

X-ray Photoelectron Spectroscopy of Polybithiophene–Polystyrene Composites

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ABSTRACT: An investigation of the structure, stability, and charge distributions of conducting polybithiophene–polystyrene composite chemically synthesized using X-ray photoelectron spectroscopy (XPS) and electron microprobe analysis is described. XPS results confirm the reduction of the oxidant (Fe^{3+} is reduced to Fe^{2+} and Cu^{2+} to Cu^+) during the bithiophene polymerization and indicate that the positive charges of doped polybithiophene are preferentially localized on the carbon atoms. Measurements versus ambient atmosphere exposure support a decreasing of the atomic ratio Cl/Fe or Cl/Cu and an increasing of the atomic ratio O/C, which could be responsible for the observed electrical conductivity instability. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1839–1845, 1997

Key words: X-ray photoelectron spectroscopy; polybithiophene; composites

INTRODUCTION

Conducting polyheterocycles are attractive research topics due to their wide range of current and potential applications. Of these polymers, the thiophene family of conducting polymers is of great interest because of its high electrical conductivity, environmental stability, and interesting redox properties associated with the heteroatoms. Most of the studies, however, have been centered on composites produced by incorporating conducting polymers into a polymer matrix as polystyrene. The obtained composites exhibit improved processability and mechanical properties.

X-ray photoelectron spectroscopy (XPS) studies are frequently used to characterize chemically or electrochemically prepared conducting polythi-

ophene. However, there are some discrepancies between the results obtained. For example, some studies¹ suggest a charge withdrawal from the ring carbon atoms only, while others² suggest partially charged carbon and sulfur species in the oxidized polymer.

Poly(2,2'-bithiophene)–polystyrene composite has been obtained by polymerization of bithiophene with FeCl_3 or $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. This study is mainly devoted to the chemical transformations occurring during the polymerization and to the distribution of the dopant FeCl_4^- and ClO_4^- within the electroactive component of the composite.

EXPERIMENTAL

Polythiophene–polystyrene composites were synthesized by the action of an oxidant [FeCl_3 or $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$] on porous crosslinked polystyrene as host polymer initially charged with 2,2'-bithiophene.³

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Table I XPS Quantitative Analysis of the PSt–PBTh–FeCl₃ Composite

PSt–PBTh–FeCl ₃	Sample Composition (%)						Relative Percentage of Fe and Cl		
	Cl	Fe	O	C	S	O/C	Cl	Fe	Cl/Fe
Fresh sample	21	4	12	61	2	19.7	84	16	5.3
Before etching									
Etched 1 min	29	8	4	55	4	7.6	79	21	3.8
Exposed to air	28	5	14	51	2	27.4	84	16	5.3
Before etching									
Etched 1 min	31	10	8	46	5	17.4	76	24	3.2

XPS measurements were carried out using a commercial photoelectron spectrometer (Leybold LHS 12) equipped with a twin-anode X-ray gun (Mg K α and Al K α lines at 1253.6 eV and 1486.6 eV, respectively) coupled to a computer for data acquisition and signal treatment. High-resolution scans were obtained with a good signal-to-noise ratio with the magnesium source operating at 10 kV and 10 mA. The energy resolution was better than 1 eV at a pass energy of 50 eV. The quantitative estimations were based on the determination of the Cl2p, Fe2p_{3/2}, C1s, O1s, Cu2p, and S2p peak areas with 0.58, 3.1, 0.2, 0.61, 5.3, and 0.44 as sensitivity factors, respectively, as given by the manufacturer. Samples (7 mm \times 5 mm) were stuck on a copper or stainless-steel sample holder (10 mm \times 11 mm \times 1 mm) with silver paste.

The change in composition with depth was studied by recording successive XPS spectra obtained after argon ion etching for short periods. Sputtering was performed at pressures lower than 5×10^{-4} Pa, with a 10 mA emission current and a 3 kV beam energy using an ion gun. The Ar⁺ ion beam could be rastered over the entire sample surface. Before sputtering, the pressure was below 5×10^{-7} Pa.

Some of the XPS peaks obtained present complex structures. The decomposition of these peaks into different components and the quantitative interpretation were made after subtraction of the background. The developed curve-fitting program permits the variation of parameters such as the Gaussian/Lorentzian ratio, the full width at half maximum (FWHM), and the position and intensity of the components.

The dopant distribution in the films and the evolution with time exposure to air of the Cl/Fe or Cl/Cu atomic ratios were checked with an electron microprobe. The morphology of the surface of the composite layers was observed with a scanning electron microscope. The microphotographs of the two types composites surfaces show the porous host polymer structure with an inhomogeneous dispersion of the dopant.

RESULTS AND DISCUSSION

For clarity in the following discussion, we refer to “fresh samples” as those kept under vacuum before XPS measurements and “exposed to air sam-

Table II XPS Quantitative Analysis of the PSt–PBTh–Cu(ClO₄)₂·6H₂O Composite

PSt–PBTh–Cu(ClO ₄) ₂ ·6H ₂ O	Sample Composition (%)						Relative Percentage of Cu and Cl		
	Cl	Cu	O	C	S	O/C	Cl	Cu	Cl/Cu
Fresh sample									
Before etching	5	1.6	41	52	0.4	0.79	76	24	3.2
Etched 1 min	30	7.5	23	37.5	2	0.61	80	20	4
Exposed to air									
Before etching	5.4	1.9	41	51	0.7	0.79	75	25	3
Etched 1 min	22	8	40.8	26.8	2.4	1.52	74	26	2.9

Table III Microprobe Analysis of the PSt-PBTh-FeCl₃ Composite

Analyzed Point	1	2	3	4
Fresh sample				
Fe (%)	29	33	33	40
Cl (%)	56	59	63	55
Atomic ratio Cl/Fe	1.9	1.8	1.9	1.8
Exposed to air				
Fe (%)	29	29	30	—
Cl (%)	50	50	49	—
Atomic ratio Cl/Fe	1.7	1.7	1.6	—

ples" as those prepared 1 week before and kept in ambient atmosphere.

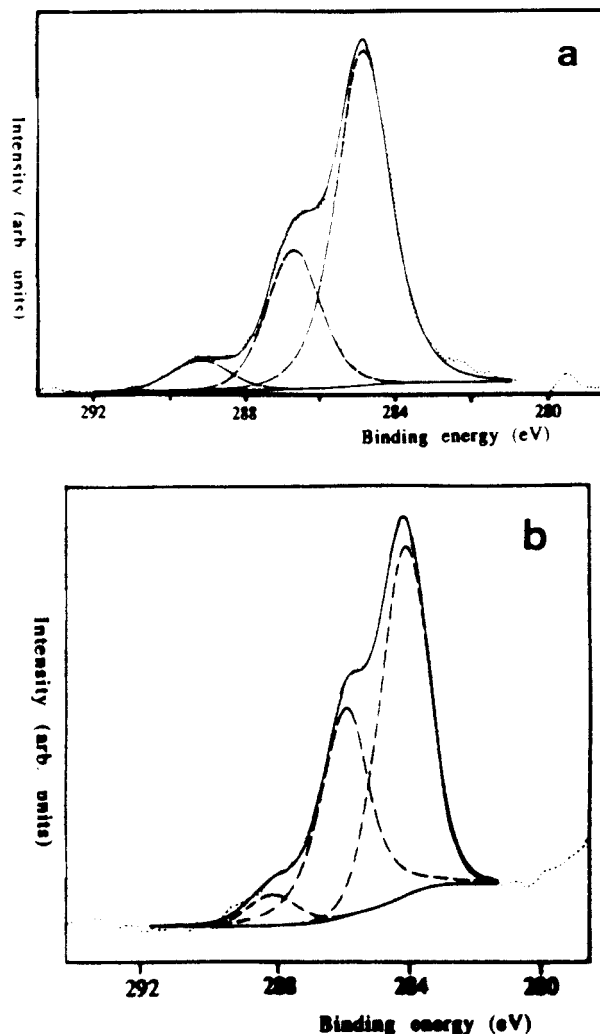
Tables I and II report the XPS studies of the evolution of the relative concentration of Cl, Fe, Cu, O, C, and S atoms as a function of the storage time in ambient atmosphere and etching.

For the exposed to air sample, it can be observed that the atomic ratio O/C of FeCl₃ composites exhibits an increase (Table I). It becomes nearly equal to 27% instead of 20% for fresh samples. In comparison, the percentage of oxygen of Cu(ClO₄)₂·6H₂O composites remains nearly constant at 41% during the same period (Table II) before increasing. These results can be correlated to the existence of oxygen-containing groups in the polythiophene chains which increase in percentage during the aging process.

As seen in Tables I and II, surface analysis of fresh and exposed to air samples show that the experimental ratio Cl/Fe or Cl/Cu is higher than the theoretical ratio (3 and 2, respectively) and remains even higher for etched surfaces. On the other hand, microprobe analysis (Table III and IV) reveals a deficit in chlorine in the bulk. However, this last result has to be analyzed more qual-

Table IV Microprobe Analysis of the PSt-PBTh-Cu(ClO₄)₂·6H₂O Composite

Analyzed Point	1	2	3	4
Fresh sample				
Cu (%)	30	36	39	36
Cl (%)	51	48	36	40
Atomic ratio Cl/Cu	1.7	1.3	0.9	1.1
Exposed to air				
Cu (%)	38	43	38	—
Cl (%)	50	45	13	—
Atomic ratio Cl/Cu	1.3	1	1.3	—

**Figure 1** XPS spectra: Cl1s peak curve fit of (a) PSt-PBTh-FeCl₃ and (b) PSt-PBTh-Cu(ClO₄)₂·6H₂O.

itatively than quantitatively since it is known that the electron beam can cause damage to the polymer surface.

All these results can be interpreted on the basis of two processes, as has been reported for PVA-PPy-FeCl₃ composite⁴:

1. the existence of Cl motion towards the surface of the film followed by its release from the composite following the formation of HCl;
2. preferential polymerization of thiophene near the surface regions.

In order to examine the chemical composition and the electronic structure of polymer surfaces, the C, O, Fe, Cu, Cl, and S core-level spectra of

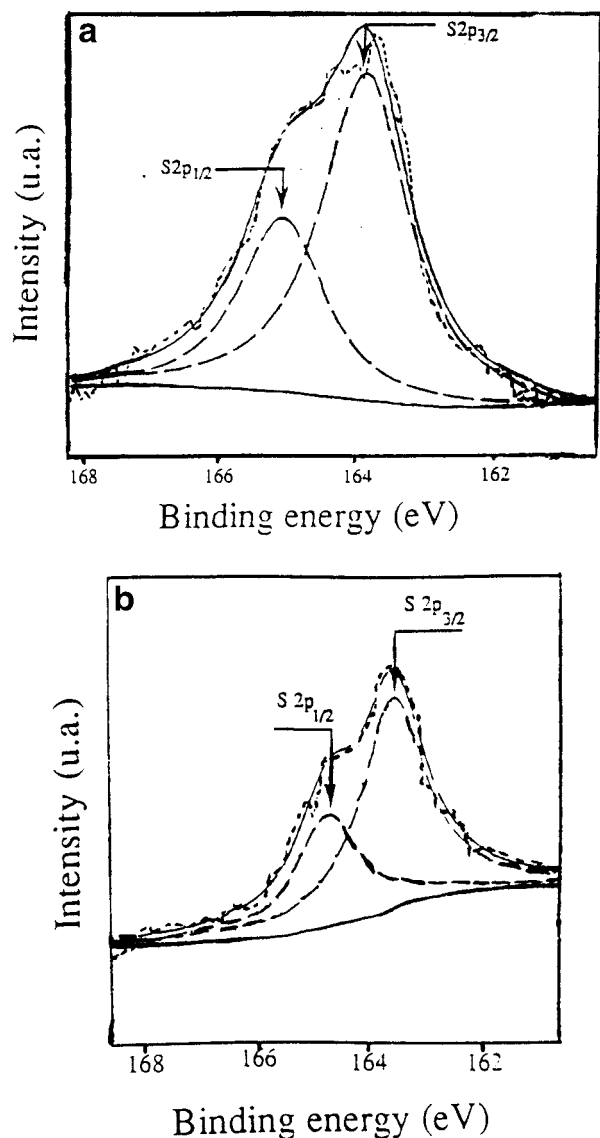


Figure 2 XPS spectra: S2p peak curve fit of (a) PSt-PBTh-FeCl₃ and (b) PSt-PBTh-Cu(ClO₄)₂·6H₂O.

the two types of composites were systematically decomposed using a routine procedure.⁵

The results obtained on PSt-PBTh-FeCl₃ fresh samples are reported in Figures 1(a), 2(a), 3(a), 4(a), and 5(a), respectively, for C1s, S2p, O1s, Fe2p, and Cl2p. The results of the decomposition are collected in Table V.

For the C1s peak [Fig. 1(a)], an asymmetric spectrum which is skewed towards the high binding-energy side is observed. The main C1s component appears at 284.8 eV. It corresponds to C—C bonds and is used as reference for other binding energies. The second component is located at 286.7 eV and can be attributed to the presence of

positively polarized carbon atoms (C^{δ+}) and C—OH groups.⁶ The third component of the C1s peak which is located at about 289.2 eV can be assigned to the presence of carboxyl or ester groups (—COOH or —COOR) and can be attributed to overoxidation occurring during the polymerization. After 1 min of etching, the shoulder around the high binding-energy side attributed to the oxidized carbon vanished. This behavior seems to confirm the oxidation of the polymer chains at the film surfaces. Nevertheless, it must be kept in mind that etching with argon ions may lead to some changes in the chemical nature of the sample surface of polymers.

The decomposition of the S2p core-level spectrum [Fig. 2(a)] leads to a sole doublet (S2p_{3/2} and S2p_{1/2}) with binding energies lying at about 163.9 and 165.1 eV, respectively, and corresponds to covalent sulfur in the ring carbon atoms. This allows us to assume that S is not positively charged⁶ and confirms that the positive charge is localized on the

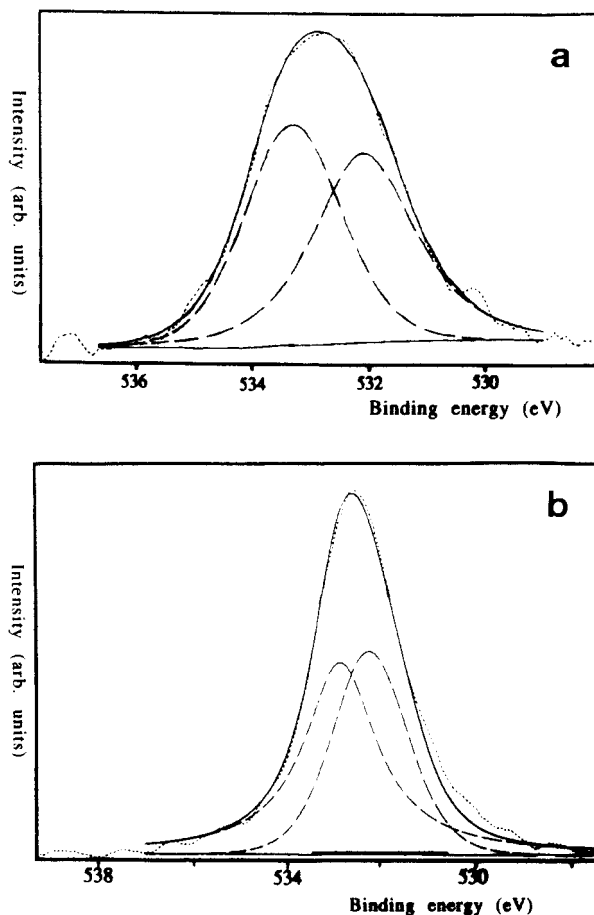


Figure 3 XPS spectra: O1s peak curve fit of (a) PSt-PBTh-FeCl₃ and (b) PSt-PBTh-Cu(ClO₄)₂·6H₂O.

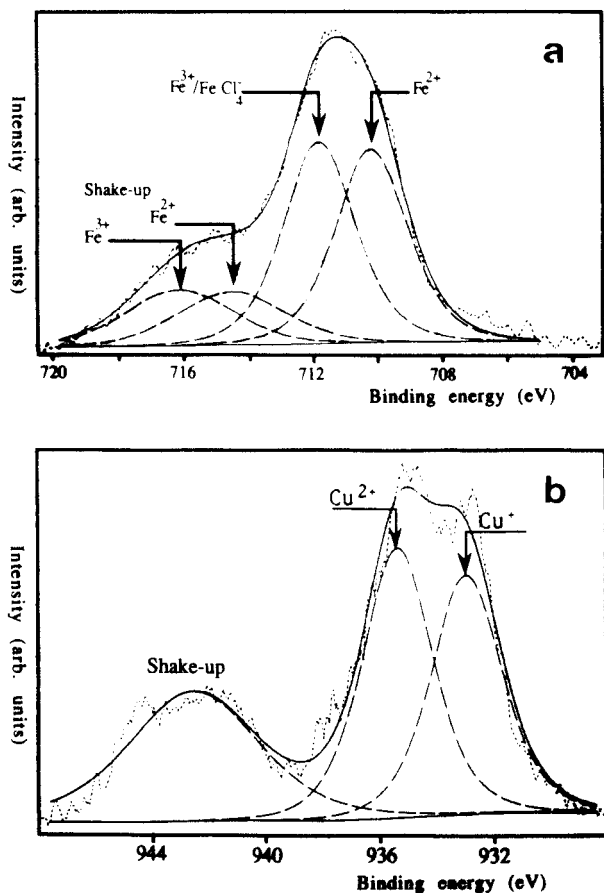


Figure 4 XPS spectra: Fe2p peak curve fit of (a) PSt-PBTh-FeCl₃ and (b) PSt-PBTh-Cu(ClO₄)₂·6H₂O.

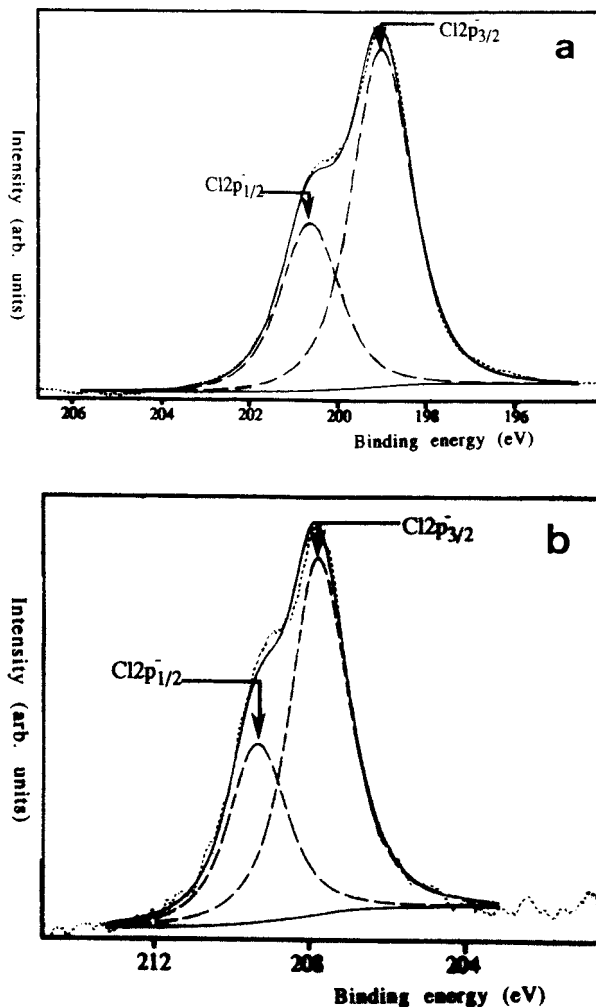


Figure 5 XPS spectra: Cl2p peak curve fit of (a) PSt-PBTh-FeCl₃ and (b) PSt-PBTh-Cu(ClO₄)₂·6H₂O.

carbon atoms. These results are consistent with those reported by Bredas and colleagues.⁷

The O1s spectrum presents two peaks situated at 532.1 and 533.3 eV [Fig. 3(a)]. The first component can be assigned to carbonyl group O=C which may be attributed to overoxidation defects occurring during the applied polymer preparation method. The second one, at the higher binding energy, corresponds to hydroxyl group C-OH in agreement with C1s results.

Concerning the Fe2p_{3/2} spectrum, it must be

recalled that the FWHM is generally broad, which makes the fitting difficult without any other information. In agreement with the polymerization reaction $2 \text{Fe}^{3+} \text{Cl}_3^- + e^- \rightarrow \text{FeCl}_4^- + \text{Fe}^{2+} \text{Cl}_2^-$, the Fe2p_{3/2} core level spectrum [Fig. 4(a)] shows the presence of four peaks. The first one, situated at 710.2 eV, is related to Fe²⁺ and indicates the par-

Table V XPS Analysis of PSt-PBTh-FeCl₃ Composite

PSt-PBTh-FeCl ₃ Assignment	C1s			S2p		O1s		Fe2p		Cl2p	
	C-C and C-H	C ^{δ+} and C-OH	-COOH or -COOR	S2p _{3/2}	S2p _{1/2}	O=C	C-OH	Fe ²⁺	Fe ³⁺ /FeCl ₄ ⁻	Cl2p _{3/2}	Cl2p _{1/2}
Binding energy (eV)	284.8	286.7	289.2	163.9	165.1	532.1	533.3	710.2	711.8	199	200.6

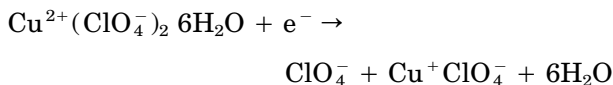
Table VI XPS Analysis of PSt-PBTh-Cu(ClO₄)₂·6H₂O Composite

PSt-PBTh-Cu(ClO ₄) ₂ Assignment	C1s			S2p		O1s		Fe2p		Cl2p	
	C—C and C—H	C ^{δ+} and C—OH	—COOH or —COOR	S2p _{3/2}	S2p _{1/2}	O=C and O (ClO ₄ ⁻)	C—OH	Fe ²⁺	Fe ³⁺ /FeCl ₄ ⁻	Cl2p _{3/2}	Cl2p _{1/2}
Binding energy (eV)	284.4	286.1	288.2	163.7	164.9	532.4	533	933.1	935.5	207.9	209.5

tial reduction of Fe³⁺ to Fe²⁺. The second peak, localized at 711.8 eV, is attributed to Fe³⁺, the presence of which results from the dopant FeCl₄⁻ and the fraction of FeCl₃ which does not react. The last two peaks correspond to a shake-up effect.

The Cl2p spectrum [Fig. 5(a)] is wide and asymmetric on the high binding-energy side. Its decomposition leads to a sole doublet with binding energies lying at about 199 (Cl2p_{3/2}) and 200.6 (Cl2p_{1/2}) eV, respectively. These values correspond essentially to the ionic form of chlorine.

Similar results have been obtained on PSt-PBTh-Cu(ClO₄)₂·6H₂O fresh samples [Figs. 1(b), 2(b), 3(b), 4(b), and 5(b) for C1s, S2p, O1s, Cu2p, and Cl2p, respectively]. However, it must be noted that the phenomenon of chlorine removal is less marked (Table II). The results of the decomposition are collected in Table VI. The Cu2p core level spectrum [Fig. 4(b)] shows the presence of three peaks. The first, situated at 933.1 eV, is related to Cu⁺ and indicates the partial reduction of Cu²⁺ to Cu⁺ according to the polymerization reaction



The second peak, located at 935.5 eV, is attributed to the presence of Cu²⁺(ClO₄)₂, which does not take part in the precedent reaction. The third peak, situated at 942.7 eV, corresponds to a shake-up effect related to Cu²⁺.

C1s and S2p core-level spectra as well confirm that the positive charge is essentially localized on the carbon atoms (Table VI).

The evolution with aging of room temperature conductivity is shown in Figure 6. In the case of PSt-PBTh-FeCl₃ samples, a drop in conductivity is observed during the first week; the decrease then becomes slower. In contrast, an improvement of the conductivity is observed during about

1 week for PSt-PBTh-Cu(ClO₄)₂·6H₂O samples, followed by a decrease which is slower than that observed for the first type of composites. These results corroborate the conclusion drawn from the XPS study that the oxidation and the decrease in chlorine concentration are the main sources of the sample aging. In the case of the PSt-PBTh-Cu(ClO₄)₂·6H₂O composites, a higher degree of electrical stability was observed during the first days of exposure to air, which could be related to the fact that the percentage of oxygen was stable during this period.

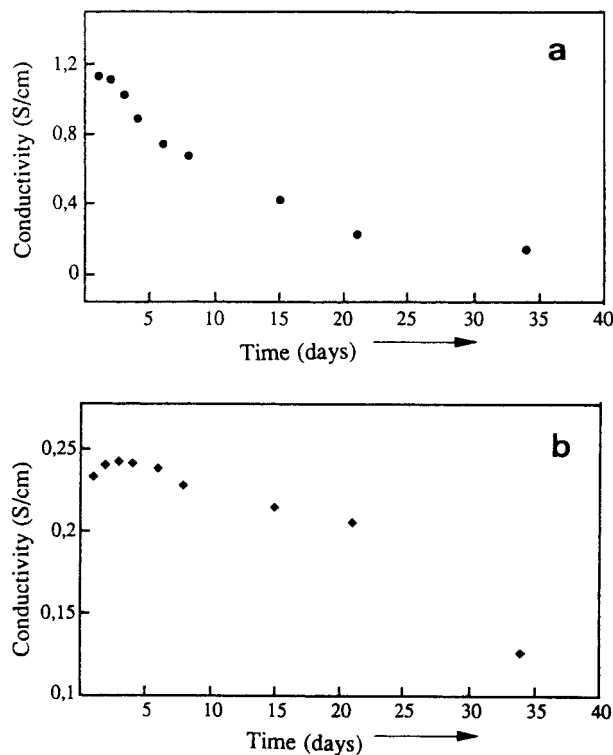


Figure 6 Evolution with time of room temperature electrical conductivity: (a) PSt-PBTh-FeCl₃ and (b) PSt-PBTh-Cu(ClO₄)₂·6H₂O.

CONCLUSIONS

The structure, the charge distributions, and the evolution with aging of chemically prepared polystyrene-polybithiophene composites were systematically analyzed by XPS, microprobe analysis, and conductivity measurements. Properly curve-fitted C1s and S2p core-level spectra revealed that the positive charges in the oxidized polymer are localized essentially on carbon rings in the polymer chain. The XPS study confirmed the reduction of the oxidant during the bithiophene polymerization and showed an oxidation by formation of O=C, —COOH, and —COOR groups at the chains' ends. The decrease with time of the electrical conductivity observed in the two types of composites can be explained by a chlorine release from the composite and an oxidation process. Therefore, the type of counterions plays an important role in the aging effect and it should

be interesting to perform similar measurements with another dopant species.

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