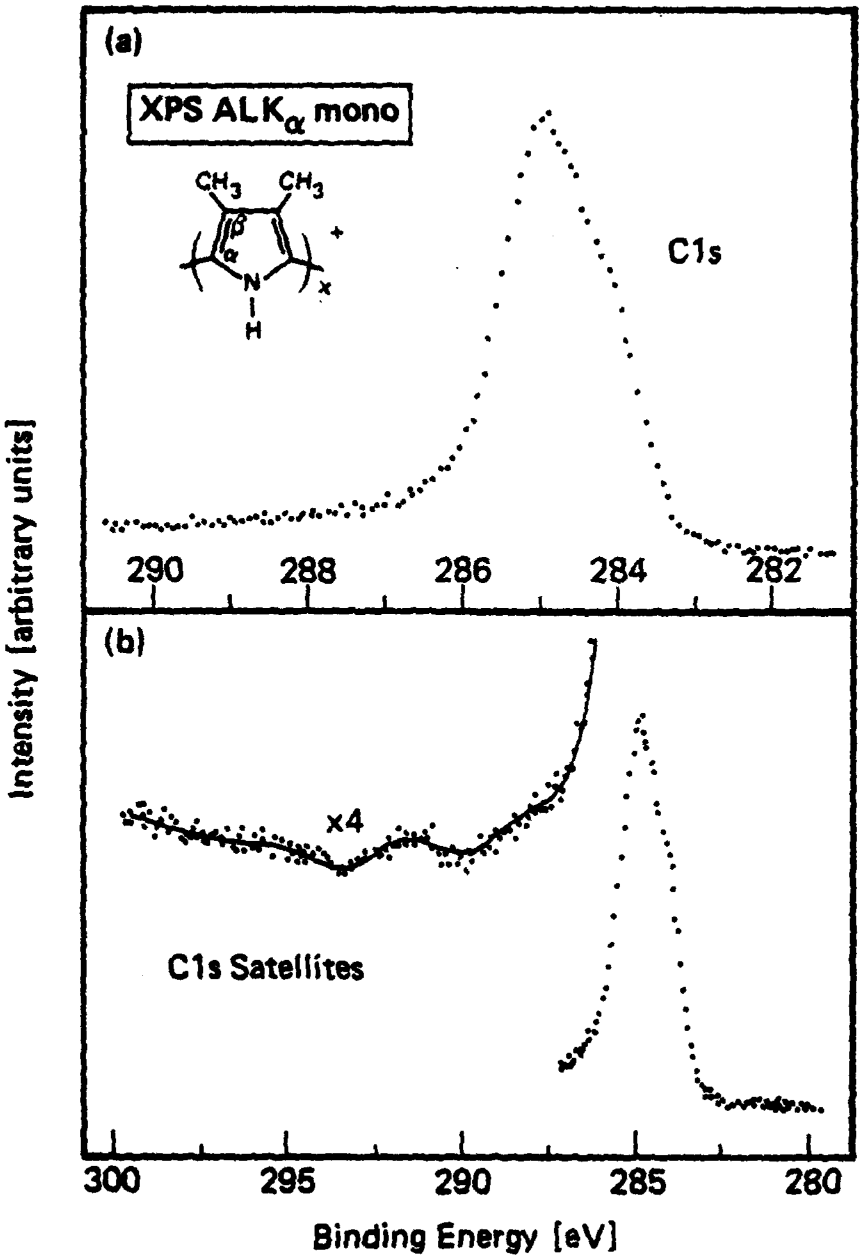


Figure 5. (a) C1s core level spectrum of poly-β-dimethylpyrrole perchlorate.

(b) C1s shake-up satellites of poly-β-dimethylpyrrole perchlorate. The line through the data points is a guide to the eye.

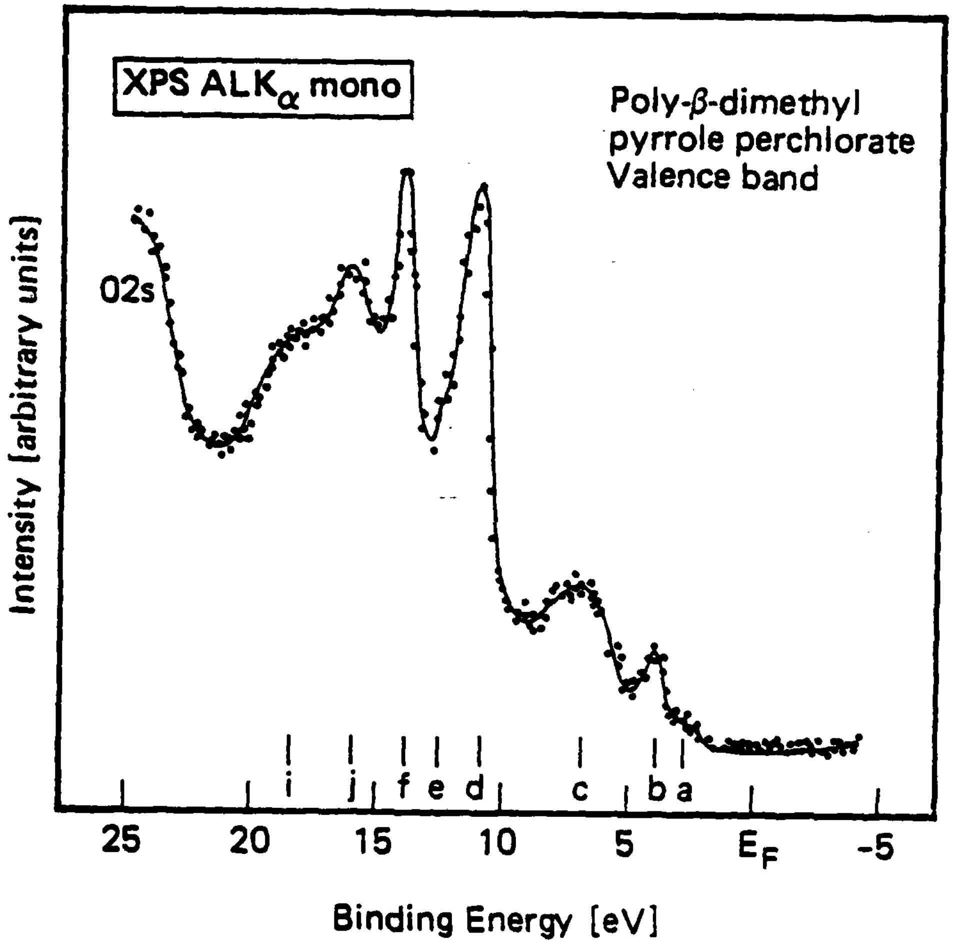


Figure 6. Valence band spectrum of poly-β-dimethylpyrrole perchlorate. The line through the data points is a guide to the eye. The structures a-i are explained in the text.

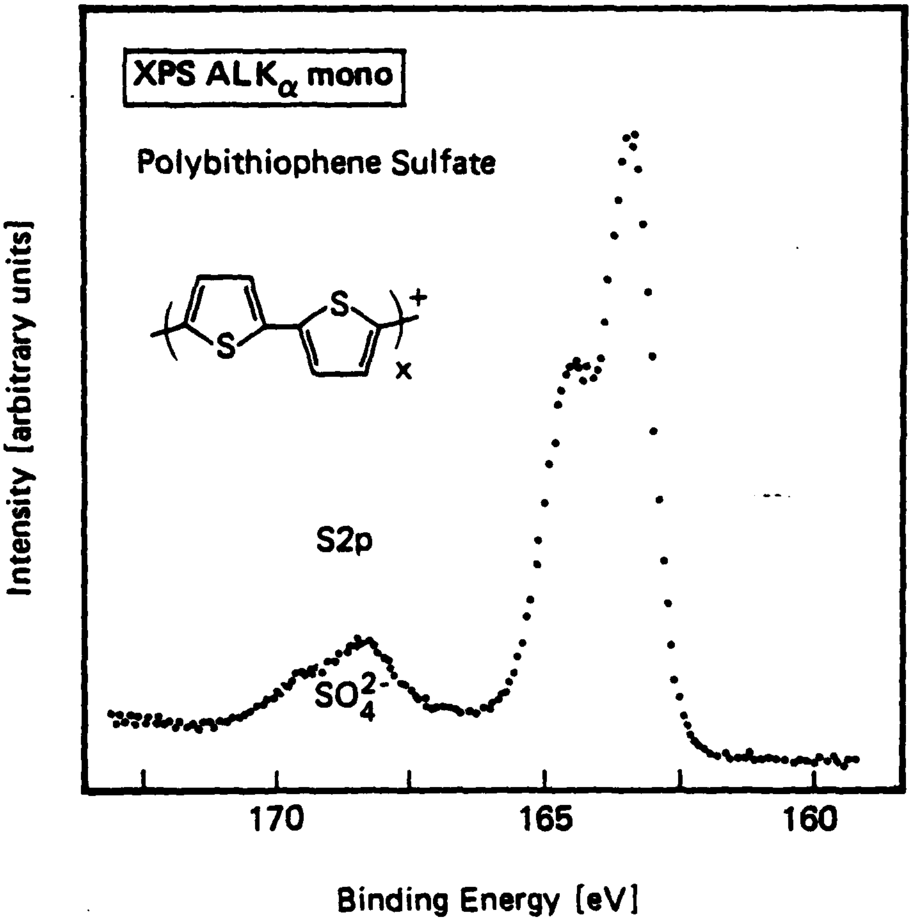
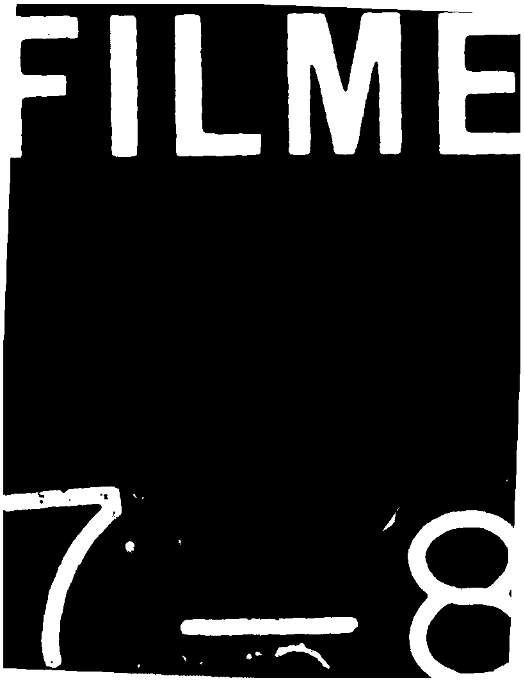


Figure 7. S2p core levels of polybithiophene sulfate. The doublet at ~164 eV is due to sulfur atoms from the thiophene rings, while the doublet at ~168 eV arises from the anions.



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