Properties of Poly(tetrabromo-*p*-phenylenediselenide) Doped with IBr, H$_2$SO$_3$, and CH$_3$COOH Acids

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ABSTRACT: Poly(tetrabromo-*p*-phenylenediselenide) (PBrPDSe) has been doped by IBr, H$_2$SO$_3$, and CH$_3$COOH acids. The samples have been studied by X-ray photoelectron spectroscopy (XPS) and electron spin resonance (ESR). Conductivity measurements have also been performed on pressed pellet samples. It has been shown by XPS and ESR that, after doping, positive charges are localized on Se atoms. The conductivity of the acid-doped PBrPDSe exhibits an increase by about four orders of magnitude. However, the limit of $10^{-7}\,\Omega^{-1}\,cm^{-1}$ appears difficult to overcome. This saturation effect could be attributed not only to charge localization on Se atoms but also to steric hindrance related to the substituent introduced on the backbone of the polymer. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2511–2517, 2000

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INTRODUCTION

Conjugated polymers have for some time been of major interest to both chemists and physicists. This interest has been greatly enhanced by the discoveries of a number of conjugated polymer systems capable of being doped.

Semiconducting polymers having chalcogenides in the chain have been known about for several years.[1–5] It is well known that, after doping with AsF$_5$, the poly(*p*-phenylenesulfide) (PPS) is a conductive polymer, while the poly(*p*-phenylenesenelide) (PPSe) is less conductive, perhaps because of the chemical reaction between Se and F[6]. However, in the family of the tetrachalcogenide fulvalene, the selenide compounds usually are more conductive than the sulfide compounds.[7] Although there are a lot of other parameters, mainly in powders, that can affect the properties of the materials, substitution of sulfur by selenium is expected to result in better conductivity because of the increased metallic character of selenium and a decrease in electronegativity.[8]

Moreover, the stability of conducting polymers seems especially important for applications. However, most of the reported conducting polymers are unstable in air, except those containing nitrogen or sulfur atoms in the polymer backbone. Consequently, heteroatoms such as N, S, or Se might be beneficial to the stabilization of doped conjugated polymers.[9] The poly(tetrabromo-*p*-phenylenediselenide) (PBrPDSe) belongs to these interesting but "unexplored" polymers.

In previous articles we have reported on the significant increase in conductivity of the PBrP-DSe after doping with SbF_5^5, I_2, or Cl_2,[10,12] as well as the effect of doping with different acids on the conductivity of this polymer.[11] The results have shown that the use of mild acids helped to avoid polymer degradation. The most promising results have been obtained with diluted CH_3COOH.

This article reports on the testing of some mild acid compounds with pH near the neutral value, with the results compared to those obtained with CH_3COOH doping in the same conditions. The doping agents used in the present work were H_2SO_3, IBr, and CH_3COOH. It has been shown that whatever the doping agent, there is a conductivity maximum that cannot be overcome, which is probably the result of the structural properties of the polymer itself.

EXPERIMENTAL

The PBrPDSe powder was obtained according to the needs of the reaction shown below, which was described in a previous article.[5] The doping acids used were diluted either in ethanol (CH_3CH_2OH) or nitromethane (CH_3NO_2); the other doping agent was iodine bromine (IBr). The concentration of the doping acid solution was 1% v/v. Some milligrams of PBrPDSe wer introduced in the solution. After 24 h or 48 h, the solutions were filtered; then the recovered powder was dried in an oven at 325 K for 24 h, this temperature being smaller than the degradation temperature of the polymer.[13] In order to dope the polymer with IBr, doping was achieved in a desiccater at ambient temperature, according to the method of Gutierrez et al.[14]

After doping the samples were characterized by X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), and conductivity measurements. The XPS apparatus (XPS analysis was carried out at Nantes, University–CNRS) and experimental conditions have been described in an earlier arcticle.[12] The quantitative studies were based on the determination of Se 3d, Br 3d, C1s, $I3d_{5/2}$, and S2p peak areas with 0.57, 0.67, 0.2, 6.4, and 0.44, respectively, as sensitivity factors (the sensitivity factors of the spectrometer were provided by Leybold, the manufacturer).

The oxygen pollution at the surface of the powder has been discussed in an earlier article.[12] Therefore, no etching was performed on the powder currently under discussion because it might modify the properties of the doped powders.

The subtraction of the background was obtained by Shirley's method.[15] Spectral decomposition were achieved using Gaussian–Lorentzian curves. After the introduction of the number of peaks, binding energies, peak height, and full width at half maximum (FWHM) were adjusted for the best overall fit.

The ESR experiments were carried out in a Bruker ER 200 spectrometer operating at X bands. The fits of g anisotropy were done by poles method integration.[16] The theoretical ESR signal was computed using a Gaussian or a Lorentzian shape, or a mixture of the two.

Conductivity measurements were performed on pressed doped polymer pellets. The upper and lower faces of the pellets were metallized by thermal evaporation of gold under vacuum. Copper wires were stuck by silver paste to the gilt faces of the pellets. An electrometer was used to measure the conductivity from 240 K to 500 K. Because pellets were quite resistive, it was difficult to measure the resistance at a lower temperature. The high-temperature limit was imposed by the polymer stability.[13]

RESULTS AND DISCUSSION

XPS study has been done without etching because ions could modify the chemical bonds of the polymer. Therefore, some contamination is present on the polymer surface. Since the samples are quite resistive, it is well known that the binding energy of the peaks increases with the resistivity of the analyzed sample, which is called the charge effect (Table II).

In order to compare the binding energy of the different components of one sample from another, the values reported in the XPS decomposition table have been estimated by using the energy of a carbon–carbon bond as a reference, as is often the case in the literature,[17] with 285 eV as binding energy.

First of all, the quantitative analyses at the surface of the samples are reported in Table I. The data of composition are presented as a percentage of the element in question to the total amount of C, Se, Br, of the elements of the dopants (I for IBr and S for H_2SO_3), and of oxygen.

It can be seen that there is a strong excess of carbon. It has already been shown that this ex-

Table I   XPS Quantitative Analysis (at. %)

Polymer (dopant)	C	Se	Br	I	S	O
PBrPDSe (pure)	55	14	24	—	—	7
PBrPDSe (IBr)	52	9	30	1	—	8
PBrPDSe (H_2SO_3, 1%)	51	9	15	—	13	12
PBrPDSe (CH_3COOH, 1%)	57	12	21	—	—	10

cess is systematically present in this family of polymers.[10] This excess can be related to surface contamination, as shown by the presence of oxygen, which is also related to this contamination. Moreover, there is a small bromine deficiency in comparison with selenium. This selenium excess could be attributed to interchain reticulation.

The other conclusion obtained from the quantitative analyses is that the concentration of some elements of the dopant agents is very high (Br in the case of IBr, S in the case of H_2SO_3), while the concentration of some others elements of these doping agents is very small (I in the case of IBr, and the increase of O in the case of H_2SO_3).

The binding energies of different atoms, including the charge effect, are reported in Table II. It can be seen that the binding energies of the elements are not strongly modified by the doping agent, as shown by comparison with the pure polymer, except in the case of IBr doping, where it can be seen that the binding energy of bromine is noticeably smaller than in the pure polymer.

The results obtained by decomposition of the peaks are reported in Table III, after subtraction of the charge effect, and Figures 1–5. They will be discussed in light of the XPS handbook of polymers.[17] First, we will discuss the binding energies of the components and then their relative contributions. It can be seen in Table III and Figure 1 that the carbon peak can be decomposed into four components. The full width at half maximum of the peaks (FWHM) is around 1.7 eV, which is the value usually obtained with the spectrometer.

As discussed earlier[12] about the PBrPDSe polymer, the peak at 285 eV should be associated with carbon contamination, while the peaks at about 286 eV and 287 eV can be assigned to the C—Se and C—Br bonds, respectively. At a minimum the fourth peak can be attributed to C—Ox contamination. The binding energy of the last component may correspond to —COOH end groups.[17] The binding energies of the peaks after decomposition of the O1s peak are around 532 eV and 533.5 eV, which is in good agreement with the —COOH group contamination.

The results in Table III show that in all the samples there is one selenium contribution at an energy of 56.5–57 eV, while a second contribution is only present after IBr (Fig. 2) and CH_3COOH doping, which is discussed below. Usually the binding energy of selenium bonded to carbon is around 55.8 eV[18]; therefore, the higher value measured here may be attributed to the electronegativity of bromine, which induces a positive partial charge on the selenium atoms. In the case of IBr and CH_3COOH doping, the second contribution at 57.8 eV should correspond to a more positive selenium atom $Se^{\delta+}$.

The binding energy of Br 3d ($\simeq$ 72 eV) corresponds to covalently bonded halogen.[19,20] However after IBr doping (Fig. 3) there is a second contribution at 70.1 eV, which can be assigned to the bromine anion Br^-[19]. In the polymer being doped with IBr there are also traces of iodine ($\simeq$ 1 at. %). The I $3d_{5/2}$ peak corresponds to two contributions (Fig. 4). The first one is situated at 618.9

Table II   Binding Energy (eV) of Different Elements in PBrPDSe After Doping and Before Charge Effect Subtraction

Dopant	C	Se	Br	I	S	O
Pure	287.12	57.59	72.22	—	—	533.51
IBr	286.4	57	71.15	620.89	—	533
H_2SO_3	287	57.30	72	—	163.5	533
CH_3COOH	287	57.3	72	—	—	532.5

Table III   XPS Decomposition (Before Charge Effect Has Been Subtracted)

Dopant	C1s				Se3d		Br3d		$I3d_{5/2}$		S2p		O 1s	
	C—C	C—Se	C—Br	C—Ox	Se	Se^+	Br^-	Br	I_3^-	I_5^-	S	SO_3^-	C=O S=O	C—O—H
Pure	285	285.7	286.7	290.3	56.5			71.7					531.5	533.5
	18	23	51	8	100			100					50	50
IBr	285	286.2	286.9	289.2	56.7	57.8	70.1	72	618.9	620.9			532	533.5
	19	27	48	6	85	15	25	75	30	70			40	60
H_2SO_3	285	286.2	287.4	290	57			72.1			163.4	169	532	534
	14	22	60	4	100			100			75	25	55	45
CH_3COOH	285	286	287	288	56.9	57.7		71.7					531.8	533.5
	32	15	37	16	80	20		100					80	20

First ligne: binding energy after correction of the charge effect (eV).
Second ligne: relative concentration (at. %).

eV and the second at 620.9 eV. In the literature[21,22] these two energies have been assigned to I_3^- and I_5^- anions, respectively.

In the case of H_2SO_3 doping, the two sulfur peaks situated at 163.4 eV and 169 eV can be attributed to neutral sulfur and the sulfite anion SO_3^-, respectively.

For CH_3COOH doping the high relative concentration value of the first component of the carbon peak should be attributed to the CH_3COOH present in the film and to carbon contamination

Therefore, the main information obtained by XPS is that there is a charge–transfer complex (C–T complex) formation between the polymer and the dopants IBr and CH_3COOH, as shown by the second contribution in the Se 3d peak ($Se^{\delta+}$).

These results are in good agreement with the ESR study. The C–T complex formation is corroborated by the ESR signal of the doping polymer, while there is no ESR signal in the pure powder. The spin-density Ns values deduced from the ESR signals are reported in Table IV. In the case of
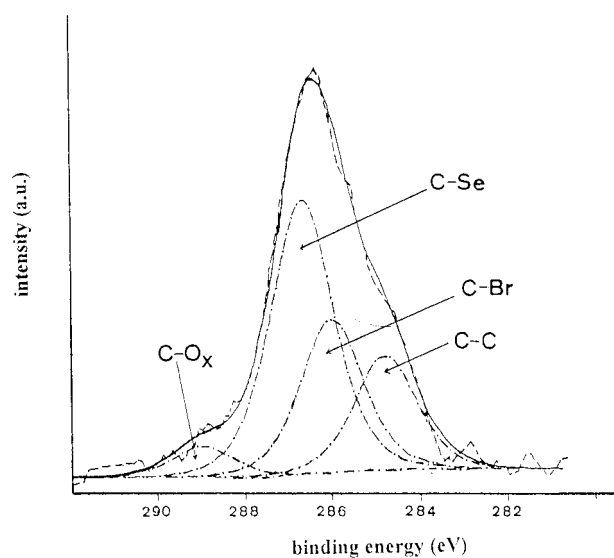

Figure 1   XPS spectra of the C1s peak in the case of IBr doping. — — — experimental result; ——— fitted curve; —·—·— different components.
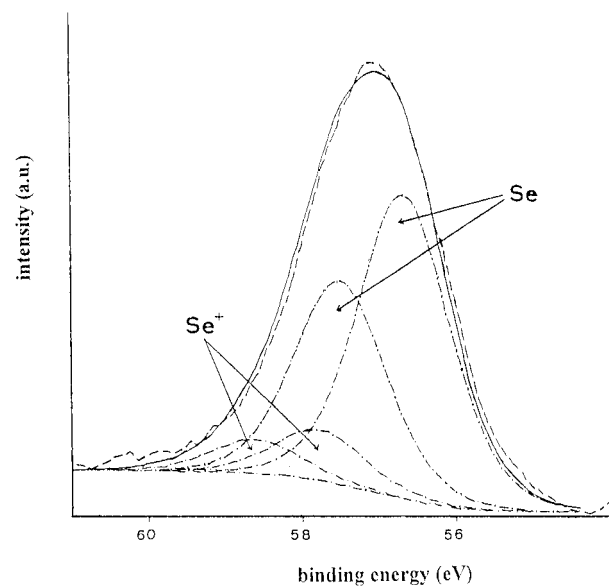

Figure 2   XPS spectra of the Se3d peak in the case of IBr doping. — — — experimental result; ——— fitted curve; —·—·— different components.
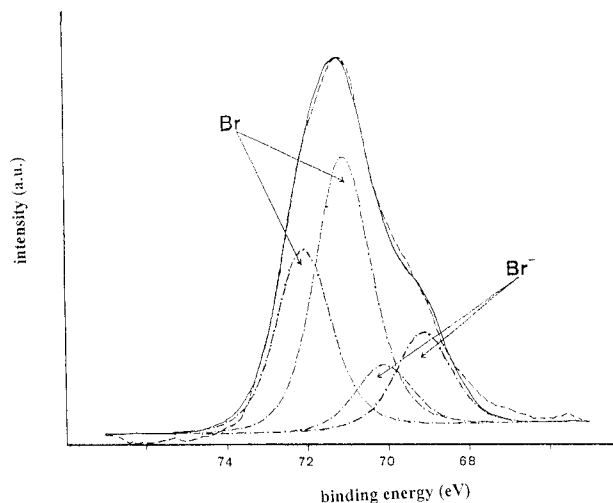
Figure 3 XPS spectra of the Br3d peak in the case of IBr doping. — — — experimental result; ——— fitted curve; —·—·— different components.

Figure 5 XPS spectra of the O1s peak in the case of IBr doping. — — — experimental result; ——— fitted curve; —·—·— different components.

H_2SO_3 It can be seen that a very small signal is obtained, which could explain why no $Se^{\delta+}$ is detected when the PBrPDSe is doped with this acid. In the two others cases the signal is stronger.

Spin density is not negligible, which explains why $Se^{\delta+}$ can be detected by XPS. The fits of the g anisotropy by poles method integration is given in Table IV, and an example in the case of CH_3COOH doping is given in Figure 6.

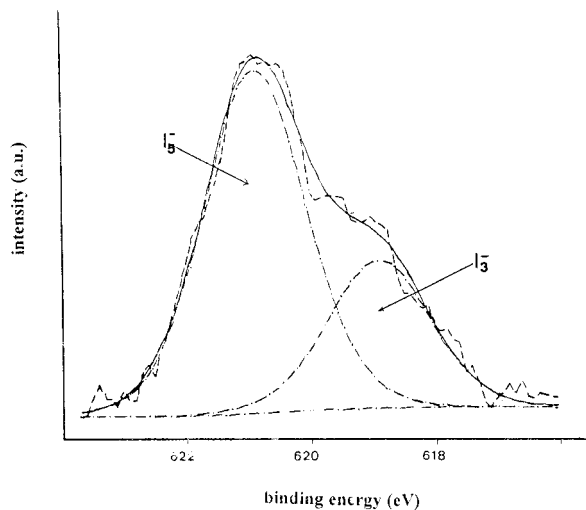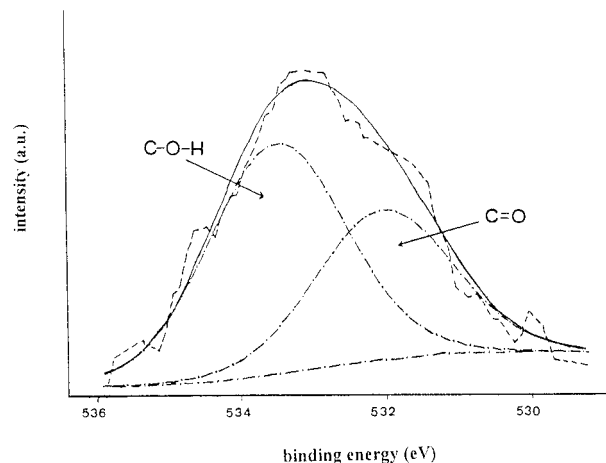The anisotropy of g values when the dopant is IBr or CH_3COOH corroborates the hypotheses of

$Se^{\delta+}$ radical formation since it has been shown that chalcogens exhibit high anisotropy of g values,[23–25] which is not the case with carbon radicals.

In the case of H_2SO_3 doping,the signal is isotropic and could correspond to carbon radicals, but it is very small. These results are in good agreement with the conductivity measurements. The conductivity increases with the spin density. However, whatever acid it is,it stays quite small. In fact, we have shown that whatever the dopant, the conductivity could not go higher than 10^{-7} $\Omega^{-1}\,cm^{-1}$ after stabilization.[10]

Therefore, since broad choice of dopant has been tested (halogens, organic and inorganic acids, etc.) it is thought that this conductivity limit is related to the properties of the polymer itself.

The molecular conformation of polymers has an important role in the electronic material properties. Their electrical conductivity properties can be explain by considering steric hindrance introduced by substitution groups. The main effect of the hindrance is to introduce a major nonplanarity of the polymer chain. Therefore, some propositions can be laid out to explain the upper limit of the conductivity:

- In the present work and also in earlier studies,[10, 11] it has been shown that the positive carriers induced by chemical doping are systematically localized on Se atoms.
- As discussed above, by fixing broad substituents such as bromine on the backbone of the

Figure 4 XPS spectra of the I3d$_{5/2}$ peak in the case of IBr doping. — — — experimental result; ——— fitted curve; —·—·— different components.

Table IV   Conductivity and ERS Measurements

Polymer	σ $(\Omega.cm)^{-1}$	Ns $(mol^{-1}\ cm^{-3})$	g
PBrPDSe	$<10^{-12}$		
PBrPDSe (CH_3COOH)	$10*10^{-8}$	9.10^{18}	$g_x = g_y = 2.0$ $g_z = 2.024$
PBrPDSe (H_2SO_3)	$0.63*10^{-8}$	$\cong 10^{16}$	$g_x = g_y = g_z$ $g_z = 2.0020$
PBrPDSe (IBr)	$2.01*10^{-8}$		$g_x = 2.078$ $g_y = 2.126$ $g_z = 2.023$

polymer chain, the coplanarity of the cycle is perturbed, which introduces some disorder in the main chain and, therefore, the localization of some carriers. Moreover, the lack of planarity has generally very important consequences on conjugated systems since it results in a lower effective conjugation length. Therefore, the averaged molecular weight is probably not very high, and in addition the chain-length distribution is probably quite broad.

- And finally the presence of possible reticulation also limits conductivity.

CONCLUSIONS

When PBrPDSe has been doped by CH_3COOH and IBr, XPS measurements have shown that the positive charge is localized on Se atoms ($Se^{\delta+}$).
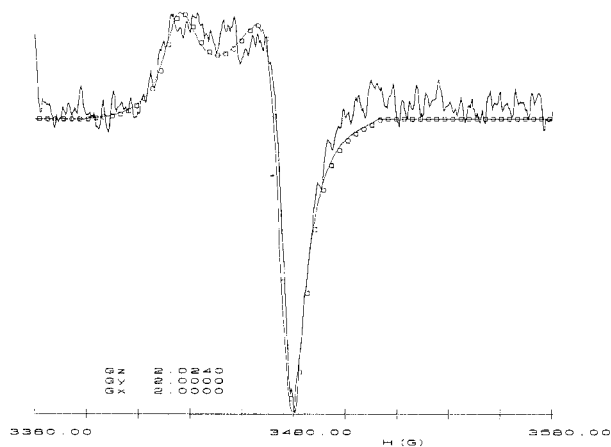
Figure 6 ESR spectra of PBrPDSe doped with CH_3COOH ——— experimental curve; —□—□— Fitted curve.

These results are in good agreement with the ESR study. In the case of H_2SO_3 doping, the signal could correspond to carbon radicals, but the response is very small. The XPS and ESR results are in good agreement with the conductivity measurements. The conductivity of acid-doped samples exhibits an increase by about four orders of magnitude. However, no matter what the dopant, the conductivity could not pass above $10^{-7}\ \Omega^{-1}.cm^{-1}$, a limit attributed to intrinsic properties of the polymer.

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