

Synthesis and Characterization of Polymers Derived from Selenophene

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ABSTRACT: The synthesis of poly(2,5-selenophen-oxo-1,4-phenylen-selenide-1,4-phenylene-oxo) (**I**) and poly(2,5-selenophen-oxo-1,4-phenylen-diselenide-1,4-phenylene-oxo) (**II**) by reaction of 2,5-bis(1,4-bromo-phenylen-oxo)-selenophene with sodium selenide or diselenide, respectively, using dimethylformamide as solvent, is described. Both monomers and polymers were characterized by elemental analysis, melting point, and FTIR spectroscopy. Polymers **I** and **II** were doped with iodine and SbF₅ and characterized by SEM and XPS. Also, the conductivity and the T_g values were determined. For both polymers the best doping agent was iodine, although polymer **II** always presented higher conductivity, reaching values of about $6 \cdot 10^{-9} \text{ S} \cdot \text{cm}^{-1}$. The T_g values suggest a likely crosslinking of the chains in polymer **II** when doped with SbF₅. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2019–2026, 2001

Key words: 2,5-selenophen-oxo-1,4-phenylen-selenide-1,4-phenylene-oxo; 2,5-selenophen-oxo-1,4-phenylen-diselenide-1,4-phenylene-oxo; poly(2,5-selenophen-oxo-1,4-phenylen-selenide-1,4-phenylene-oxo); poly(2,5-selenophen-oxo-1,4-phenylen-diselenide-1,4-phenylene-oxo); selenophene derivatives

INTRODUCTION

Since the conducting properties of polyacetylene doped with different agents were discovered,^{1,2} a new and important research area began. The main challenges are, first, the search for new organic conductors, and second, the possibility of tailoring polymers for a wide field of applications.³ This situation has been corroborated by

the preparation of aromatic polymers such as poly(*p*-phenylene)⁴ or poly(*p*-phenyl-vinylene),⁵ which, after doping, switched their conductivity from insulator to conductor.

D. J. Sadman et al.⁶ contributed to this series of compounds working with poly(*p*-phenylen-selenide) which, when doped with different agents, increased its conductivity by up to seven orders of magnitude with respect to poly(*p*-phenylene) doped with the same materials. In this way, the possibility of introducing chalcogens in the polymeric chain with the purpose of studying their effect on the conductivity was established.

Based on these results, we report here the synthesis of polymers derived from selenophene containing selenium in the main chain. These poly-

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mers were characterized before and after doping with *n*- or *p*-doping agents.

EXPERIMENTAL

Elemental analysis was performed in an Elemental Analyzer C, H, N, O, Mod. EA 1108. Melting points were measured in a Kofler microscope with gradual increase of the temperature. The FTIR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer by the KBr pellet method. The conductivity measurements were carried out on pellets of the doped and undoped polymers, using a Keithley 610 electrometer. The glass transition temperature of the polymers was obtained on a Perkin-Elmer DSC-1B differential scanning calorimeter under nitrogen.

The X-ray photoelectron spectroscopy (XPS) measurements were conducted at the University of Nantes, CNRS, Nantes, on a Leybold Heraeus apparatus with Mg $K\alpha$ radiation (1253.6 eV). High-resolution scans with a good signal-to-noise ratio were obtained with the source operating at 10 kV and 10 mA in the Se 3d, C 1s, and O 1s region of the spectrum. The samples were fixed to the substrate holder by pressing onto a sheet of indium. The quantitative analysis was based on the determination of Se 3d, C 1s, and O 1s areas using sensitivity factors of 0.57, 0.20, and 0.61, respectively (the sensitivity factors of the spectrometer are given by the manufacturer). The deconvolution of the C 1s peak and its interpretation was carried out using Shirley's method.⁷ The adjustment program of the curves allows the variation of parameters such as the Gaussian/Lorentzian ratio, width of the band in half peak position, and intensity of the contribution.

The morphological analysis was carried out by Scanning Electronic Microscopy (SEM) with a field effect JEOL scanning electron microscope, Model JSM-6400 F. Polymers were fixed to brass plates of 3.1 cm² with silver lacquer. The microphotographs were obtained under a pressure in the range of $1.3 \cdot 10^{-6}$ Pa.

Synthesis of the Monomer 2,5-bis(4-Bromophenyl-oxo-selenophene)⁸

Selenium oxychloride (0.0625 mol) was mixed with 0.125 mol of 4-bromo-acetophenone in 50 mL of diethyl ether as solvent. After 1 h, white and bright needles of dichloroselene-bis-*p*-bromo-

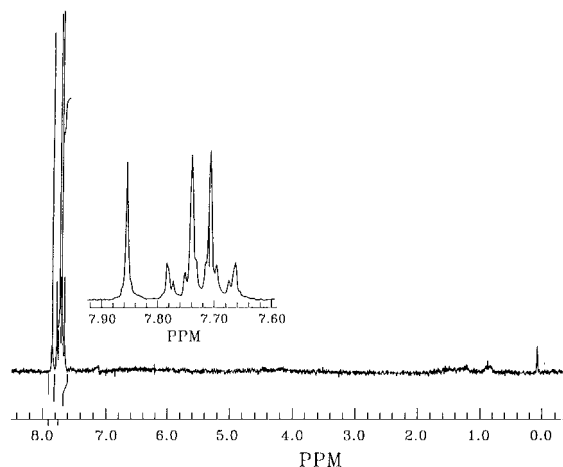


Figure 1 NMR of 2,5-bis(4-bromo-phenyl-oxo-selenophene).

tophenone are formed. The product was collected by filtration and then characterized.

Dichloroselene-bis-*p*-bromo-acetophenone was added, in small portions, to a mixture of 50 mL of benzene and 50 mL of a 10% aqueous sodium dithionite solution. A yellow powder of di(*p*-bromophenacyl)selenide was obtained. Yield 69%. m.p.: 140–140.5°C. Elemental analysis (%): calc.: C: 60.57; H: 4.42; Se: 24.92; found: C: 60.35; H: 4.61; Se: 24.98. FTIR (KBr) (cm⁻¹): 1640–1660 R—CO—Ar; 1460–1480 —CH₂—.

Di(*p*-bromophenacyl)selenide was added to a previously refluxed mixture of trimeric glyoxal in ethanol, and then a 0.35M KOH solution in ethanol was added slowly and refluxed by 2 h. The mixture was cooled and filtered. The solid was extracted with dichloromethane to eliminate residues of black selenium to afford 15.7 g of a brown-yellowish powder of the 2,5-bis(4-bromophenylene-oxo-selenophene)monomer. Yield: 73%. m.p.: 249–250°C. ¹H RMN (CDCl₃) (δ): 7.68– and 7.76, 8H (arom *p*-sust) and 7.86 s 2H selenophene (Fig. 1).

Polymer Synthesis

Black selenium (0.1749 g for polymer **I** and polymer **II**) was mixed with 20 mL of *N,N*-dimethylformamide, DMF, in a round-bottom flask at 130°C; then, 0.15 g (or 0.3 g) of metallic sodium was slowly added maintaining the temperature for 5 min.⁹ The mixture was added to a solution of 1.13 g of 2,5-bis(4-bromo-phenyl-oxo-selenophene) in 20 mL of DMF and heating at 130°C for 1 h. The mixture was poured into methanol con-

taining HCl, and the precipitate formed was filtered and washed with water and methanol, affording 0.8 g of a green-yellowish solid (polymer I) or 0.8 g of a brown solid (polymer II). The products were characterized by elemental analysis and FTIR spectroscopy.

Polymer I: Elemental analysis (%): calc.: C: 51.93; H: 2.40; Se: 37.97; found: C: 51.68; H: 2.56; Se: 37.91. FTIR (KBr) (cm^{-1}): 1620–1635 Ar–CO–Ar; 826–860 arom. *p*-sust.

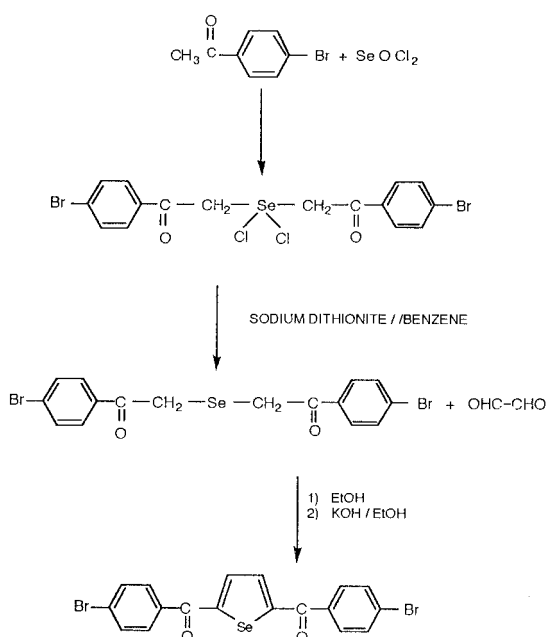
Polymer II: Elemental analysis (%): calc.: C: 43.65; H: 2.02; Se: 47.87; found: C: 43.57; H: 2.60; Se: 47.31. FTIR (KBr) (cm^{-1}): 1630–1650 Ar–CO–Ar; 826–850 arom. *p*-sust.

Doping with Iodine¹⁰

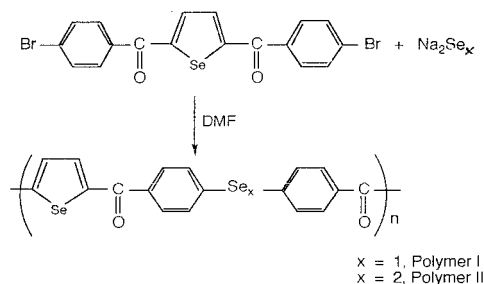
Poured samples were exposed to iodine vapor until saturation (constant weight), and then placed in a vacuum oven for 6 h at room temperature. After this treatment it prepared pellets to conductivity measurements.

Doping with Antimony Pentafluoride¹¹

Polymers were placed in contact with the condensed phase of SbF_5 . The system was heated between 140–150°C for 3–7 h and then placed in a vacuum oven at 50°C for 12 h, to eliminate the



Scheme 1 Synthesis of 2,5-bis(4-bromo-phenylen-oxo-selenophene).



Scheme 2 Polymers synthesis.

excess of SbF_5 . After this process it prepared pellets to conductivity measurements.

RESULTS AND DISCUSSION

The monomer 2,5-bis(4-bromo-phenylen-oxo-selenophene) was synthesized according to Scheme 1 and characterized by elemental analysis, FTIR and $^1\text{H-NMR}$. The results have been presented in the Experimental part.

Polymers were synthesized from the monomer 2,5-bis(4-bromo-phenylen-oxo)selenophene and sodium selenide or diselenide according to Scheme 2 and characterized by elemental analysis and FTIR spectroscopy.

Figures 2 and 3 depict the XPS analysis and the bands corresponding to C 1s of polymer I and II. These bands were asymmetric and presented an inflection, indicating the presence of several types of carbon. The bands obtained for both polymers were deconvoluted using Shirley's method⁷ and the resulting peaks are also exhibited in these figures.

For both polymers a value of 285.6 eV was found for the C–C bond. As the reference value of

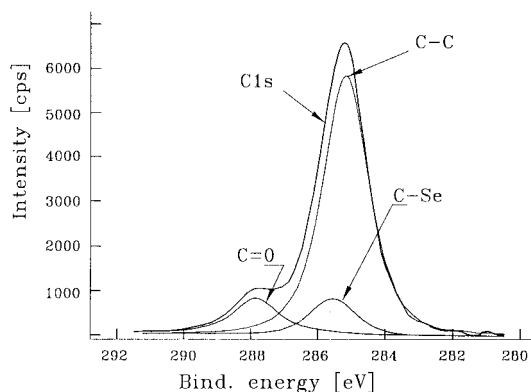


Figure 2 Deconvolution of C 1s peaks of polymer I.

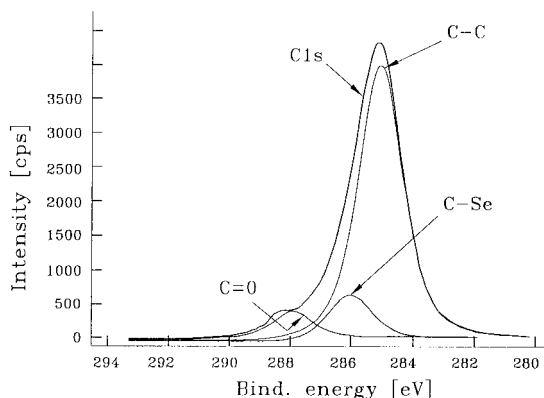


Figure 3 Deconvolution of C 1s peaks of polymer II.

the spectrophotometer used is 285 eV, if we subtract this to the obtained value, it is possible to see that there is a charge effect of 0.6 eV.¹²

A second peak is observed for both polymers, at 285.4 eV for polymer **I** and at 286 eV for polymer **II**, corresponding to the C—Se bond, with a lower intensity than that corresponding to C—C. And finally, a third very small peak, corresponding to C=O, with a bond energy of 287.8 eV, was observed.

Detection of bromine by conventional analysis was not possible in these polymers, and it was impossible for a molecular weight determination because polymers are insoluble in all solvents.

Bonding energy obtained for the different polymeric atoms are summarized in Table I. The values of these bonding energy show that selenium, as well as the other atoms, are covalently bonded in the polymeric chain.

Also, for both polymers, the analysis of Se 3d indicates a small percentage of ionized selenium. This ionization could have been produced in the polymerization step, wherein the sodium selenide or diselenide substitutes bromide in the aromatic ring to generate the polymeric chain. In the formation of selenide or diselenide, the limiting reagent is sodium, and, consequently, a small excess of elementary selenium remains. During the polymerization process, when the two reaction

Table I XPS: Bonding Energy of Polymers **I** and **II** [eV]

Polymer	C—C	C—Se	C=O	Se 3d
I	285.0	285.6	287.9	56.5
II	285.0	286.0	287.7	56.5

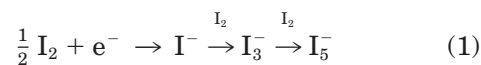
Table II Analysis of Polymers **I** and **II**, from XPS Values

Polymer	Element % (Theoretical) Found		
	C	Se	O
I	(78.3) 78	(13.0) 8	(8.7) 11
II	(82) 82	(9) 7.5	(9) 10.5

mixtures are combined, a large amount of bromide is liberated, that could be oxidized to bromine by elemental selenium, bringing about a small doping of the polymer. This small amount of doping could not be avoided due to the low solubility of the macromolecules in the reaction medium and in the washing solvent. This situation should appear in the XPS curves, because, as mentioned above, a small percentage of ionized selenium was actually detected.

Table II summarizes the percentage obtained for each element by XPS. These results show the presence of a small percentage of atmospheric oxygen, while the selenium content is somewhat lower than the calculated value.

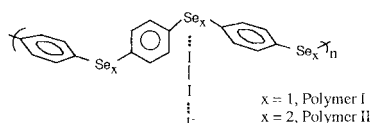
The conductivity values obtained for the doped and undoped polymers **I** and **II**, are summarized in Table III. An important conductivity increase after doping with iodine is observed for both polymers, but with antimony pentafluoride, only polymer **II** presents a higher conductivity, which could be ascribed to a charge-transfer complex formed between the more electronegative atom of the chain (Se) and any of the likely species that the doping agent (iodine) forms:



Iodine is a relatively weak electron-acceptor substance, but in a medium rich in electrons, due

Table III Conductivity Values of Doped and Undoped Polymers

Polymer	Conductivity $\times 10^{12}$ [S \cdot cm ⁻¹]		
	Undoped	I ₂ Doped	SbF ₅ Doped
I	0.0385	22.20	0.237
II	0.0700	6150	1016



Scheme 3 Tri-iodine coordination to the polymers.

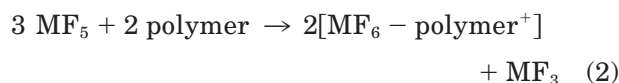
to the presence of electronegative atoms such as selenium, it quickly forms iodides. Because the system is saturated with iodine vapor, the tri-iodide anion is originated and, if the exposition is sustained, it may generate the penta-iodide anion.

Molecular iodine would behave like Lewis acid and would coordinate Lewis bases such as iodine and tri-iodide, generating the species described above. This phenomenon has been widely studied, mainly by Mössbauer¹³ and Raman spectroscopy,^{13,14} and, according to the literature regarding iodine-doped polymers, it has been established that the predominant anion is tri-iodide.¹⁵

On the other hand, Se is a large atom with metallic characteristics, and does not have a high charge density. Nevertheless, this charge is enough to coordinate tri-iodide or penta-iodide anions because, despite these ions being large, they are linear and can approach to selenium atoms of the chain, coordinating to the charge-transfer complex. This situation, like a similar structure proposed for PPS,¹⁶ is depicted in Scheme 3.

The above-mentioned explains that iodine doping is more extensive in polymer **II**. It can be corroborated through FTIR spectra depicted in Figure 4: only for a recently doped polymer it can be appreciate the bands between 1400–2000 cm^{-1} and near 3900 cm^{-1} [Fig. 4(b)], which diminishes with time when iodine doping decreases [Fig. 4(a)].

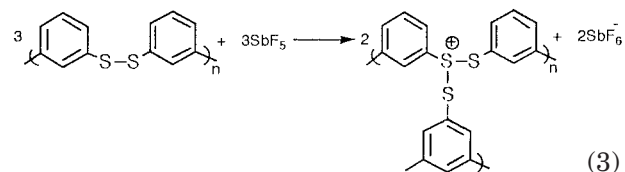
The lower conductivity obtained for polymers doped with SbF_5 , can be ascribed to the large size of the species that would form the counter-ion of the oxidized chain. This type of reaction has been proposed by Masse⁵:



where M is P, As, or Sb. The best results were those obtained with As and Sb. Any polymer having a chalcogenic atom in its structure would behave likewise. As the counter-ion in this reaction

is the bulky SbF_6^- , the coordination of Se atoms into the polymer chain is hindered.

Bertinelli¹⁰ investigated this type of doping in poly(*m*-phenylenedisulfide) (PMPDS) and pointed out that, for long exposure of the polymer to SbF_5 , chemical changes occur, leading to a crosslinking of the chains, according to the following oxidation reaction:



Bertinelli bases his proposition from results obtained by IR spectroscopy.

If we consider that Se belongs to the sulfur group, but with a higher metallic character, i.e., Se is a better electron-donor than S, then a similar or even more favorable process would be expected. This could explain the different conductivity of polymers **I** and **II**.

One of the necessary conditions to be met by an energetic oxidizer, such as SbF_5 to produce this reaction¹⁷ is the presence of two adjacent chalcogen

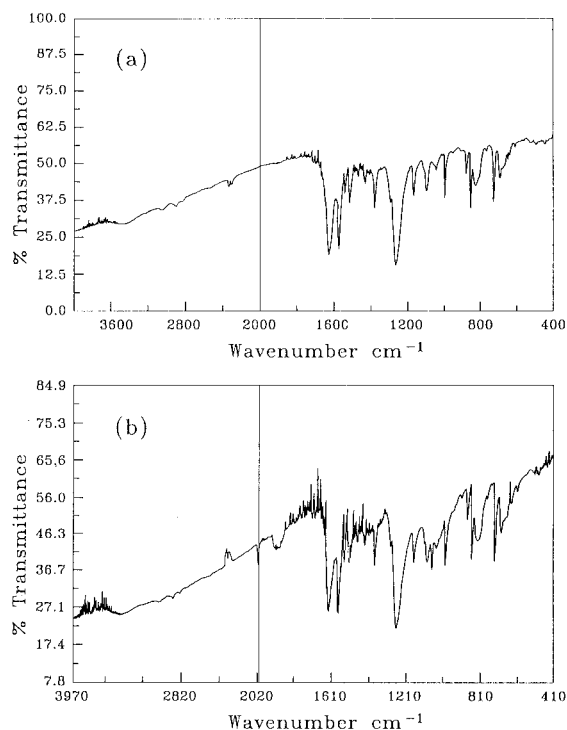
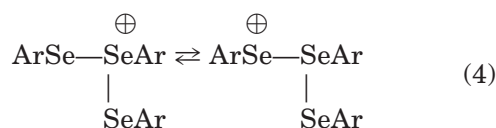


Figure 4 FTIR spectra of (a) undoped polymer I; (b) I_2 doped polymer I.

Table IV T_g of Undoped and SbF_5 Doped Polymers

Polymer	T_g (°C)		
	Undoped	SbF_5 Doped (3 h)	SbF_5 Doped (5 h)
I	86.6	87.2	96.9
II	100.1	109.9	114.2

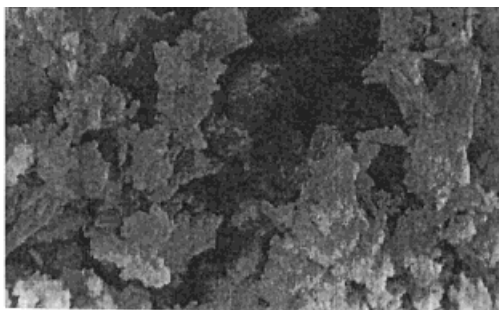
gens bond to a third one to generate a balance, such as that presented in the following equation:



The crosslinking was experimentally demonstrated by the T_g values of the doped and undoped polymers. If crosslinking exists, the chain will be more rigid and the T_g and the conductivity should increase. The obtained values are exhibited in Table IV.

An increase of T_g is observed for both polymers, being higher in the case of polymer **II**, in good agreement with the conductivity value. This was not so for polymer **I**, wherein the increase may be due to occlusion of nonreacted SbF_5 into the polymeric chain. This allows to corroborate Bertinelli's assumption, because in the absence of adjacent chalcogens, the equilibrium described above is not reached and, therefore, the conductivity of polymer **I** practically does not change.

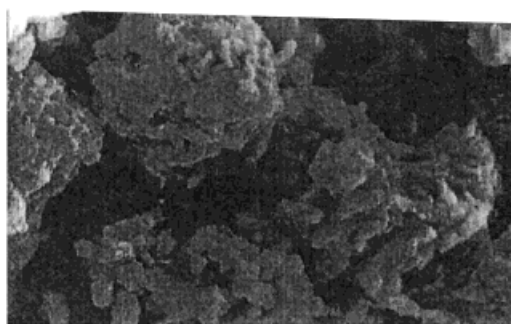
Another way to confirming the doping is through the morphological change that should experience the polymers after the doping process. Visually, after the doping with iodine, noticeable



(a)



(b)



(c)

Figure 5 Microphotographs of (a) undoped polymer I; (b) I_2 doped polymer I; (c) SbF_5 doped polymer I.

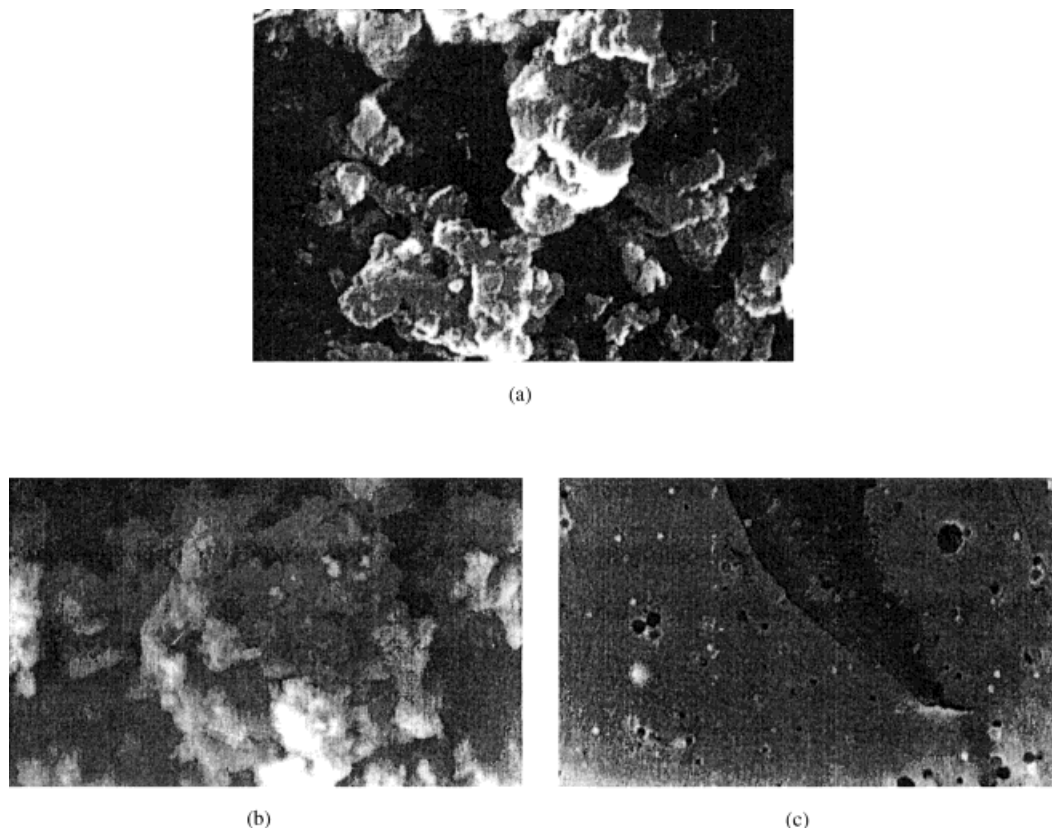


Figure 6 Microphotographs of (a) undoped polymer II; (b) I₂ doped polymer II; (c) SbF₅ doped polymer II.

color change is observed. When the doping process is made with iodine, polymer **I** varies its color from yellow-greenish to brown-reddish, and polymer **II** from brown to black. On the other hand, when the doping is carried out with SbF₅ polymer **I** undergoes only a change in its appearance, while polymer **II** changes its color from brown to very bright black. These phenomena are clearly evidenced in the corresponding microphotographs showed in Figures 5 and 6.

On the other hand, none of the polymers presented T_m , although the temperature reached 650 K. Furthermore, both polymers decompose at 430 K with H₂Se evolution.

In addition, both polymers presented low T_g values, because aromatic substituted selenophenes are separated by only one Se. This would also explain why the T_g is higher in polymer **II** than in polymer **I**, and also the most amorphous character of polymer **II**, as a result of its higher freedom of movement when two adjacent Se are present in the chain.

The crosslinking theory postulated for the doping with SbF₅, is corroborated by the T_g values found for both polymers, as shown in Table IV.

From these data it can be inferred that for polymer **I** a change exists only when the doping process lasts 5 h. Saturation of the system with SbF₅ may account for this behavior. On the other hand, an important increase of the T_g after 3 h of doping is observed for polymer **II**, which is even higher after 5 h, corroborating the existence of the crosslinking proposed for this polymer. With an excess of doping agent, the chains would increase the degree of crosslinking, increasing the T_g owing to the lower freedom of movement of the chains, which makes the accommodation to become slower and more difficult, leading to a decrease of the conductivity.

CONCLUSIONS

Iodine is a better doping agent than SbF₅ for both polymers, due to its higher capacity of coordinating to Se. Higher conductivity is obtained for polymer **II**, irrespective of the type of doping, due to the high amount of Se in the structure and to a lower steric hindrance to form the charge-transfer

complex. Also, from the T_g values found, crosslinking of the polymeric chains after the doping with SbF_5 has been corroborated.

Although it is possible to increase the conductivity of polymer **II**, this only reaches the semiconductor quality, because of the carbonyl group present in its structure.

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