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Physico-chemical characterization of poly(seleno-*p*-arylene diamine)s doped with chlorine

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After synthesis, poly(seleno-*p*-arylene diamine)s were doped with chlorine. The polymers were studied before and after doping by X-ray photoelectron spectroscopy (X.p.s.), electron spin resonance (e.s.r.) and conductivity measurements. It is suggested that chain ends may be partly terminated by groups containing oxygen. After doping, there is charge transfer complex formation as shown by X.p.s. analysis. In some polymers, the e.s.r. study provided evidence that doping induces carbon radical formation. However, the conductivity remains quite low, whatever the material. This can be explained by small chain lengths and chlorine attack of the chains.

(Keywords: diamines; characterization; doping)

Introduction

Polymers having non-carbon elements in the chain will provide conducting materials when the delocalization of electrons is possible[1]. Polymers containing N–S linkage are of interest due to their good electrical conduction[2,3]. In 1980, Apostolescu *et al.*[4] described the synthesis of poly(*N*-seleno-*p*-phenyldiamine). After doping, this material has semiconductive properties[4].

Therefore it should be interesting to study the properties after doping of new polymers with N–Se linkage. The synthesis of poly(seleno-*p*-arylene diamine)s has been described previously[5,6]. It was shown that doping with I_2 or SbF_5 increases the conductivity of these materials, but the values obtained remain quite low, and after 2 months under ambient atmosphere there is a strong decrease in the conductivity.

Here, the more promising polymers of the family are doped with a more electronegative dopant, chlorine (Cl). X-ray photoelectron spectroscopy (X.p.s.), electron spin resonance (e.s.r.) and conductivity measurements show that chlorine is more effective as a dopant than the materials used previously.

Experimental

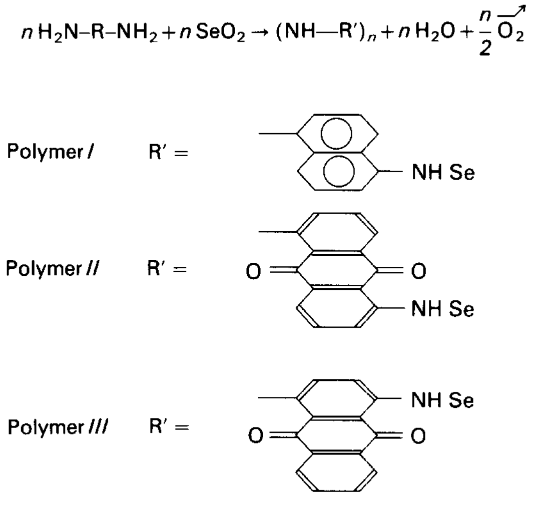
Three polymers were synthesized in the present study. The poly(n-seleno-*p*-arylene-diamine) powders were obtained by the reactions shown in *Scheme 1*, which have been described previously[5,6].

All chemicals and solvents used during the process were obtained from Aldrich, Merck and Fluka and were purified before use by normal procedures[5,6].

In order to dope the polymers with Cl, the powder was exposed to chlorine at room temperature in a glass tube under chlorine pressure.

The resulting powders, before and after doping, were characterized by X.p.s., e.s.r. and by conductivity measurements. X.p.s. analysis was carried out at the University of Nantes – CNRS, on a Leybold LHS-12 spectrometer. The data were obtained with a magnesium source of radiation (1253.6 eV) operating at 10 kV and 10 mA, and the pass energy was set to 50 eV. High resolution scans with a good signal-to-noise ratio were obtained in the Se3d, Cl2p, C1s, N1s and O1s regions of the spectrum. In order to decrease the charge effect, the powders were fixed to the substrate holder by pressing the polymer powder onto a sheet of indium.

The quantitative analyses were based on the determination of the Se3d, Cl2p, C1s, N1s and O1s peak areas with sensitivity factors of 0.57, 0.58, 0.2, 0.36 and 0.61, respectively. The sensitivity factors of the spectrometer were given by the manufacturer. The vacuum in the



$$n\,H_2N\text{–}R\text{–}NH_2 + n\,SeO_2 \rightarrow (NH\text{—}R')_n + n\,H_2O + \frac{n}{2}O_2\nearrow$$

Scheme 1

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Table 1 X.p.s. quantitative analysis of polymer *I* relative to the constituents and to oxygen

	C	N	Se	O
Theoretical	76.9	15.39	7.69	
Before doping	(86.5)	4.5	(9)[a]	
	78	(8)[a]	4	(10)[a]
After doping	79	(9)[a]	(3.5)[a]	
	(87.5)[a]	8	3	(10)[a]

[a] Data on composition are presented as the ratio (in per cent) of the element in question to the total amount of C, N, Se and O

analysis chamber was around 10^{-6} Pa. All spectra were recorded under identical conditions. The decomposition of the X.p.s. peaks into different components, and the quantitative interpretation, were made after subtraction of the background using the Shirley method[7]. The developed curve-fitting programs permit the variation of parameters such as the Gaussian/Lorentzian ratio, the full width at half maximum (*FWHM*), the position and the intensity of the contribution. These parameters were optimized by the curve-fitting program, in order to obtain the best fit.

The influence of the surface contamination was checked by recording successive X.p.s. spectra obtained after ion etching for short periods. Sputtering was performed at pressures of less 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 scanned over the entire sample surface, therefore the sputtered area had a larger diameter than the analysed one. It should be noted here that etching with argon ions may lead to drastic changes in the chemical nature of the sample, since this technique can create radical structures which lead to heavy crosslinking and produce structurally ill-defined material. Therefore the etching is used only to check whether oxygen is a surface contamination or whether it is also present in the bulk.

The e.s.r. experiments were carried out in a Bruker ER 200 spectrometer operating at X bands.

The electrical measurements were carried out on pressed pellets. Electrical contacts were obtained by vacuum deposition of gold on each side of the pellets. Then copper wires were stuck onto the gold-coated faces of the samples using silver or gold paste. The resistance measurements were performed by using an electrometer (Keithley 617).

Results

X.p.s. analysis. X.p.s. quantitative analyses are reported in *Table 1*. It can be seen that at the surface of the samples there is oxygen contamination and a carbon excess. Typical X.p.s. spectra of all the polymers show the presence of C, O, N and Se peaks. As shown by the quantitative analysis, parts of the oxygen and carbon peaks are due to surface contamination, which will be discussed subsequently, but no other contaminating element is detected in any of the powders.

The C1s and O1s peaks exhibit shoulders and large *FWHM*, therefore, they have decomposed (*Figures 1*, *2* and *Table 2*). After doping, the Cl2p peak has also decomposed (*Figure 3*, *Table 2*). The carbon–carbon bond present in the polymers has been taken as the reference in order to estimate the charge. In the literature[8], this

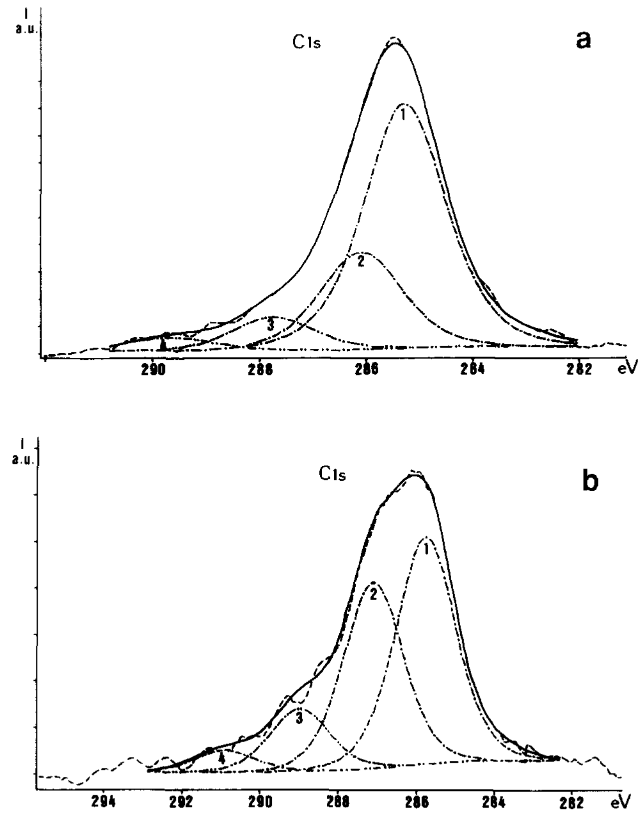

Figure 1 Result of curve-fitting of C1s peak of polymer *I*: (a) before doping, (b) after doping. —··—·—, Decomposition; ——, fitted curve; - - -, experimental curve

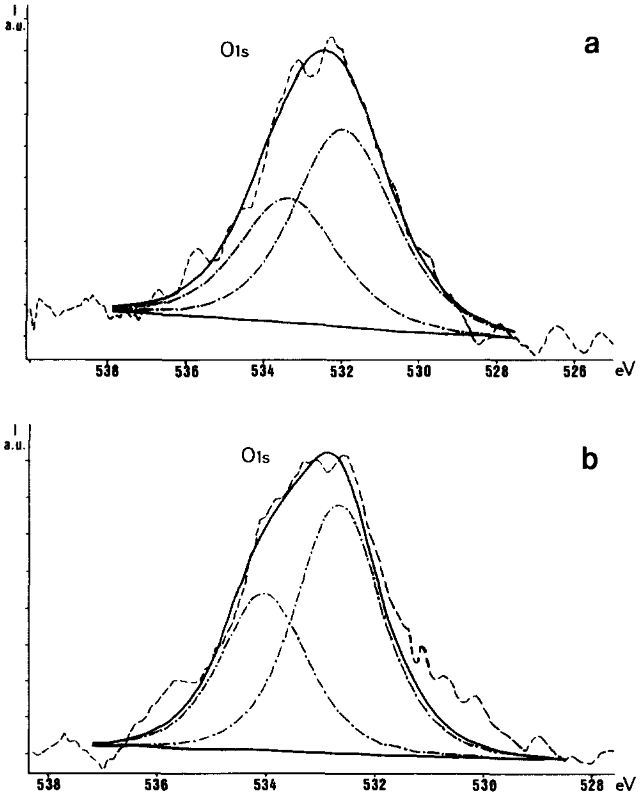

Figure 2 Result of curve-fitting of O1s peak of polymer *I*: (a) before doping; (b) after doping. —·—·—, Decomposition; ——, fitted curve; - - - -, experimental curve

Table 2 X.p.s. analyses and room temperature conductivity of polumers *I–III*

Sample	Room temp. conductivity (Ω^{-1}cm^{-1})	C1s peak decomposition: First value: binding energy (eV) Second value: relative %				Se3d (eV)	N1s (eV)	O1s First value: binding energy (eV) Second value: relative %		Cl2p First value: binding energy (eV) Second value: relative %	
		C–C	C–N	C–O–H	C=O			C=O	C–O–H	Cl$^-$	Cl
I before doping	18×10^{-13}	285	286.7	288.7	289.7	55.2	398.6	531.8	533.2		
		80	10	7	3			60	40		
I after doping	2×10^{-10}	285	286.1	287.4	288.9	55	398.7	531.8	533.2	198.8	200.8
	to 2×10^{-9}	49	33	10	8			60	40	45	55
II before doping		285	285.8	287.4	288.7	55.3	398.7	531.8	533.2		
		73	12	6	8			70	30		
II after doping	2×10^{-11}	285	285.9	287.6	289	55.1	399.3	531.6	532.6	199.8	
		47	37	11	5			45	55		
III before doping	2×10^{-15}	285	286.5	288	289.5	55.3	398.5	531.7	532.9		
		79	11	7	3			80	20		
III after doping	2×10^{-11}	285	286	288	289.7	55.9	399.5	533	534.6	199.6	201.6
		15	60	15	10			80	20	50	50

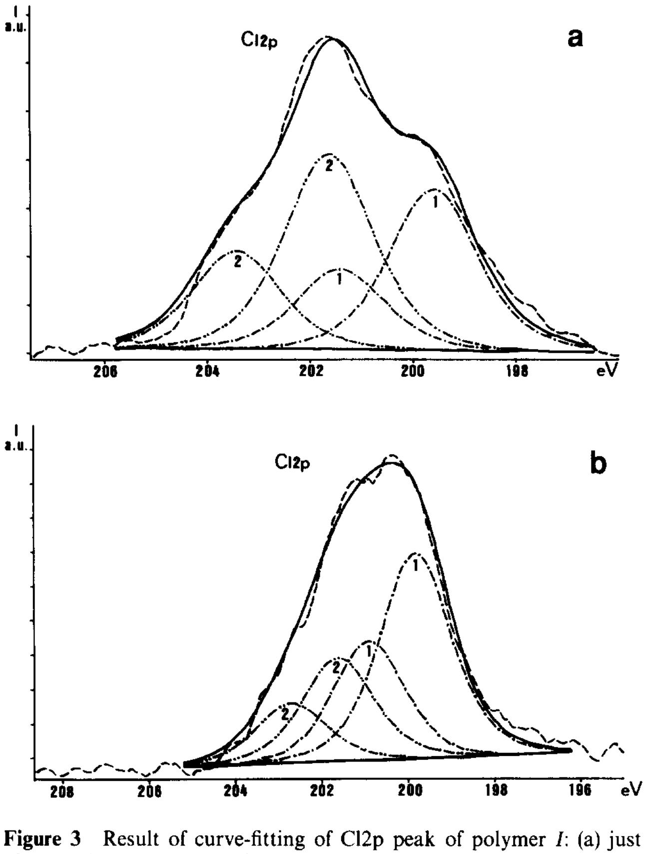

Figure 3 Result of curve-fitting of Cl2p peak of polymer *I*: (a) just after doping; (b) 8 days after doping. —··—·—, Decomposition; ——, fitted curve; - - - -, experimental curve

Table 3 X.p.s. quantitative analyses of polymers *I–III*

Sample	Oxygen (%)	
	Before etching	After 1 min etching
I before doping	10	5
I just after doping	10	5
II before doping	25	25
II just after doping	20	20
III before doping	20	10
III just after doping	20	10

band has a well defined position at 285 eV and this value has been taken as reference. So a charge effect has to be subtracted from the binding energies of the experimental curves shown in *Figures 1, 2* and *3*.

The quantitative analyses show that the percentage of oxygen and of carbon excess does not change during the doping process (*Table 3*). The C1s peak can be decomposed into four peaks (*Figure 1*). The first corresponds to the carbon and hydrocarbon bonds. The second, before doping (*Figure 1a*), can be attributed to the C–N bonds. However, after doping, while the O_2 and N_2 concentration in the powder does not change drastically, the relative intensity of the C–N bond increases strongly (*Table 1, Figure 1b*), while the *FWHM* values estimated by the fit are quite similar (1.8 eV before doping and 1.9 eV after doping). Therefore this increase cannot be attributed to oxidation by oxygen, but to positively charged carbon having a strong electrostatic interaction with the new Cl^- anion incorporated into the sample by doping. Then the second peak of the fitted C1s peak probably corresponds to two unresolved peaks, or perhaps three peaks, since we cannot exclude the possibility that some O–H bonds are present before and after doping.

The third peak may be attributed to the carbonyl bond. In Polymer *I*, this bond is assigned to surface contamination while in the other polymers it can be attributed to the carbonyl groups present in the chain, but also to contamination. The fourth peak may correspond to carboxyl and/or COOR group contamination[9]. These carbonyl and carboxyl groups may be attributed to surface contamination since there is a surface excess of oxygen and carbon; however, it has been shown in others polymers that the chains can be terminated via reaction with oxygen to form a terminal carbonyl group[10,11]. After

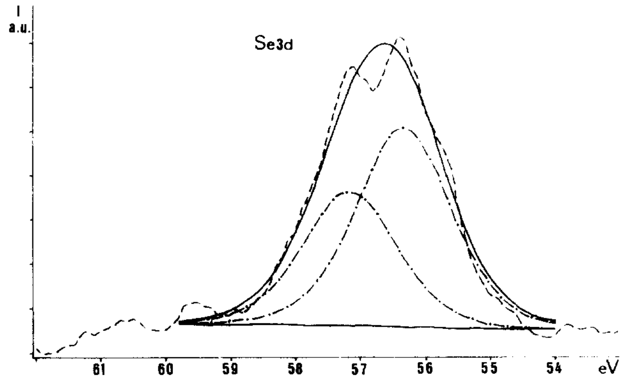

Figure 4 Se3d X.p.s. peak of polymer *I*. — · · · , Decomposition: . fitted curve: – – – –, experimental curve

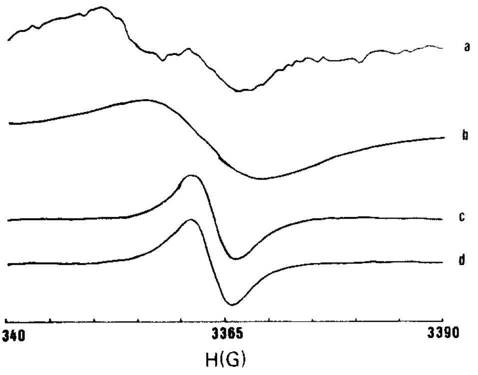

Figure 5 Normalized e.s.r. spectrum of: (a) polymer *I* before doping; (b) polymer *I* after doping; (c) polymer *III* before doping; (d) polymer *III* after doping

etching for 1 min, the oxygen percentage is still high even in polymer *I* (*Table 3*), which is in good agreement with the formation of chain ends with oxygen, since after etching the surface contamination should be ruled out.

The two peaks obtained after decomposition of the O1s peak can be attributed to C=O and C–O–H bonds (*Figure 2*).

After doping, it is seen that the chlorine peak can be decomposed into two peaks (*Table 2, Figure 3*). The peak situated at around 199 eV can be attributed to the chlorine anion while the other corresponds to covalently bonded chlorine. There is a relatively high concentration of the covalent bond (*Table 2*) which can be attributed to the presence of chlorine gas inclusions inside the powder, since the analysis has been performed just after doping. This hypothesis is corroborated by the fact that 8 days later, the relative percentage of covalently bonded chlorine has decreased (*Figure 3b*).

Before or after doping, the binding energy of the Se3d peak (*Table 2, Figure 4*) is slightly higher than the value obtained in $(C_5H_5)_2Se_2$ (ref. 12). This corresponds to a partial positive charge of the selenium, which may be explained by the electronegativity difference between N ($\chi_N = 3$) and Se ($\chi_{Se} = 2.4$).

E.s.r. study and conductivity measurements. The structure of polymer *II* is quite similar to that of polymer *III* and the results obtained with these materials were identical. Therefore the results obtained with samples *I* and *III* only are presented. The samples were studied with and without chlorine dopant. The spectra obtained are shown in *Figure 5* (*Table 4*).

It can be seen that while the shape of the spectrum of sample *I* is strongly affected by chlorine doping, that of sample *III* is not. The g and ΔH_{pp} values are not affected by doping in the case of polymer *III*. In the case of polymer *I*, before doping we can fit the line with two isotropic values g, $g = 2.0010$ and $g = 2.0070$, while $\Delta H_{pp} = 8$ and 9, respectively. The former can be attributed to the carbon radical while the other, with a greater g value, can be attributed to the nitrogen radical since, in the case of Se radical, the g spectrum is strongly asymmetric[3-5]. In *Figure 5* the signals have been normalized but, in fact, there is a strong increase (× 100) of the signal of polymer *I*. After doping, there is not only a strong increase in the e.s.r. signal but also a change of the e.s.r. line shape is noted. There is only one g value for this sample, $g = 2.0018$, as there is no need for decomposition of the e.s.r. spectrum, this e.s.r. line ($g = 2.0018$) seems to correspond to a carbon radical (usually with $g = 2.0026$). This is in close agreement with the decomposition of the C1s peak of X.p.s. after doping.

The room temperature conductivity measurements of the samples before and after doping are reported in *Table 2*. It can be seen that after doping with chlorine, there is an increase of about three orders of magnitude of the conductivity in each polymer studied.

Microprobe analyses were performed on the different powders. It has been shown that the relative atomic ratio Cl/Se varies strongly from one point to another ($1 < Cl/Se < 1.4$).

Discussion and conclusion

X.p.s. measurements have shown that there is probably not only surface contamination, but also oxidation of the polymer. This oxidation can be attributed to the chain

Table 4 Values of g and ΔH_{pp} from e.s.r. spectra

Polymer	g values	ΔH_{pp} (gauss)
I before doping	$g_1 = 2.0010$	8
	$g_2 = 2.0070$	9
I after doping	2.0018	14
III before doping	2.0011	5.5
III after doping	2.0010	5.1

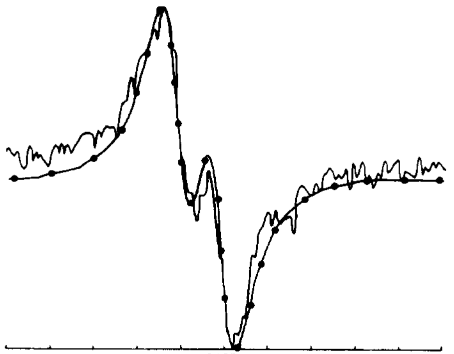

Figure 6 E.s.r. spectrum fitting of polymer *I* before doping: . experimental curve; —●—, fitted curve

ends[9,10]. After doping, it has been shown that the carbon peak is strongly affected while the nitrogen peak is not. More specifically, the peak attributed to the C–N bonds increases strongly. Since the oxygen concentration during doping does not change, this increase can be attributed to the carbon peak modification by doping. This assumption is corroborated by the fact that the chlorine is essentially in the anion configuration. That is to say, after doping there is a complex salt formation between chlorine and some carbons of the polymers. The anisotropy of the e.s.r. signal of undoped polymer *I* is not unexpected in powder samples. As has been shown, this anisotropy can be attributed to some carbon and nitrogen radicals. After doping, the new e.s.r. line corresponds to a carbon radical, which is also in agreement with X.p.s. results as shown by the decomposition of the C1s peak. The doping induces a strong increase of the e.s.r. line, i.e. a strong increase of the radical density.

In the case of polymer *III*, the signal can be attributed to the carbonyl bonded to the phenyl rings. The signal is quite strong and therefore there is not a strong increase of the signal after doping.

It has been shown that even immediately after doping, there is a quite significant concentration of oxygen in the polymer. A part of this oxygen probably terminates the chains. Therefore the high concentration of oxygen in polymers, even after etching, may be attributed to very short polymer chains. This small length of the polymer chains may explain the small value of the conductivity of this polymer even after doping. If the new carriers are free in the chains, they have to jump from one chain to another during the conduction process. Therefore the conductivity of the material is controlled by hopping between the chains more than by carrier motion in a chain. This small mobility of the carrier is in good agreement with the relatively high value of ΔH_{pp} for the e.s.r. signal. In the case of polymer *III*, the initial signal corresponds to that of the carbonyl grain. Therefore the e.s.r. signal is quite important even before doping.

The improvement of the signal after doping is small and cannot be distinguished from the carbonyl contribution. This probably shows that the number of free carriers obtained after doping is small, which, with the short chains, can explain the very low value of the conductivity even after doping.

In these three polymers it has been shown that the repartition of chlorine is not homogeneous. Therefore we can imagine that highly doped (conductive) domains are juxtaposed to poorly doped (insulating) domains, which may also explain the poor conductivity of the doped samples.

Another possible explanation for the relatively small increase in conductivity of the polymers after doping may be related to chain rupture by chlorine attack[16]. Therefore a systematic study by X.p.s., e.s.r. and conductivity measurements, with storage time as a function, is under way in the laboratory.

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