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Synthesis and Characterization of Poly[bis(3-aminophenyl) diselenide] and Poly[bis(3-aminophenyl) diselenide-co-aniline]

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Summary

Bis(m-aminophenyl)diselenide was synthesized by diazotation of m-nitroaniline followed by incorporation of potassium selenium cyanate, and the reduction of the nitro groups by addition of tin and concentrated HCl. This dihydrochloride monomer was polymerised using ammonium persulphate in 0.25 M HCl as oxidizing agent. Copolymers of aniline with bis(m-aminophenyl)diselenide were prepared by oxidation of diselenide and aniline mixtures, at several mole ratios of aniline in the feed (f_1), with the same oxidizing agent. In the all the range of polymers analysed there are more diselenide comonomer units than aniline units. The polymer and copolymers were characterized by FTIR, elemental analysis, thermal stability and electrical conductivity, showing a high thermal stability, with a weight loss of 10% at 400 °C and there is an important effect of groups diselenide on the electrical properties, because conductivities are highly modified when the substitution is in m-position in the aniline ring. Therefore, it is necessary to add a high mole ratio of aniline in the feed to obtain copolymers with conductivities within the semi-conduction range.

Introduction

Polyaniline (Pani) is a conducting polymer, which can be easily prepared in doped state and has a very good stability [1-7]. In the literature there are many examples reported about the use of electrodes modified by derivatives polyaniline[8-11]. The homopolymer, Pani, have electrical and redox properties make it useful in electronic devices, such as diodes and transistors [12-14], and specially in electrodes for electrocatalytic reactions [15] and rechargeable batteries [16-20]. The batteries require materials with redox properties that could difuse ions into materials. The conductivity of those materials can be elecrical and/or ionic [21]. On the other hand, dicalcogenide nanotube has been reported [22] and a variety of small organodisulfides molecules like RSSR (R= phenyl, methyl, difluorophenyl), have been used as cathode in batteries. Furthermore, lithium batteries using these materials have reached energy density values up to 140 Whkg^{-1} [23-26]. A different approach has been described by Naoi *et al.* [26,27]. They propose to use a material with polymer chains interconnected by S-S bonds, because in that case, the cleavage and recombination of S-S bonds is expected to be easy. This is a good way for potential rechargeable batteries because it is possible to have electrodes with supported polymers with S-S and Se-Se bonds. Those polymers might have high charge density by area unit, such as those of very small molecules. Having this aim in mind poly[bis(2-aminophenyl) diselenide] and poly[bis(2-aminophenyl) disulfide] have been chemically synthesized by us, but the products show poor electrical conductivity [28,29]. Thus, in the present work, we report the chemical synthesis and characterization of poly[bis(3-aminophenyl) diselenide] and copolymers between aniline and bis(3-aminophenyl)diselenide which have the Se-Se bridge in *meta*-position in the aniline ring, to compare the electrical conductivity of these products with those previously reported with the Se-Se substitution in *o*-position. Thermal stability of the homo- and copolymers is also reported.

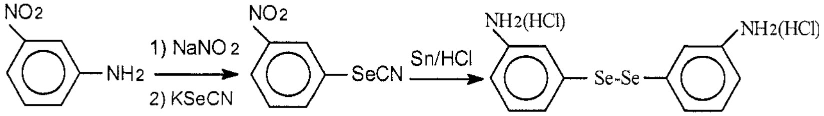
EXPERIMENTAL

C, H, N elemental analysis was performed on a Fisons Elemental-Analyzer EA-1108. FTIR spectra were obtained from KBr pellets and recorded in a Perkin Elmer 1310 spectrophotometer. The amount (weight %) of total chloride in the polymer was determined by the ASTM standard method [30] and the amount (weight %) of selenium was established by the following procedure: 50-60 mg of the sample was treated with 5 mL of *supra*pure concentrated HNO_3 and 1 mL of *supra*pure concentrated HCl and maintained during 12 h at room temperature in a closed 50 mL flask. Later, the flask was placed in a water bath at 90 °C (± 1°C) during 1 hour, cooled at room temperature and then added 4 mL of bidistilled water and filtered, if necessary. Finally, Se% was measured by atomic absorption using the hydride generation method. Conductivity measurements were carried out on pellets, using the four probe method in a Elchema CM-508 conductimeter. Pellets were obtained by pressing the samples at about 24,000 Psi. Thermograms were recorded under nitrogen atmosphere, at a 12°C min^{-1} rate.

Potassium selenocyanate and 3-nitroaniline were obtained from Aldrich. The latter was re-crystallized from ethanol/acetone (2 + 0.5, v/v) and charcoal, and potassium selenocyanate was used without previous purification.

Monomer synthesis

The monomer bis(3-aminophenyl) diselenide dihydrochloride was synthesized according to Pyman's modified method [31], in two steps as shown in scheme 1:



Scheme 1: two steps in synthesis of monomers

In an ice bath, 20 g of 3-nitroaniline were dissolved in 110 mL of water containing 15 mL of 37% HCl. Then, 35 g of ice and 11.9 g of $NaNO_2$ were added slackly under stirring. The mixture was speed filtered using a Buchner funnel immersed in the ice bath and 29 g of sodium acetate were added to the filtered, under stirring. Then, 20.9 g of potassium selenocyanate dissolved in the minimum amount of water were added. The solution was rested for 2 h. Ethylic ether was added and the water removed by decantation. The ether-phase was filtered, dried with Na_2SO_4 and the solvent (ether) removed by distillation. It was obtained 10.2 g of 3-nitro phenyl selenocyanate (yield 31%). The red compound was dissolved in 150 mL of hot ethanol and 10.8 g of tin and 136 mL of 32 % HCl were added slowly (15 min) to the boiling reaction mixture. The mixture was refluxed during 1.5 h and then 80 mL ethanol removed at reduced pressure, generating a green-yellow solid at room temperature. If not solid is obtained, 6.5 g of tin, 60 mL of ethanol and 50 mL of 32 % HCl are added and the mixture refluxed during 1 hour. The solvent is then totally removed in a rota-vapour (bath temperature less than 60 °C), and water added on the green-yellow solid up to 400 ml, then filtered and 20 mL of water and 25 mL of 3M NaOH were added to the yellow solid and filtered again. The filtered was acidified (pH=0) dropping 14 mL of 5M HCl under stirring. This acidic solution was stored one day, and filtered. The yellow-orange solid was vacuum dried during 1 day at 50 °C. It was obtained 3.7 g (Yield 40.0%). Melting point 184-185 °C.

The most representative FTIR bands associated to the monomer bis(3-aminophenyl) diselenide dihydrochloride were (cm^{-1}): 3456 (N-H stretching); 1581 (C=C stretching); 1468 (aromatic ring stretching); 188 (Se-Se-C bending); 282 (Se-Se stretching) [32]. ^1H-NMR (DMSO-D_6) signals were (ppm): 7.64 (s 1H); 7.58 (d1H); 7.40 (t 1H); 7.22 (d 1H); 4.7 (wide NH, H_2O). Elemental analysis: theoretic (experimental); C=34.7% (34.2%); H= 3.40% (3.11%); N=6.7% (6.51%); Se=38.05 %(35.3%); Cl = 17.1% (19.0%).

Homopolymer (diSe) synthesis

0.305 g (0.74 mmol) of dusted monomer were dissolved in 120 mL of 0.25 M HCl and 0.34 g (1.49 mmol) of ammonium persulphate in 14 mL of 0.25 M HCl was added under stirring at 63-65 °C. The reaction mixture was maintained under stirring at this temperature for 170 minutes, and then, filtered and washed with hot 0.5 M HCl. The product was vacuum dried at 60 °C during 2 days and the yield was 42.9%.

Copolymers synthesis

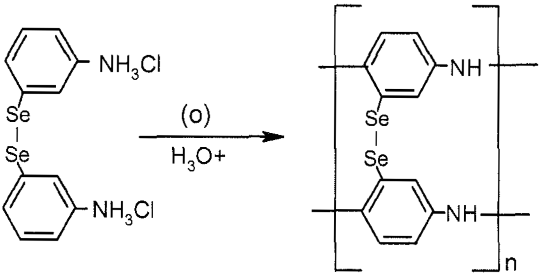
The copolymers of bis(3-aminophenyl)diselenide and aniline were prepared by chemical oxidation of aniline and the diselenide comonomer at several molar ratios of aniline in the feed (f_1). The procedure was as follows: a bis(3-aminophenyl)diselenide dihydrochloride / aniline solution (f_1=1:1) was prepared dissolving 0.35 g (0.84 mmol) of dusted diselenide comonomer and 0.079 g (0.85 mmol) of aniline in 138 mL of 0.25 M HCl and heated to 63-65 °C in an oil bath. Then, 0.386 g (1.69 mmol) of ammonium persulphate in 16 mL of 0.25 M HCl were added to the comonomers solution under constant stirring. The solution was stirred and maintained at 63-65 °C during 170 min and then filtered and washed with hot 0.5 M HCl. The copolymers were vacuum dried at 60 °C during 2 days.

In all the synthesis reported here the mol ratio diselenide comonomer / ammoniunm persulphate was 1 / 2.

With the aim to compare these results, aniline homopolymer (Pani) was also synthesized under identical conditions to that of poly[bis(3-aminophenyl) diselenide], but using 1M HCl.

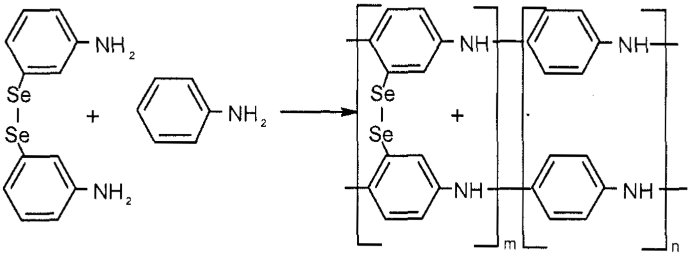
RESULTS AND DISCUSSION

Poly[bis(3-aminophenyl)diselenide] was synthesized from the monomer in 0.25 M HCl and ammoniun persulphate according to scheme 2:



Scheme 2: Synthesis of homopolymer

Copolymers were synthesized by an analogue route, but at several mol ratios of aniline in the feed, according to scheme 3:



Scheme 3: Synthesis of copolymers

Copolymers composition was determined by elemental analysis, considering the Carbon and Selenium atom %. Figure 1 shows mol ratios of bis(*m*-aminophenyl)diselenide dihydrochloride / aniline in the feed (f_1) *versus* copolymers composition (F_1), defined as mol ratio of diselenide / aniline units in the copolymers.

For f_1 values in the range of 2.0 to 0.35, copolymer composition is practically constant. If aniline quantity is increased in the feed (f_1=0.17 and f_1= 0.10), copolymer composition is similar ($F_1=0.23$ and $F_1=0.25$, respectively). In all copolymers the mole ratio diselenide comonomer / aniline (F_1) is higher than diselenide comonomer ratio in the feed (f_1). Nevertheless, if f1 is higher than 0.17, F_1 values are higher than f_1. These results show that diselenide comonomer reactivity is greater than that of aniline in all the f_1 range.

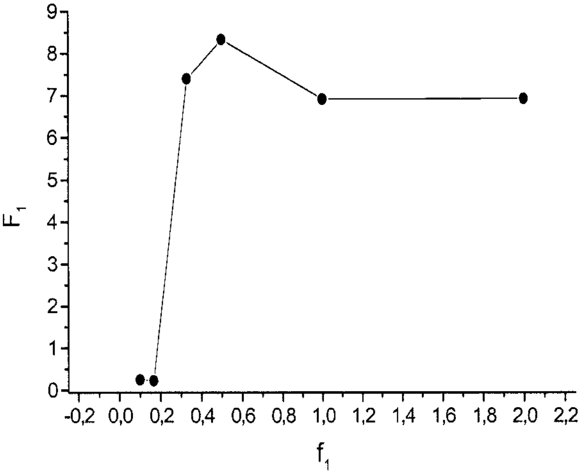


Figure 1: Mole ratio of diselenide comonomer / aniline in the feed (f_1) *vs* copolymer composition (F_1)

Table 1: Polymers and copolymers doping level and electrical conductivity

polymer (F_1)	doping level Cl^-/N	electrical conductivity σ ($S\cdot cm^{-1}$)
diSe	0.64	$1.9\cdot10^{-10}$
(8.33)	0.75	$3.6\cdot10^{-10}$
(7.40)	0.72	$2.8\cdot10^{-10}$
(6.93)	0.81	$3.6\cdot10^{-10}$
(6.92)	0.82	$1.5\cdot10^{-10}$
(0.23)	0.65	$4.1\cdot10^{-7}$
(0.25)	0.61	$3.9\cdot10^{-7}$
Pani	0.45	$1.7\cdot10^{-3}$

Table 1 shows that all these polymers have a doping level higher than that of Pani. The four copolymers of higher composition in diselenide units (F_1=8.33, 7.40, 6.93 and 6.92) have a doping level higher than the copolymers of lower composition (F_1=

0.25 and F_I= 0.23) indicating that protonation in the nitrogen atom of diselenide units is more favourable with respect to aniline units.

The electrical conductivity of homo- (diSe) and copolymers from F_I=6.93 to F_I= 7.40 are in the same order of magnitude (app. 10^{-10} Scm^{-1}), but in copolymers with higher aniline units (F_I=0.23 and F_I= 0.25), electrical conductivity increases. The electrical conductivity of copolymers is much lower than Pani ($1.7 \cdot 10^{-3}$ Scm^{-1}). We believe that increasing the copolymer composition in aniline units (F_I < 0.25), the electrical conductivity would significantly increase. We have previously reported analogous polymers with Se-Se and S-S bonds in *orto*-position [28,29]. When dichalcogen bond is in *orto*-position, the chloride and bisulphate ions doping level are near 0.50 and the electrical conductivities are in the range of 10^{-9} Scm^{-1}. Therefore, the Se-Se bond of diselenide units in *o*- or *m*-positions does not favour the conductivity, and the doping level increase is not necessarily shown in an electrical conductivity increase.

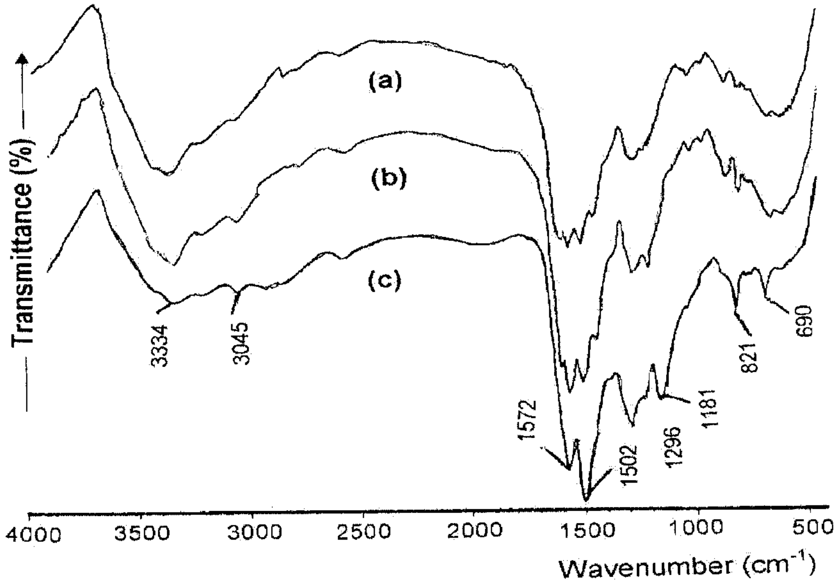


Figure 2: FT-IR spectra of: (a) diSe; (b) copolymer (F_I=6.93); (c) copolymer (F_I=0.25)

Figure 2 shows FTIR spectra of homo- and copolymers with different composition. The characteristic band at 1611 cm^{-1} arises mainly from both C=N and C=C quinoid diimine unit stretching, while the band near 1513 cm^{-1} is attributed to the C-C aromatic ring stretching of the benzenoid diamine units [33-36].

FT-IR spectrum of diSe homopolymer is similar to FT-IR spectra of copolymers of composition F_I= 8.33, 7.40, 6.93 and 6.92. If aniline composition is increased (F_I=0.25 and F_I=0.23), the relative intensity of the bands between 1300 and 1000 cm^{-1} increases in relation to the intensity of bands between 1600-1500 cm^{-1} (see figure 2 c). McDiarmid *et al.* [37] reported that the bands between 1300-1000 cm^{-1} are associated to C-N stretching and the electrical conductivity of polymers depends on the intensity of these bands. This observation is consistent with the results here obtained, because the increase of FTIR bands intensity in this spectral region can be precisely associated to the corresponding conductivity increase of copolymers.

Figure 3 shows the homopolymer (diSe) thermal stability curve, which is similar to that obtained for all the doped copolymers synthesized in this study. Table 2 shows the temperatures of weight loss for the homo- and copolymers. It can be seen that all these polymers show high stability, which can be attributed to the diselenide units in the aniline ring. The aniline units increase in the copolymers (F_l=0.23 and F_l=0.25), producing a change in the 10 % loss weight temperature from 400 to 300°C.

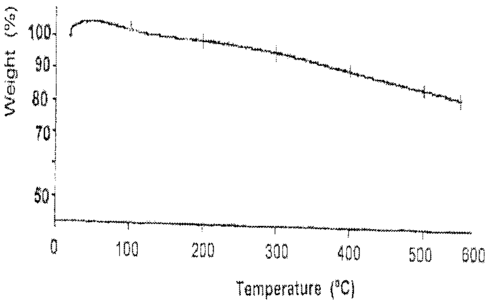


Figure 3: Thermal stability of doped homopolymer (diSe)

Table 2: Weight loss temperature of doped polymers

polymer (F_l)	10 % weight loss temperature (°C)	20 % weight loss temperature (°C)
diSe	400	550
(8.33)	400	550
(7.40)	400	520
(6.93)	400	550
(6.92)	400	550
(0.23)	300	500
(0.25)	300	500

Conclusions

Poly[bis(*m*-aminophenyl) diselenide] was synthesized from the respective monomer. Moreover, copolymers were prepared between aniline and this diselenide comonomer. The diselenide comonomer shows high reactivity with itself, and it is necessary to introduce high aniline quantity in the feed with respect to the diselenide comonomer to obtain copolymers with electrical conductivity in the semiconducting range. So, it was demonstrated that the diselenide bond in *m*-position highly affects the conductivity.

The homo- and copolymers show high thermal stability, reaching 400 °C with a 10 % loss of weight.

These polymers can be potentially studied in the area of rechargeable batteries and their electrical conductivity can be increased including aniline units in the copolymers.

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