Poly(tetrahalo-*p*-phenylenechalcogenide)s: synthesis and properties

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(Received 1 October 1991; revised 16 January 1992)

Poly(tetraiodo-*p*-phenyleneselenide), poly(tetrachloro-*p*-phenylene telluride) and poly(tetrabromo-*p*-phenylenetelluride) were synthesized from the corresponding hexahalobenzenes. The polymers were characterized by elemental analysis and i.r. spectroscopy. Conductivity measurements were carried out and showed that the polymers were semiconducting materials when doped with SbF_5.

(Keywords: poly(tetrahalo-*p*-phenylenechalcogenide)s; synthesis; properties)

Introduction

In 1972 Kawasura and Taketomi[1] described a method for obtaining poly(tetrahalo-*p*-phenylenesulphide)s with conductivities dependent on the nature of the halogen used (10^{-10}–10^{-16} Ω^{-1} cm^{-1}). Later, Sandman *et al.*[2] synthesized poly(*p*-phenylenetelluride) from *p*-diiodobenzene and sodium telluride prepared *in situ*, and found that this polymer had insulating characteristics, but behaved as a semiconductor when doped with iodide[3]. However, it is known that tetraselenafulvalenes are better conductors than the corresponding tetrathiafulvalenes[4,5]. In 1989 Díaz *et al.*[6] described the synthesis of poly(tetrahalo-*p*-phenylenmonoselenide)s and the corresponding diselenides with Cl or Br, which showed semiconductor characteristics when doped with SbF_5. These results led to the synthesis of poly(tetraiodo-*p*-phenylenselenide), and the introduction of Te instead of Se in the polymeric chain to study the behaviour of Te, which has more metallic character than Se.

Experimental

All chemicals and solvents were obtained from Aldrich, Merck and Fluka and were purified prior to use by standard procedures.

Elemental analyses were performed in a C, H Heraeus Mikrostandard analyser. Halogen determinations were carried out by the ASTM method[7,8], Se analyses by the Fredga method for insoluble organic compounds[9] and Te analyses by an electrometric method[9,10].

The i.r. spectra were obtained in KBr pellets using Perkin-Elmer model 567 and 1310 spectrophotometers; the band positions were expressed in wavenumbers[11]. The ^{13}C n.m.r. spectra were obtained using a Varian 90 MHz spectrophotometer.

The electrical conductivity measurements were performed in a Keithley 620-A electrometer with pellets made of polystyrene or teflon and connected to Cu terminals[12]. The pellets were obtained by pressing the powdered polymers at 24000 psi (165 MPa).

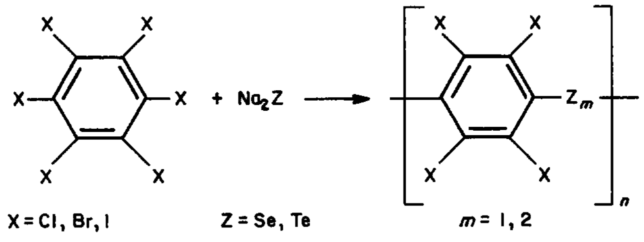
Poly(tetraiodo-*p*-phenyleneselenide) (PIPSe) was synthesized by the following procedure: hexaiodobenzene (0.2 mmol) dissolved in *N*-methyl-2-pyrrolidinone (NMP, 16 ml) was mixed with a solution of sodium selenide prepared *in situ* from Na (1 mmol) and black Se (0.5 mmol) in NMP (5 ml). The mixture was refluxed at 80°C for 2 h and then the solution precipitated in aqueous HCl with ice. The orange precipitate was filtered, washed and dried under vacuum until constant weight (yield 12%).

Sodium telluride was synthesized by the following procedure: Na (17.3 mmol for poly(tetrachloro-*p*-phenylenetelluride), PClPTe or 13.0 mmol for poly(tetrabromo-*p*-phenylenetelluride), PBrPTe) was added to Te (7.8 mmol for PClPTe or 3.9 mmol for PBrPTe) in *N*,*N*-dimethylformamide (DMF, 10 ml). The mixture was heated at 110–120°C until a yellow precipitate was produced[13]. The reaction mixture was evacuated and purged with nitrogen.

PClPTe and PBrPTe were synthesized by the following procedure: hexachlorobenzene (7.7 mmol) was dissolved in a mixture of DMF/pyridine 50/50 (for PClPTe) and hexabromobenzene (3.4 mmol) in pyridine (30 ml) mixed with DMF until dissolution (for PBrPTe). These reaction mixtures were added slowly (under nitrogen) to a solution of sodium telluride, prepared as above. The mixture was refluxed for 3 h (for PClPTe) and 2 h (for PBrPTe) at 80–90°C and then precipitated in aqueous HCl with ice. The dark precipitated polymers were filtered, washed and dried under vacuum until constant weight (yields 47% for PClPTe and 30% for PBrPTe).

Results and discussion

Polymers were obtained according to *Scheme 1*, which is the same mechanism as that described for the synthesis of poly(*p*-phenylenesulphide)[14], and characterized by i.r.



Scheme 1

0032-3861/92/112454-02

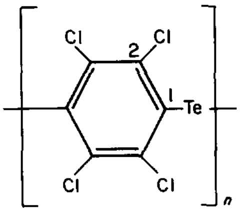
Table 1 I.r. spectra and elemental analyses of the polymers

	I.r. (cm^{-1})			C (%)		X (%)		Z (%)	
Polymer	Ar-X	C-X	C-Z	Calc.	Found	Calc.	Found	Calc.	Found
PIPSe	1255, 1245	430	590	10.9	12.7	77.1	78.0	12.0	13.6
PClPTe	1370, 1290	685	480	21.1	20.9	41.5	43.5	37.4	39.1
PBrPTe	1270, 1250	590	–	13.9	13.7	61.6	63.4	24.6	26.3

Table 2 Conductivities of polymers doped with I_2 and SbF_5

Polymer	Without doping ($\times 10^{13}\ \Omega^{-1}\ cm^{-1}$)	Doping with I_2 ($\times 10^{8}\ \Omega^{-1}\ cm^{-1}$)	Doping with SbF_5 ($\times 10^{9}\ \Omega^{-1}\ cm^{-1}$)
PIPSe	0.24	0.00062	11.0
PClPTe	4.50	7.5	5.0
PBrPTe	5.00	4.7	10.0

spectroscopy and elemental analysis. The results obtained were in agreement with the proposed structures (*Table 1*). The polymers were insoluble in all common organic solvents and only PClPTe was slightly soluble in $CHCl_3$, which was characterized by ^{13}C n.m.r. giving the following signals (δ): 127.9 (s, 4C) and 131.4 (s, 2C) ppm. These signals were in good agreement with the ^{13}C n.m.r. signals for diphenylsulphide[15]:



Conductivity measurements of the powdered polymers were obtained without doping and after doping with I_2 according to the method of Gutierrez *et al.*[16]. In order to dope the polymers with SbF_5, they were exposed to SbF_5 vapour over their condensed phase at 60°C[17]. *Table 2* summarizes the conductivity values obtained. The conductivity studies showed that the products are insulators. The conductivity values increase after doping with I_2 and SbF_5 in the semiconductor range.

In a previous paper[6], the values of the conductivities of poly(tetrachloro-*p*-phenyleneselenide) and poly(tetrabromo-*p*-phenyleneselenide) obtained were 0.2×10^{-10} and $0.61 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$, respectively. PIPSe has lower conductivity than the poly(tetrahalo-*p*-phenyleneselenide)s, probably due to the bulky iodine atoms.

Poly(tetrachloro-*p*-phenyleneselenide) and poly(tetrabromo-*p*-phenyleneselenide) doped with SbF_5 have conductivities in the range of $10^{-6}\ \Omega^{-1}\ cm^{-1}$. However lower conductivity values were obtained for the corresponding telluride polymers[6].

These chalcogenides were synthesized in order to complete the series of poly(tetrahalo-*p*-phenylenechalcogenide)s. However, the synthesis of poly(tetraiodo-*p*-phenylenetelluride) was not achieved.

Acknowledgement

The authors acknowledge financial support from the Fondo Nacional de Investigación Científica y Tecnológica (FONDECYT).

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