3630 *Macromolecules* **1991,** *24,* 3630–3637

Modification of Polybithiophene by Electrochemical Cycling Studied by ToF-SIMS and XPS

Gemma Morea,[*,†] **Luigia Sabbatini, and Pier Giorgio Zambonin**

Analytical Chemistry Laboratory, Department of Chemistry, University of Bari,
4, Trav.200 Re David, 70126 Bari, Italy

Andrew J. Swift, Robin H. West, and John C. Vickerman

The Centre for Surface and Materials Analysis, UMIST, P.O. Box 88,
Manchester M60 1QD, U.K.

Received August 7, 1990; Revised Manuscript Received November 27, 1990

ABSTRACT: A parallel ToF-SIMS/XPS study of electrochemically grown polybithiophene was carried out on both doped (ClO_4^-) and undoped pristine polymers and on samples electrochemically cycled from the conducting to the insulating form. The potential of ToF-SIMS in the analysis of this class of polymers was exploited for the first time and invaluable chemical information on the structure of both doped and undoped pristine samples was obtained. Moreover, the power of coupling SIMS and XPS techniques has been shown with reference to the investigation of the polymer "surface modifications" with cycling. On the basis of information obtained on the surface chemical composition, a first attempt to elucidate the degradation process of these polymers was made, with particular reference to the key role of the amount of water in the solvent.

Introduction

Surface analysis of polymeric materials has been usually performed in the past by X-ray photoelectron spectroscopy (XPS). XPS provides qualitative and quantitative information on atomic species present at the surface of the investigated material and supplies oxidation state data by signal chemical shift analysis. Nevertheless the latter capability is difficult to exploit in the surface characterization of polymers since the common elements that constitute these materials, e.g. carbon, nitrogen, oxygen, silicon, etc., do not always display easily discernible chemical shifts. This lack of molecular sensitivity often compels many workers to employ surface derivatization prior to analysis of these materials by XPS. This approach, however, has inherent disadvantages, introducing modifications and contaminations at sample surfaces.

A direct approach to molecular information can be achieved by using static secondary ion mass spectrometry (SSIMS).[1] This technique employs a beam of accelerated ions to bombard the specimen. Both positive and negative charged fragments and neutrals are generated as a consequence of the impact and the emitted ions are analyzed by mass. Static SIMS in recent years has provided valuable complementary surface information to electron spectroscopy and is finding increasing application in the investigation of polymer surfaces. The technique has an inherently greater surface specificity and sensitivity to molecular structure than XPS.

It has been widely demonstrated by a number of workers[2–9] that the mass spectra of secondary ions of polymers and biopolymers obtained by static SIMS provide unique information about the molecular arrangements at the surface of complex polymer systems. Reproducibility is assured provided the ion dose employed during the analysis is kept below a critical level, enabling the beam-induced damage effects to be neglected. This regime is known as the "static" SIMS mode.[4] Recently many aspects of polymer structure have been successfully investigated by static SIMS. For example, distinction of homologous polymers with different side chains[2] and information on the average chain length,[5] structure of chain ends,[6] monomer sequences in copolymers,[7] and influence of treatments on polymers surface structure.[8]

Table I

(a) pbt/ClO_4^- oxidized pristine
(b) pbt reduced pristine
(c) pbt/ClO_4 oxidized, 5 cycles
(d) pbt reduced, 5 cycles

Table II
XPS BE (eV) for the Main Signals of pbT

sample	C 1s	S 2p	Cl 2p A	Cl 2p B	O 1s
a	284.6	163.6	207.2		532.1
b	284.6	163.6	208.3		532.9
c	284.6	163.8	107.2	200.3	532.3
d	284.6	163.5	108.5	200.3	532.9

Table III
Atomic Ratios from XPS Signal Areas[a]

sample	S/Cl A	S/Cl B	C/S	N/S
ox. prist (350 μA/cm^2)[b]	2.7		5.0	0.25
red. prist (350[b]–150[c] μA/cm^2)	11.1		4.7	0.02
ox. 5 cycles (350[b]–50[d] μA/cm^2)	2.7	9.1	5.3	0.41
red. 5 cycles (350[b]–50[d] μA/cm^2)	3.3	10.0	5.6	0.40

[a] Uncertainty 10%. [b] Synthesis current. [c] Discharge current. [d] Cycling current.

One of the more recent developments of static SIMS, time of flight SIMS (ToF-SIMS) with its advantages of simultaneous detection and high transmission, has raised the sensitivity of SSIMS by 4–5 orders of magnitude compared with mass analysis using a typical quadrupole mass spectrometer. Moreover, the high mass capability of this technique often enables the direct evaluation of polymer structure, while the use of a pulsed primary ion source makes beam-induced damage insignificant.

In this work a particular class of polymers has been examined.

[†] Present address: The Centre for Surface and Materials Analysis, UMIST, P.O. Box 88, Manchester M60 1QD, U.K.

0024-9297/91/2224-3630$02.50/0

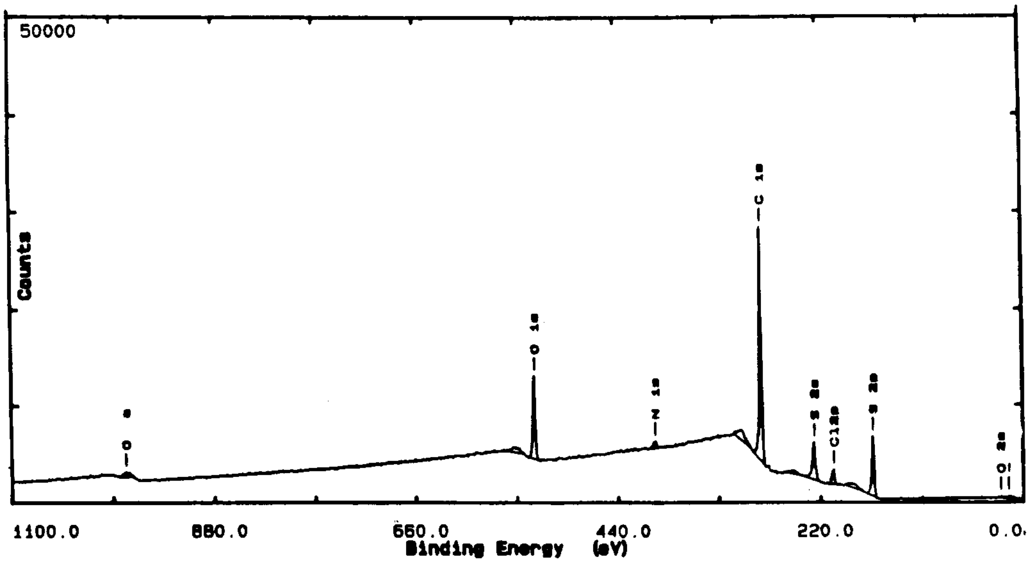


Figure 1. Overall XPS spectrum for an oxidized pbT/ClO_4^- film.

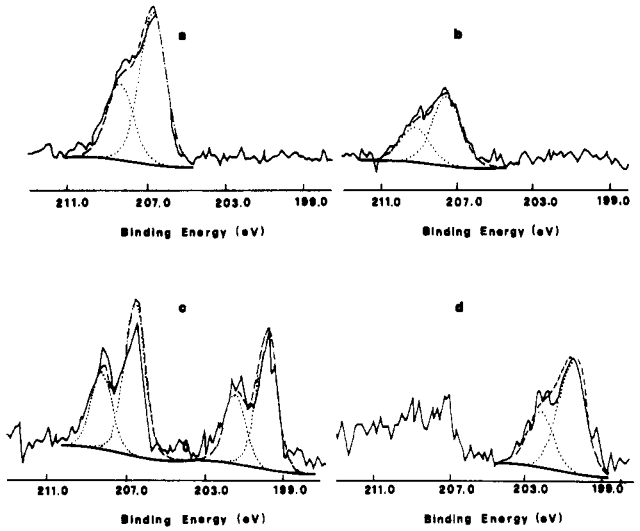


Figure 2. Cl 2p regions for (a) oxidized pristine pbT, (b) reduced pristine pbT, (c) oxidized cycled pbT, and (d) reduced cycled pbT.

Conducting polymers are novel materials whose practical applications, such as electrodes in secondary batteries, gas sensors, electrochromic materials, or corrosion protective films, are receiving growing attention. In these applications, moreover, the surface of samples plays a primary role. Many heterocyclic molecules like pyrrole, thiophene, etc. have been incorporated in conducting polymers.[10] The most common conducting form of these polymers is the oxidized form, which is thought to consist of polycations of the polymer. The electroneutrality of the system is restored by the intrusion of anions into the polymer lattice.

The synthesis and/or doping of polyheterocycles has been performed both electrochemically and chemically. In the electrochemical synthetic route (constant current, constant potential, cyclic voltammetry) the synthesis and doping are performed simultaneously (ref 11 and references therein). Growth of polycation occurs during the anodic polarization of the working electrode, following a radical mechanism,[12] and electroneutrality is achieved by the entry of anions from the background electrolyte (ClO_4^-, BF_4^-, etc.). The electrochemical route has been found to give better results in terms of the purity and conductivity of the polymer.

Polybithiophene (pbT) is a polymer showing good conductivity (few Ω^{-1} cm^{-1}) upon doping with negative ions. Its use as a cathode in secondary batteries is receiving growing interest, although poor resistance on charge–discharge cycles and spontaneous undoping in working conditions still prevent full development of polybithiophene-based batteries. A better understanding of such problems could be reached by a systematic characterization of such polymers by surface analysis.

The surface chemistry of polybithiophene has been studied by several workers.[13-15] X-ray photoelectron spectroscopy (XPS) has been employed as a quantitative technique to evaluate the surface stoichiometry and the doping ratio of polybithiophene. Moreover, the spectra have been used to gain a better understanding of band structure, order, and charge location in polybithiophene. In contrast, the authors are not aware of any static SIMS work on conducting polymers.

Recently, a systematic XPS investigation has been performed in our laboratory[16] with the aim of testing the chemical stability of the pbT upon cycling. Heavy modifications of the surface chemistry of the polymer were found under particular experimental conditions.

In this context an XPS and ToF-SIMS study of polybithiophene was performed and is reported in the present paper, in order to examine the potential of these techniques toward the analysis of such samples and with the aim of clarifying the chemical identity of the new species that form on pbT when cycled.

Experimental Section

Sample Preparation. All polybithiophene samples were electrochemically deposited in their oxidized doped form onto 1-cm^2 Pt anodes using a constant density current of 350 $\mu A/cm^2$, from a solution containing 10^{-2} M bithiophene (resublimed under vaccum at 20 °C) and 0.5 M $LiClO_4$ (desiccated at 120 °C under vacuum for 2 h) in acetonitrile (HPLC grade). The water concentration in $LiClO_4^-$ solutions used was found to be generally 0.1 M. All chemicals were supplied by Aldrich. Nitrogen was bubbled through the cell prior to use and a nitrogen environment was kept over the cell during polymerization. The samples were repeatedly washed in pure acetonitrile after synthesis and cycling and stored under nitrogen. The working electrode potential was monitored by a reference electrode of Ag/Ag^+ (0.1 M) in acetonitrile (+0.230 V versus SCE) and an EG&G Model 273 potentiostat/galvanostat. The quantity of charge for deposition was generally 65 mC, giving a film thickness of about 32.5 nm. The *reduced pristine* samples were prepared by applying a cathodic constant current of 150 $\mu A/cm^2$ immediately after the synthesis in the same monomer solution, for the time necessary for the anodic potential to reach the value of −0.3 V (versus Ag/Ag^+). At this stage the doping charge was calculated. The monomer quantities deposited were determined by considering the difference between the deposition and doping charge, based on the assumption that two electrons per monomer unit were consumed in growing the polymer,[16] and were typically 3×10^{-7} mol. *Cycled samples* were obtained by charging and discharging the film in a monomer-free solution at 50 $\mu A/cm^2$ current density and with a quantity of charge corresponding to the doping charge found after synthesis (~10 mC). A cycle corresponded to a discharging plus a charging experiment. Table I summarizes the nature of the sample examined in this work.

Measurements. XPS measurements were performed on an SSI M-Probe instrument operating with a base pressure less than 10^{-9} Torr. Monochromatized Al Kα X-rays were focused into a spot size of 1000×400 μm for source radiation.

ToF-SIMS analyses were performed on a VG IX23SQ instrument fitted with a pulsed liquid metal ion source (Ga^+, 30 kV) and a Poschenrieder energy compensating electrostatic analyzer. Both positive and negative secondary ion spectra were generated by using a total primary ion dose of 2×10^{11} ions cm^{-2}.

FT-IR measurements were performed on a BIO-RAD 3240-SPC spectrometer. The ATR arrangement was obtained by employing an RIIC multireflection ATR unit TR 25.

Results

XPS Results. Figure 1 shows a wide-scan spectrum for an oxidized sample of polybithiophene/ClO_4^-. Photoelectron peaks originating from C 1s, O 1s, S 2p, S 2s, Cl 2p, Cl 2s, and N 1s levels are detected. The binding energy (BE) values for the set of analyzed samples are reported in Table II, and Table III displays some atomic ratios as obtained by signal area measurement corrected by sensitivity factors.[18,19] Calibration of spectra was performed by taking as an internal reference the carbon 1s electron peak (BE = 284.6 eV) due to the ring carbons of pbT.

Figure 2a shows the *Cl 2p region* of the oxidized pristine sample. The signal at 207.2 eV BE in the pristine sample is indicative of a perchlorate species. Often the presence of two partially overlapping Cl 2 p doublets (spin orbit splitting $\Delta E = 1.6$ eV) was observed and a tentative curve fitting for these identified two chlorine species at 208.3 and 207.2 eV. Reduced pristine (Figure 2b) samples showed a signal of variable intensity at 208.3 eV. After cycling, two chlorine-containing components separated by 7 eV are evident (Figure 2c,d). The peak at higher BE can be assigned to ClO_4^-. Also in this case two chlorine species as described earlier can often be identified. The assignment of the peak at 200.3 eV is less straightforward. The oxidation state of this chlorine species is likely to be −1 from the relative BE value. Therefore Cl^- or C–Cl are the most likely possibilities for the signal at 200.3 eV. The reduction of ClO_4^- concurrently with the polymer during the cycling was suggested[16] to account for the presence of the lower oxidation state chlorine, although the nature of the final reduction product is still not clear. The presence of Cl^- as a counterion, together with ClO_4^-, would lead to dopant concentrations that are higher than the amount of charge used in the oxidation and found in the film after the XPS analysis.

Figure 3 displays a typical *C 1s signal* for a cycled sample. A curve fitting was performed and at least three different carbon species were identified[16,20] at 284.6, 286.4, and 288.4 eV. The main peak (284.6 eV) has been attributed to α and β *carbons* of the polymeric backbone.[17] The peak at 286.4 eV (much less intense on reduced pristine samples) is thought to correspond to those carbon atoms that interact with dopant molecules or are possibly bonded to the low oxidation state chlorine.[16,20] The third peak (288.4 eV) is thought to be C≡N from trapped acetonitrile. The relative intensity of the three peaks changes on going through oxidized and reduced pristine and oxidized and reduced cycled samples.[16]

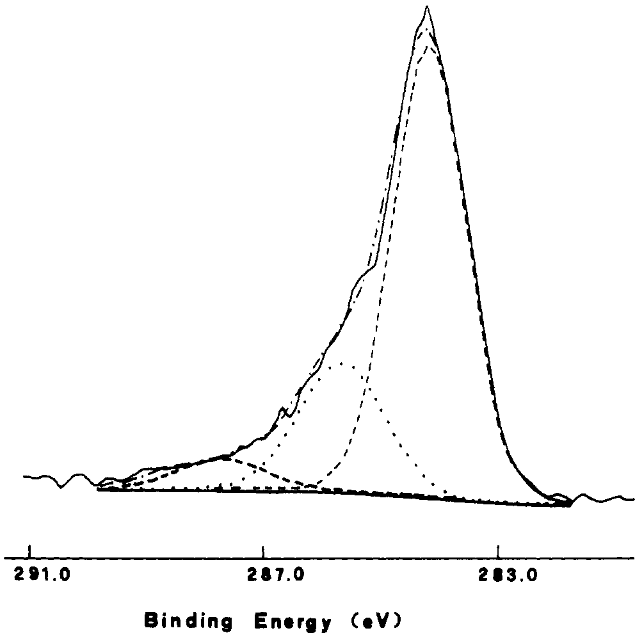


Figure 3. C 1s region relevant to pbT: oxidized cycled sample.

Figure 4 displays the *S 2p region* for both an oxidized and a reduced sample. The broadening of this signal on the higher BE side following oxidation has been reported previously[13] and explained in terms of a shift of shake-up satellites, corresponding to the generation of occupied states in the band gap on doping. An explanation that considers a positive charge localization on sulfur in oxidized samples has been also proposed,[16,20] since curve fitting produces two sulfur species whose ratio is in agreement with doping ratio.

The *O 1s signal* always shows perchlorate oxygen (532.1 eV) together with another component at higher BE, which is thought to be trapped water.

SIMS Results. Samples summarized in Table I were also analyzed by ToF-SIMS. As a general trend both positive and negative ion yields were found to be greater for oxidized samples compared to reduced samples. There are at least two explanation:

(i) The matrix effect[21] which is directly related to the chemical and electronic state of the surface. In this case the secondary ion yields from oxidized pbT are increased by the presence of positive and negative charges respectively on the polymer backbone and the dopant.

(ii) Sample charging effects. These are expected to be more evident for reduced samples than for oxidized samples due to the different conductivity. This could contribute to lower the negative ion yields[22] of reduced pbT.

The differences in ion yields becomes more evident in cycled samples because of the modified morphology of the surface with respect to pristine samples due, for example, to a further growth or crosslinking of the polymer on cycling.[16,20]

Oxidized Pristine. Figure 5 shows the positive ion spectrum relevant to the oxidized pristine sample. No clusters directly attributable to polybithiophene fragmentation are evident in the lower mass range (0–300 amu). The base peak is generally $C_2H_3^+$ ($m/z = 27$) or Li^+ (6 and 7 mass units) from residual electrolyte ($LiClO_4$).

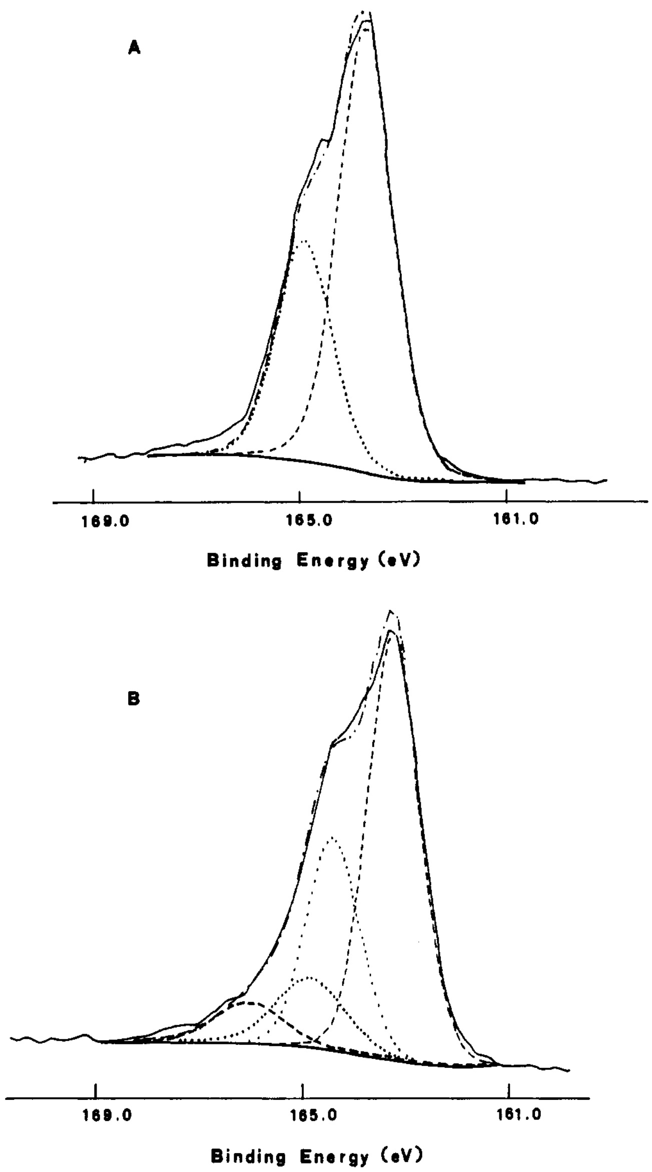


Figure 4. S 2p region relevant to (A) reduced and (B) oxidized pbT.

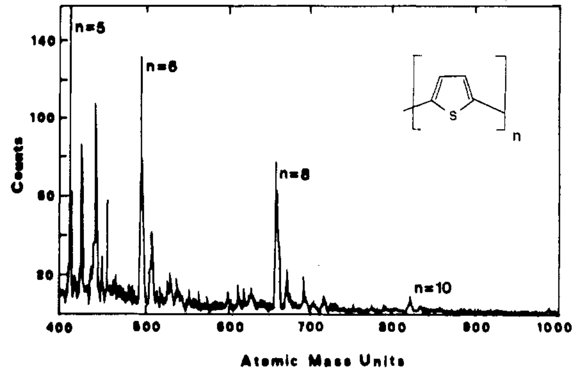
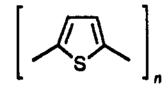


Figure 5. Oxidized pristine polybithiophene. Positive ion ToF-SIMS spectrum.

At higher m/z groups of clusters diagnostic of polybithiophene can be identified. The molecular weights of thiophene oligomers are reported for reference in Table IV. In particular the following cluster ions appear as intense peaks: m/z = 413 (five thiophene units + H); m/z = 494 (six thiophene units); m/z = 657 (eight thiophene units − H); m/z = 821 (10 thiophene units − H); m/z = 986 (12 thiophene units). Other clusters are evident, which appear to be directly related to these ions and display an isotopic distribution similar to that of the next neighbor oligomeric cluster. Their m/z values generally correspond to oligomeric units with pendant hydrocarbon groups, probably originating from the adjacent rings of the polymer.

Table IV
Thiophene Oligomer Masses



n	*M*	*n*	*M*
2	166	8	658
3	248	9	740
4	330	10	822
5	412	11	904
6	494	12	986
7	576		

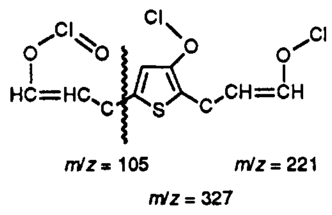
Table V
Negative Ion Groups of Clusters from $LiClO_4$

mass (m/z)	structure	mass (m/z)	structure
35–37	Cl^-	173–175–177	$LiCl_2O_6^-$
51–53	ClO^-	189–191–103	$LiCl_2O_7^-$
67–69	ClO_2^-	205–207–209	$LiCl_2O_8^-$
83–85	ClO_3^-	311–313 etc.	$Li_2Cl_3O_{12}^-$
99–101	ClO_4^-	340–342 etc.	$Li_2Cl_3O_{12}COH^-$
125–127–129	$LiCl_2O_3^-$	417–419 etc.	$Li_3Cl_4O_{16}^-$
141–143–145	$LiCl_2O_4^-$	446–448 etc.	$Li_3Cl_4O_{16}COH^-$
157–159–161	$LiCl_2O_5^-$		

The negative ion spectrum of the pristine oxidized sample shows, together with the typical intense carbon peaks (C^-, CH^-, C_2H^-, $C_2H_2^-$, etc.), ions characteristic of the sample itself. The base peak is generally C^- (m/z = 12) or S^- (m/z = 32). A chain fragment at m/z = 58, $(C_2H_2S)^-$, is the only peak, apart from S^-, that can be directly attributed to the polymer chain. Instead peaks directly attributed to the dopant species (ClO_4^-) were observed: Cl^- (m/z = 35–37); ClO_3^- (m/z = 81–83); ClO_4^- (m/z = 99–101); $Li(ClO_4)_2^-$ (m/z = 205–207–209). Their assignment was confirmed by reference to the SIMS spectrum of $LiClO_4$ (Table V).

Some other Cl-containing peaks (Figure 6) are present whose origins are not directly attributable to the doping/contamination by ClO_4^-. Thus an organic nature was hypothesized for them. They are (a) m/z = 105–107 (one chlorine, $C_3H_2O_2Cl$); (b) m/z = 221–223–225 (two chlorines, $C_7H_3O_2SCl_2$); (c) m/z = 327–329–331 (three chlorines, $C_{10}H_6O_4SCl_3$); and (d) m/z = 343–345–347 (three chlorines − (c) + oxygen).

The previous ions would be then consistent with the following fragmentation pattern:



Reduced Pristine Sample. The positive ion spectrum for reduced pristine polymer shows a very similar fragmentation pattern as for the oxidized pristine polymer. The total ion intensity is lower (discussed earlier). The negative ion spectrum also displays lower total ion intensity and similar intensity distributions of inorganic and organic ions.

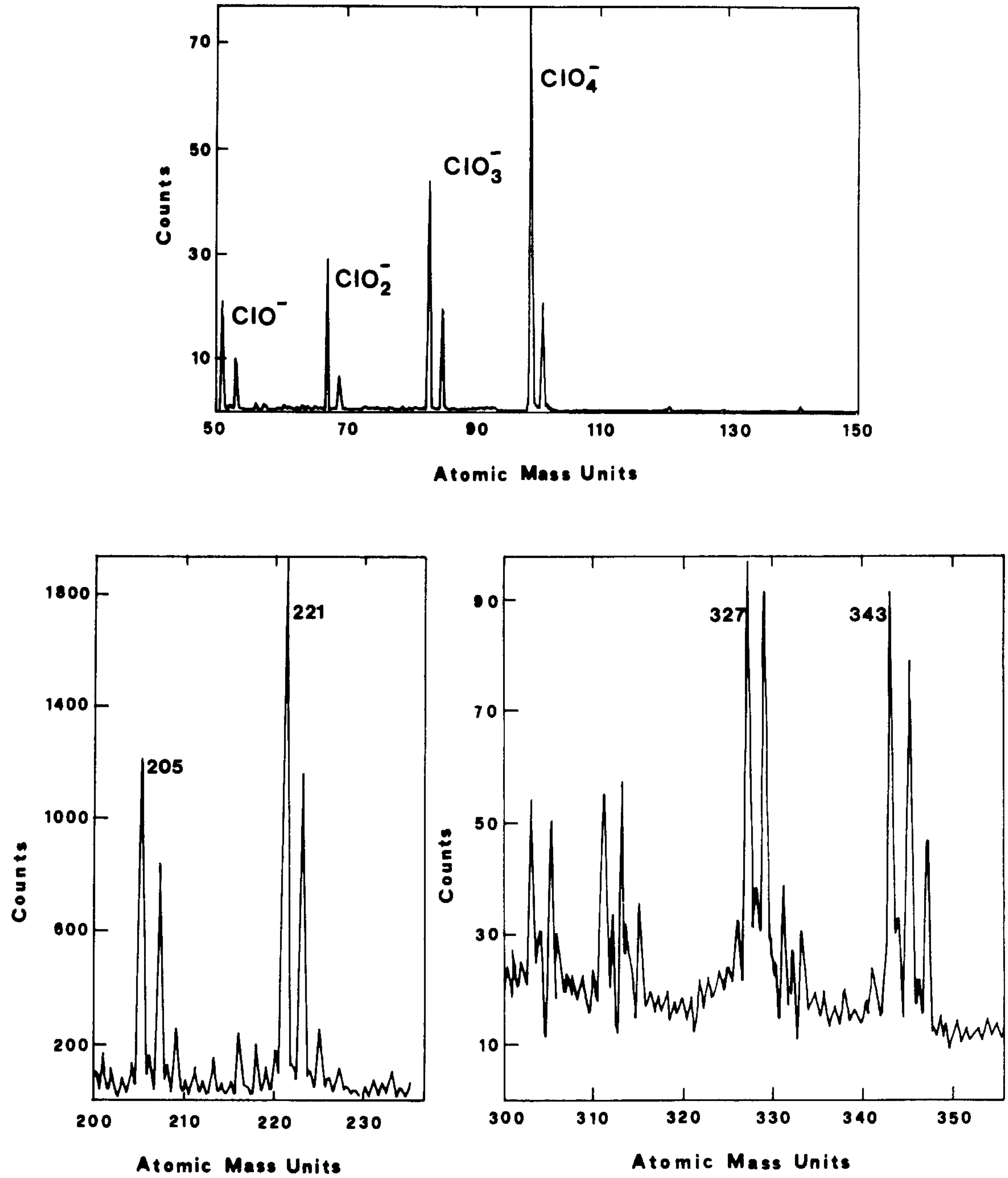
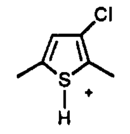


Figure 6. Oxidized pristine polybithiophene. Negative ion ToF-SIMS spectrum.

$LiClO_4$. SIMS analysis of $LiClO_4$ was performed in order to aid the assignment of the chlorine-containing clusters appearing in the spectra of polybithiophene samples. The main peaks of the positive ion spectrum for this sample are Li^+ (m/z = 6–7) and $(Li_2ClO_4)^+$ (m/z = 113–115).

The negative ion spectrum, instead, shows a large range of ions that originate from the salt and can be assigned on the basis of the characteristic isotopic distribution of chlorine-containing clusters (Table V).

Oxidized Sample. Five Cycles. Figure 7 shows the positive ion spectrum for the oxidized cycled sample. The general appearance of this spectrum is very much different from that of the pristine sample. The base peak of the spectrum is now $OH_2^{\bullet +}$ (m/z = 18); see the O 1s XPS spectrum. At higher m/z a sequence of seven groups of peaks, separated by a m/z difference of 117, is evident. The first member of this series is a doublet at m/z = 135–137 and shows the typical isotopic distribution of chlorine (e.g., M:M + 2 = 3:1). The subsequent member of the sequence is m/z = 252–254–256 with an intensities ratio of 9:6:1, diagnostic of the presence of two chlorine atoms. The third member is a quadruplet at m/z = 369–371–373–375 with an intensities ratio indicative of the presence of three chlorine atoms and so on. The unit m/z = 117 containing one chlorine atom could be assigned to



m/z = 117

The first member of the series has a m/z difference of 117 from the ion at m/z = 18, which has been attributed to $H_2O^{\bullet +}$ and could be considered the real first member of the series. A molecular structure could thus be suggested

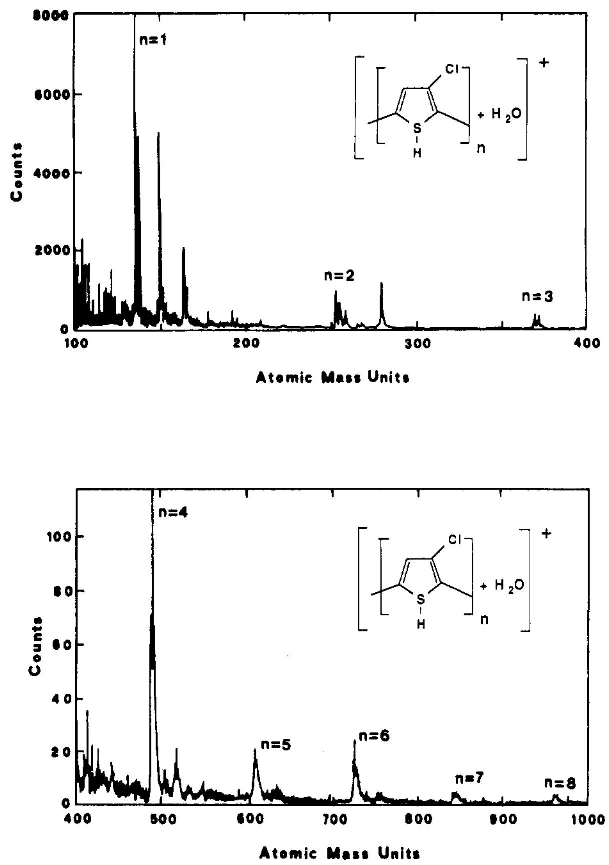
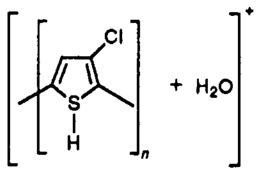


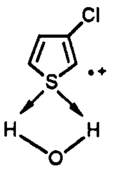
Figure 7. Oxidized cycled polybithiophene. Positive ion ToF-SIMS spectrum.

for the ion at m/z = 135–137.



n = 1–7

Thus the series of clusters would be diagnostic of a polymeric structure such as



m/z = 135–137

At lower and higher m/z around the ion at m/z = 135, weaker peaks (one chlorine containing) are evident. They are at m/z = 121–123, m/z = 163–165, m/z = 177–179, and m/z = 191–193 so that their mass separation is m/z = 14 or 28, which are thought to correspond to CH_2 units or CO.

Unlike in the spectra for the pristine samples, no evidence of unmodified oligomeric clusters has been detected when analyzing cycled samples. Figure 8 shows the negative ion spectrum for the oxidized cycled sample. The most intense ion of the spectrum is Cl^- (m/z = 35–37) and the usual fragments originating from ClO_4^- (ClO_2^-, ClO_3^-, ClO_4^-) are also present. At higher m/z values a series of intense peaks separated by a 117 units are present.

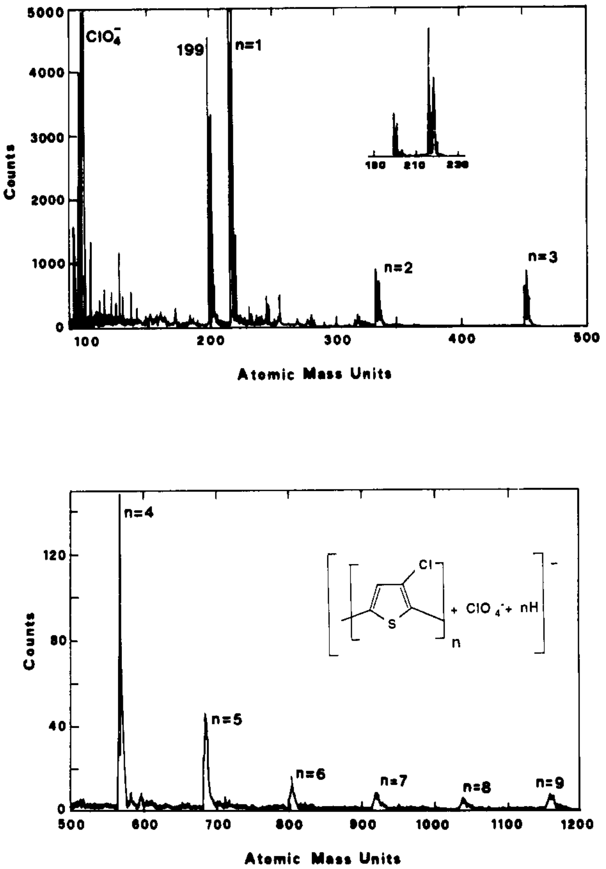
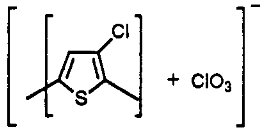


Figure 8. Oxidized cycled polybithiophene. Negative ion ToF-SIMS spectrum.

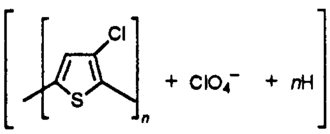
The series starts with the triplet at m/z = 216–218–220 (intensity ratios 9:6:1, two chlorines) and follows by analogy to the positive ion spectrum up to m/z = 1152. The structure of the unit of mass 117 has been already assigned, and since the first cluster of the series (m/z = 216–218–220) is separated by 117 units of mass from ClO_4^- (m/z = 99–101), the latter can be considered the real first member of the series.

This hypothesis could explain the presence of a two-chlorine-containing group of clusters at m/z = 199–201–203 in terms of the following structure:



m/z = 199–201–203

This series of clusters would then correspond to



n = 1–8

The structures suggested for the polymeric chains that would fragment to give the observed clusters in the spectra attribute to respectively water and ClO_4^- a stabilizing role toward emitted cations and anions analogous to the cationization[23] process observed for metal atoms. Alternatively, these small molecules are actually the terminal groups in the polymer chains.

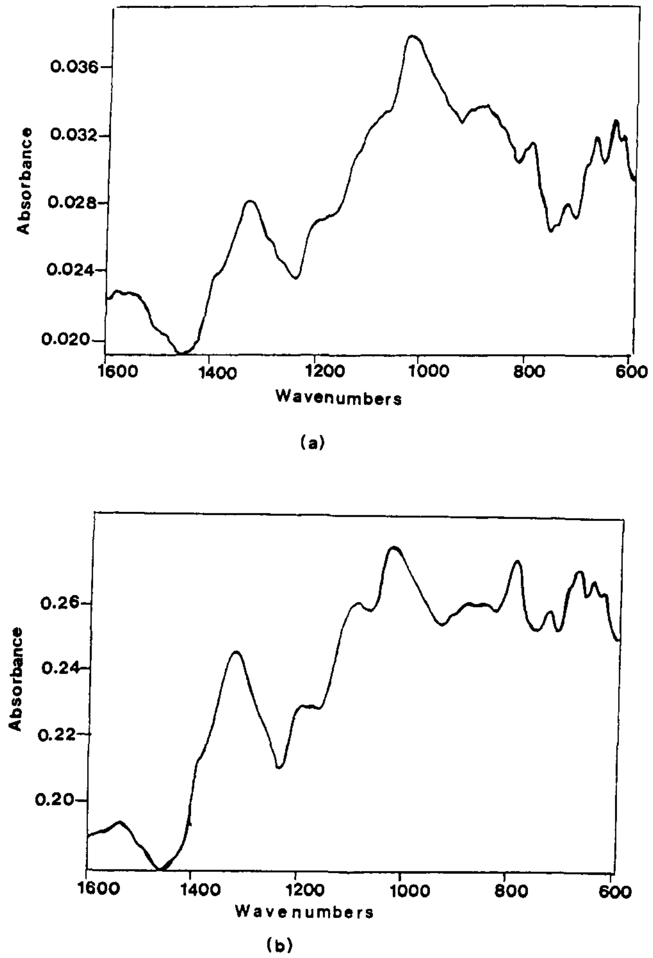


Figure 9. ATR-FTIR spectra of polybithiophene: (a) oxidized pristine and (b) oxidized cycled.

Table VI
IR Frequencies (cm^{-1}) for Doped Pristine and Cycled pbT

pbT			
pristine	cycled	mode	ref
1331	1323	C-C stretch	23
1197	1198	C-C stretch	23
1129, 1088	1094	ClO_4^-, C-C stretch	24, 23
1031	1025	C-C stretch	23
793	789	C-H bend (2,5-sub)	25
669	671	C-H bend (2-sub)	25
637	641	ClO_4^-	24

IR Results. Figure 9 shows the FT-IR spectra relative to both oxidized pristine and oxidized cycled pbT, prepared as under Experimental Section. Typical transitions in the 500–1500-cm^{-1} range were recorded in the ATR mode and are reported in Table VI. The four bands between 1330 and 1030 cm^{-1} are reported[24] to be characteristic of doped polythiophenes and correspond to C—C and C=C stretching vibrations of charged polythiophenes chains. They appear, at different frequencies, on both the samples. These bands are likely to overlap with the vibrational modes of the doping species ClO_4^-.[25]

At lower frequencies the C–H out-of-plane bending vibrations are reported to appear at 790 and 690 cm^{-1} respectively for 2,5-substituted and 2-substituted thiophene rings.[26] The ratio between these two bands is employed to estimate the average chain length of the polymer.

Finally the band at 640 cm^{-1} has been attributed to ClO_4^- vibrations.[25]

The shift of some bands toward lower frequencies observed on cycling may be attributed to the presence of β-substituted rings. This could represent indirect evidence of the presence of C–Cl bonds in the cycled polythiophene as suggested by the above ESCA and SIMS results. On the contrary, no direct evidence of C–Cl vibrations has been observed in the range of frequencies (800–500 cm^{-1}) expected.[27] This result could be interpreted by either one or both the following explanations: (a) Infrared spectroscopy is ineffective in detecting the presence of bonded chlorine on polybithiophene substrata because of the overlapping of rings and C–Cl vibrations. (b) C–Cl bonds are present only on the uppermost layer of cycled pbT and thus a bulk technique like IR is ineffective for revealing them.

Discussion

It has been clearly demonstrated[2-9] that structural information can be gained by employing static SIMS in the characterization of polymers. The use of low ion fluence[4] typical of static SIMS prevents damage of the materials or mixing effects, thus giving mass spectra truly representative of the surface structure of the analyzed polymers. In light of this we have employed ToF-SIMS along with XPS in the study of the surface modification of pbt on electrochemical cycling.

The XPS results from polybithiophene/ClO_4^- samples showed evidence of a reduction reaction for ClO_4^- during the doping/undoping cycles, since a lower oxidation state chlorine appeared in the cycled sample.[16] The nature of the chlorine was not clear from these data since the relative value of the BE of the second chlorine component does not allow distinction between an ionic and an organic bonded chlorine. Indirect data (doping charge versus chlorine concentration, anion exchange experiments) suggested[16] that organically bound chlorine is more likely. The SIMS results presented here reinforce this picture and, furthermore, allow a more precise evaluation of the structure of these polymers either before or after cycling.

The positive ion spectrum of the pristine sample displays oligomeric clusters corresponding to even numbers of thiophene units (apart from the ion at m/z = 413,5 thiophene rings). Furthermore no short fragments (one to four thiophene units) were detected, whereas clusters that could be attributed to a chain breaking mechanism were present (at high m/z). Two approaches can be taken to understand these results: (a) Detected oligomeric ions are daughter ions of longer chains. This would mean that high mass ions are more stable than low mass ions and so they are the main product of fragmentation. Moreover, ions with an even number of thiophene rings are more stabilized than clusters with an odd number of thiophene rings. (b) Detected ions are molecular ions (apart from m/z = 413) of oligomers of pbT. In this view no fragmentation of possibly longer pbt chains would be detectable.

In the negative ion spectrum for oxidized pristine polymer the presence of few organic ions (m/z = 105, 221, 327, etc.) containing chlorine seems to confirm the XPS-based hypothesis[16,20] of a dopant–polymer backbone interaction that causes a chemical shift of carbon atoms (peak at 286.4 eV). These clusters are much less intense on reduced pristine samples in agreement with XPS results.

The appearance of both positive and negative spectra for oxidized cycled samples corroborates the XPS data of a considerable surface modification of the polymer structure upon cycling under the given experimental conditions. The large increase in the relative intensity of Cl^- ions in cycled samples with respect to pristine samples provides the most direct evidence for such a modification. The presence of water (even in small quantities) in the cycling solution has already been suggested to be one of the causes of ClO_4^- reduction[16] and competition of water with acetonitrile in counterion solvation has been identified by analyzing the amount of nitrogen trapped in the film.[16] A direct detection of water in the film from XPS data is complicated by the close proximity, in the O 1s peak, of signals originating from ClO_4^- and H_2O. More direct evidence of the effect of water in pbT degradation on cycling can be claimed from the SIMS results. A very intense $H_2O^{\bullet +}$ peak ($m/z = 18$) is detected *only* on the cycled samples. Water has also been suggested to be the highly polarized molecule that would stabilize the emission of positive ions from cycled samples.

Finally, the absence of unmodified oligomeric clusters from the surface of cycled pbT could be explained by the transformation of the whole uppermost layer of pbT into a polymer with attached chlorine. Moreover the cycling could induce chain growth and cross-linking reactions, modifying the polymer structure.[16] Such modification of the polymer structure could hamper the fragmentation and represent another cause of the absence of pbT oligomeric clusters in spectra of cycled samples.

Extensive investigation by FT-IR has not been able to confirm the picture so far assembled. This is due to the lack of sensitivity toward the detection of C–Cl bonds in modified pbT, which may be explained either by the overlap of C–Cl adsorptions with predicted polythiophene bands or simply by the fact that this technique does not afford adequate sensitivity to surface changes specifically. Since IR monitors effects many micrometers into the material bulk, unless special facilities are used, it is unlikely that surface change would be detected.

It is clear that to investigate the surface modification of polymers surface sensitive techniques have to be employed. The present paper highlights the potentials in this field.

Conclusions

A parallel XPS/ToF-SIMS work has been performed to examine the surface chemistry of electrochemically prepared polybithiophene and to monitor its modifications upon electrochemical cycling. A coherent picture has been drawn on the basis of these data, which confirms the effectiveness of static SIMS in surface analysis of polymeric materials and promotes this analytical method as a useful tool in the investigation of surface chemistry of conducting polymers.

Acknowledgment. Dr. C. Malitesta of the University of Bari is greatly acknowledged for his assistance in sample preparation and for helpful discussion on XPS data. Work carried out with the financial support of Italian Ministero Pubblica Istruzione.

References and Notes

(1) (a) Benninghoven, A.; Rudenauer, E. G.; Werner, H. W. *Secondary Ion Mass Spectrometry*; John Wiley & Sons: New York, 1987. (b) Vickerman, J. C. *Chem. Br.* **1987**, *10*, 969. (c) Brown, A.; Vickerman, J. C. *Surf. Interface Anal.* **1984**, *6*, 1. (d) Brown, A.; Vickerman, J. C. *Surf. Interface Anal.* **1988**, *8*, 75.
(2) Hearn, M. J.; Briggs, D. *Surf. Interface Anal.* **1988**, *11*, 198.
(3) Davies, M. C.; Short, R. D.; Khan, M. A.; Watts, J. F.; Brown, A.; Eccles, A. J.; Humphrey, P.; Vickerman, J. C.; Vert, M. *Surf. Interface Anal.* **1989**, *14*, 115.
(4) Briggs, D.; Hearn, M. J. *Vacuum* **1986**, *36* (11), 1005.
(5) Reference 1a, p 742.
(6) Lub, J.; Weremeus Buning, G. H. *Polymer* **1990**, *31*, 1009.
(7) Benninghoven, A. *J. Vacuum Sci. Technol.* **1985**, *A3* (3), 45.
(8) Fakes, D. W.; Davies, M. C.; Brown, A.; Newton, J. M. *Surf. Interface Anal.* **1988**, *13*, 233.
(9) Briggs, B.; Brown, A.; Vickerman, J. C. *Handbook of Static SIMS*; Wiley: Chichester, 1989.
(10) Skotheim, T. A. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986.
(11) Waltman, R. J.; Bargon, J. *Can. J. Chem.* **1986**, *64*, 76.
(12) Diaz, A. F.; Kanazawa, K. K. *Chem. Scr.* **1981**, *17*, 145.
(13) Tourillion, G.; Yugnet, Y. *J. Chem. Phys.* **1988**, *89* (4), 1905.
(14) Nelson, A. J.; Glenis, S.; Frank, A. J. *J. Chem. Phys.* **1987**, *87* (8), 5002.
(15) Yoshino, K.; Onoda, M.; Manda, Y.; Yokoyama, M. *Jpn. J. Appl. Phys.* **1988**, *27* (9), L1606.
(16) Morea, G.; Malitesta, C.; Sabbatini, L.; Zambonin, P. G. *J. Chem. Soc., Faraday Trans.* **1990**, *86* (22), 3769.
(17) Tourillion, G. In *Handbook of Conducting polymers*; Skoteim, T. A., Ed.; Marcel Dekker: New York, 1986; p 296.
(18) Wagner, C. D. *Anal. Chem.* **1972**, *44*, 1050.
(19) Sabbatini, L.; Malitesta, C.; Desimoni, E.; Zambonin, P. G. *Ann. Chim.* **1984**, *74*, 341.
(20) Morea, G.; Malitesta, C.; Sabbatini, L.; Zambonin, P. G., work in preparation.
(21) Benninghoven, A. *Surf. Sci.* **1975**, *53*, 596.
(22) Briggs, D. *Surf. Int. Anal.* **1982**, 4.
(23) Benninghoven, A. In *Secondary Ions Mass Spectrometry-SIMS II*; Benninghoven, A., Evans, C. A., Powell, R. A., Shimizen, R., Storms, A. A., Eds.; Springer-Verlag: Berlin, 1979; p 116.
(24) Yong, C.; Renyuan, Q. *Solid State Commun.* **1985**, *54* (3), 211.
(25) Rao, C. N. R.; Hansen, G.; Schultze, J. W. *Ber. Bunsenges. Phys. Chem.* **1988**, *92*, 710.
(26) Furakawa, Y.; Akimoto, M.; Harada, I. *Synth. Met.* **1987**, *18*, 151.
(27) Socrates, G. *Infrared Characteristic Group Frequencies*; John Wiley & Sons: New York.

Registry No. $LiClO_4$, 7791-03-9; polybithiophene, 80029-99-8.