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Polymerization of Diphenyl Disulfide by the S–S Bond Cleavage with a Lewis Acid: A Novel Preparation Route to Poly(*p*-phenylene sulfide)

Eishun Tsuchida,* Kimihisa Yamamoto, Hiroyuki Nishide, Shu Yoshida, and Mitsutoshi Jikei

Department of Polymer Chemistry, Waseda University, Tokyo 169.

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ABSTRACT: Poly(*p*-phenylene sulfide) (PPS) is efficiently and conveniently produced by a cationic and oxidative polymerization. Diphenyl disulfide is allowed to react with a Lewis acid such as antimony pentachloride at room temperature and is polymerized to PPS. The polymer is isolated as a white powder, whose 1,4 structure is confirmed by IR. Phenylbis(phenylthio)sulfonium ion acts as an active species, which is formed by oxidation of the S–S bond of diphenyl disulfide with the Lewis acid, and is electrophilically substituted on the phenyl ring. The polymerization mechanism is discussed and compared to a model reaction using dimethyl disulfide.

Introduction

Poly(*p*-phenylene sulfide) (PPS) deserves much attention as an engineering plastic or conductive polymer of excellent performance.[1,2] Lenz and co-workers reported that PPS is synthesized by the polycondensation of *p*-halothiophenoxy alkali-metal salts at high temperature.[3-6] PPS has been commercially produced with the polycondensation of *p*-dichlorobenzene and sodium sulfide in *N*-methyl-2-pyrrolidone.[7,8] These polymerizations proceed under high pressure and temperature. Recently much effort was given to the study of new preparation routes of PPS. It has been reported that PPS-like polymers such as poly(thianthrylene sulfide) have been prepared by the reaction of benzene and sulfur with aluminum trichloride[9,10] and by the oxidation of thiophenol with aluminum trichloride and thionyl chloride[11,12] or with concentrated sulfuric acid.[13] However, these polymers showed no melting point, and these preparations resulted in formation of cross-linked and branched structures during the polymerization. Few papers have reported that PPS was prepared at room temperature and through a polymerization of diphenyl disulfide as a starting material. We preliminarily reported that diphenyl disulfide reacts with a Lewis acid in dichloromethane and is easily polymerized through cleavage of its S–S bond to yield a linear PPS at room temperature and atmospheric pressure.[14-16] In this paper the structure of the formed polymer is described and the polymerization mechanism is discussed and compared to the reactions of nonpolymerizable dimethyl disulfide as a model compound.

Experimental Section

Materials. Diphenyl disulfide was purified by recrystallization from ethanol and drying in vacuo for 1 day at 30 °C and replace white needles, mp 59 °C. Dimethyl disulfide was also purified by distillation. A reagent-grade antimony pentachloride stored in a sealed ampule was used without further purification under dry nitrogen atmosphere. Solvents dichloromethane, nitromethane, nitrobenzene, acetonitrile, and *N*-methylpyrrolidone were purified by distillation in the usual manner.

Polymerization. A total of 0.01 mol of diphenyl disulfide was dissolved in 50 mL of dichloromethane and was rapidly poured into the dichloromethane solution containing 0.02 mol of $SbCl_5$ under dry nitrogen atmosphere. The color of solution turned to deep black. The mixture was stirred at 20 °C under nitrogen atmosphere for 20 h. Grayish powder separated out and the deep black of the solution faded during the time passage. The reaction mixture was poured into 500 mL of 5 wt % hydrochloric methanol. Precipitated white powder was collected and washed with methanol and 0.1 N potassium hydroxide aqueous solution several times. The product was further washed with hot water for 12 h and was completely dissolved in hot *N*-methyl-2-pyrrolidone and reprecipitated by methanol. After filtration and washing with methanol, the product was dried in vacuo at 70 °C for 1 day to yield >80% of a white powder.

Isolation of Methylbis(methylthio)sulfonium Antimony Hexachloride (1). A solution of antimony pentachloride (0.5 mol) in dry dichloromethane (50 mL) was poured into a solution of dimethyl disulfide (0.5 mol) at 0 °C. The mixture changed to a yellowish slurry with time. To complete the precipitate formation, dry ether (100 mL) was added. The precipitate was filtered off in dry atmosphere and was recrystallized

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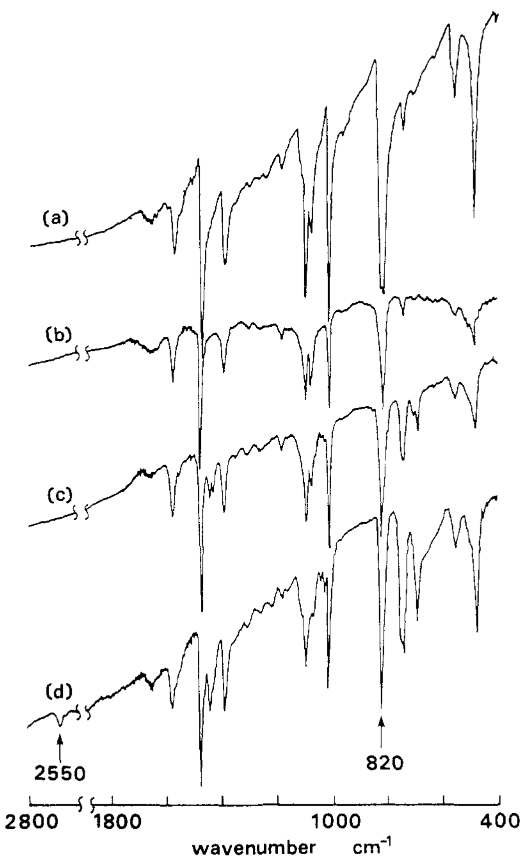


Figure 1. IR spectra of chemically available PPS (noncuring type) (a), cyclic hexamer (b), the obtained polymer (c), and the reduced product of the dichloromethane-soluble part of the obtained polymer (d).

in dichloromethane. A slightly yellowish microcrystalline produce was obtained with analytical purity and 91% yield.

Reaction Procedure of Methylbis(methylthio)sulfonium Antimony Hexachloride (1) with Diphenyl Sulfide. Methylbis(methylthio)sulfonium antimony hexachloride (1; 0.1 mol) and diphenyl sulfide (0.1 mol) were dissolved in 50 mL of dichloromethane. After 5 h, 100 mL of potassium hydroxide aqueous solution (10 wt %) was added to the reaction mixture. The soluble reaction products in the dichloromethane layer were separated by column chromatography (*n*-hexane, silica gel).

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a 90-MHz JEOL FX-100. ^{1}H and ^{13}C NMR spectra of disulfides with $SbCl_5$ were measured in double-compartment cell probes of which the internal and standard sample was CD_3OD/tetramethylsilane. IR spectroscopy was carried out with a JAS IR-810 spectrometer. Mass spectra were measured using an ionization energy of 20 eV on a JMS-DX300 spectrometer. Gas chromatography was carried out by using a SE-30 (polysiloxane) column with a heating rate of 10 °C/min; the product yield was determined with a thermal conductivity detector. Melting points were determined on the hot stage of a microscope with a heating rate of 2 °C/min. DSC was measured with a SEIKO SSC/580 thermal analyzer with a heating rate of 20 °C/min. The molecular weights of the *N*-methylpyrrolidone-soluble products were measured with gel permeation chromatography standardized with polystyrene.

Spectroscopic Data. Poly(*p*-phenylene sulfide). Anal. Calcd for $C_6H_4S_1$: C, 66.67; H, 3.7; S, 29.63. Found: C, 66.51; H, 3.85; S, 29.55. IR (KBr, cm^{-1}): 3025 (ν_{C-H}) (Figure 1). MS: *m/e*[17] 756, 648, 540, 434, 326, 218, 110. This suggests that the monomer unit of mol wt 109 exists. The weight-average molecular weight of the *N*-methylpyrrolidone-soluble part of the polymer is 1500. The X-ray diffraction pattern is $2\theta = 19, 21$.

Poly(3-methyl-1,4-phenylene sulfide). Anal. Calcd for $C_7H_6S_1$: C, 68.85; H, 4.92; S, 26.23. Found: C, 68.51; H, 4.73; S, 25.98. IR (KBr, cm^{-1}): 2950, 2875 (ν_{C-H}); 1575, 1540, 1480 ($\nu_{C=C}$); 860, 820 (δ_{C-H}). ^{13}C NMR ($CDCl_3$, ppm): 20.5 (methyl C); 127.3, 130.1, 131.2, 134.0, 136.5, 141.1 (phenyl C). ^{1}H NMR ($CDCl_3$, ppm): 2.3 (methyl 3 H); 7.1, 6.9 (phenyl 3 H). MS: *m/e* 612, 490, 168, 243, 121. The weight-average molecular weight of the *N*-methylpyrrolidone-soluble part of the polymer is 3500.

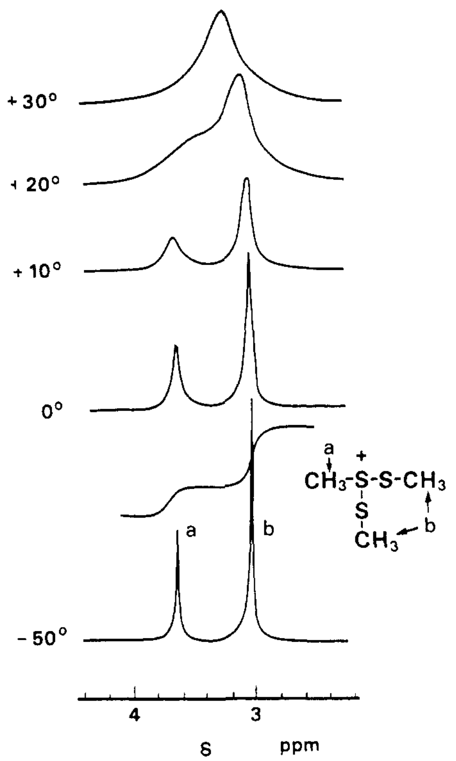


Figure 2. ^{1}H NMR spectra of a mixture of dimethyl disulfide and $SbCl_5$ in dichloromethane at different temperatures.

Methylbis(methylthio)sulfonium Antimony Hexachloride (1). Yellow needle like solid. Mp: 118–120 °C. Anal. Calcd for $C_3H_9S_3Sb_1Cl_6$: C, 7.57; H, 1.89; S, 20.22; Sb, 25.60; Cl, 44.70. Found: C, 7.81; H, 1.98; S, 19.86; Sb, 25.90; Cl, 44.69. IR (KBr, cm^{-1}): 3020, 2925, 2850 (ν_{C-H}); 1415, 1310, 1115, 1040, 995. ^{1}H NMR (CH_2Cl_2, −20 °C, ppm): 3.0, 3.6 (Figure 2). UV (CH_2Cl_2, nm): λ_{max} 272.

4-(Methylthio)phenyl Phenyl Sulfide (2a). ^{1}H NMR ($CDCl_3$, ppm): 2.43, 7.17, 7.23. ^{13}C NMR ($CDCl_3$, ppm): 15.9, 126.7, 127.5, 129.1, 130.4, 132.2, 132.5, 136.5, 138.1. IR (KBr, cm^{-1}): 3060, 2920, 2850 (ν_{C-H}); 1475, 1580 ($\nu_{C=C}$); 820, 710 (δ_{C-H}). MS: *m/e* 232, 217, 184, 124, 108. TLC: R_f (*n*-hexane) 0.25.

Bis[4-(methylthio)phenyl] Sulfide (2b). ^{1}H NMR ($CDCl_3$, ppm): 2.44, 7.18, 7.20, 7.24. ^{13}C NMR ($CDCl_3$, ppm): 16.2, 128.0, 131.6, 132.9, 138.1. IR (KBr, cm^{-1}): 3050, 2920, 2850 (ν_{C-H}); 1480 ($\nu_{C=C}$); 820 (δ_{C-H}). MS: *m/e* 278, 263, 231, 216, 184. TLC: R_f (*n*-hexane) 0.19.

4-(Methylthio)phenyl Phenyl Ether (3a). ^{1}H NMR ($CDCl_3$, ppm): 2.45, 6.98, 7.20, 7.24, 7.31. ^{13}C NMR ($CDCl_3$, ppm): 17.4, 118.7, 119.6, 123.2, 129.5, 129.7, 132.4, 155.5, 157.3. IR (KBr, cm^{-1}): 3040, 2920, 2850 (ν_{C-H}); 1580, 1485 ($\nu_{C=C}$); 825, 760 (δ_{C-H}). MS: *m/e* 216, 201, 139. TLC: R_f (*n*-hexane) 0.20.

Bis[4-(methylthio)phenyl] Phenyl Ether (3b). ^{1}H NMR ($CDCl_3$, ppm): 2.46, 7.00, 7.20, 7.30. ^{13}C NMR ($CDCl_3$, ppm): 17.3, 119.4, 129.6, 132.6, 155.5. IR (KBr, cm^{-1}): 3000, 2925, 2850 (ν_{C-H}); 1490 ($\nu_{C=C}$); 820 (δ_{C-H}). MS: *m/e* 262, 247, 232, 200, 168. TLC: R_f (*n*-hexane) 0.09.

4-(Methylthio)phenyl Phenyl Disulfide (4). MS: *m/e* 264, 217, 184, 155, 109. TLC: R_f (*n*-hexane) 0.48.

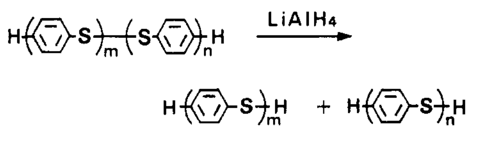
Methyl Phenyl Disulfide (5). IR (KBr, cm^{-1}): 3050, 2920 (ν_{C-H}); 1580, 1475 ($\nu_{C=C}$); 740, 690 (δ_{C-H}). MS: *m/e* 156, 141, 109. TLC: R_f (*n*-hexane) 0.31.

4-(Methylthio)phenyl Methyl Disulfide (6). MS: *m/e* 202, 155, 109.

Results and Discussion

Structure of the Formed Polymer. Diphenyl disulfide is allowed to react with $SbCl_5$ in dichloromethane for 20 h at room temperature. The polymer

Scheme I



is isolated in over 80% yield as a white powder having an empirical formula $C_6H_4S_1$. The polymer is completely soluble in hot *N*-methyl-2-pyrrolidone but not in any common solvents. The structure of the 1,4-phenylene unit is confirmed by IR (Figure 1c). The absorption attributed to C–H out of plane deformation vibration of 1,4-disubstituted benzene at 820 cm^{-1} indicates a linear or 1,4-conjugated phenylene sulfide. This agrees with that of a reference PPS prepared by the polycondensation of *p*-halothiophenoxy alkali-metal salt.[5] Lack of an absorption at ca. 850 cm^{-1}, associated with an isolated ring hydrogen, excludes any significant amount of branching and cross-linking. This IR spectrum is also consistent with that of a commercially available PPS (Figure 1a). A weak absorption of a C–H out of plane vibration of monosubstituted phenyl rings appears at 680 cm^{-1}, which indicates at least a fraction of relatively small molecular weights of PPS. As a reference (Figure 1d)[18] the cyclic hexamer of phenylene sulfide shows no IR absorption of a C–H out of plane vibration as in the monosubstituted phenyl rings. IR spectroscopy in the 1000–1150-cm^{-1} region reveals significant and diagnostic differences between the cyclic and the linear PPS.[19] This means that the formed polymer is principally linear. This region of the spectrum also shows that the formed polymer does not contain detectable sulfoxide or sulfone structures. No thianthrene structures are detected by IR.[20]

In order to address the existence of the S–S bond in the polymer, the soluble PPS was reduced by lithium aluminum hydride in dichloromethane. The reduction product shows the new absorption at 2550 cm^{-1} (Figure 1d), which is ascribed to the stretching vibration of the mercaptan group. This indicates that the prepared polymer contains a disulfide bond in the polymer chain. The melting point of the reaction product was reduced. The S–S bond is cleaved to SH by the reduction (Scheme I). It is considered on the basis of the polymerization mechanism described below that a polymer chain contains a S–S bond.

The X-ray diffraction pattern was similar to that of commercial PPS Ryton. The molecular weight of the cool *N*-methylpyrrolidone-soluble part of the prepared PPS (ca. 20 wt %) was about 10^3, which was estimated by the relationship between the molecular weight and the melting point of PPS.[21]

Polymerization Behavior. The polymerization of diphenyl disulfide with $SbCl_5$ was carried out in various solvents (Table I). The yield is higher in low-basicity solvents such as dichloromethane and nitromethane. But the polymerization does not proceed in basic or high donor number solvents such as dimethyl sulfoxide and acetonitrile. This result suggests that this polymerization proceeds via a cationic mechanism. The basic solvents nucleophilically react with cationic species, or deactivate the ability of $SbCl_5$, and suppress the polymerization. The polymer yield was not affected by the presence of added oxygen, which often deactivates a radical species. Polymerization of various sulfides with $SbCl_5$ is listed in Table II. Diphenyl disulfide yields PPS. Similarly bis(3-methylphenyl) disulfide is polymerized to yield poly(3-methyl-1,4-phenylene sulfide) whose molecular weight was ca. 5 × 10^3. However, diphenyl disulfide substituted at the para position with, for instance, a *tert*-butyl or halide group does not polymerize. Experiments using diphenyl sulfide and diphenyl sulfoxide do not give any polymer. These results suggest that the S–S bond of diphenyl disulfide, of which the bond energy is smaller than those of C–S or C–SO bonds,[22] reacts with $SbCl_5$ to form a C–S–C bond at the para position.

Table I
Polymerization[a] of Diphenyl Disulfide with $SbCl_5$ in Various Unreactive Solvents

solvent	donor no.	PPS yield, wt %	mp, °C
CH_2Cl_2		89	185
$(CHCl_2)_2$		67	140
C_6H_{14}		77	113
CH_3NO_2	2.7	89	191
$C_6H_5NO_2$	4.4	26	194
CH_3CN	14.1	0	
DMF[b]	26.1	0	
DMSO[c]	29.8	0	

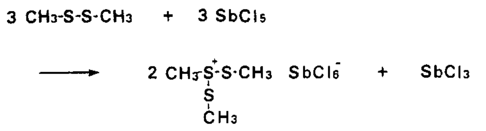
[a] 20 h at 20 °C. [b] *N,N*-Dimethylformamide. [c] Dimethyl sulfoxide.

Table II
Polymerization of Various Disulfides with $SbCl_5$

sulfide	PPS yield, wt %
diphenyl disulfide	89
bis(3-methylphenyl) disulfide	63
diphenyl sulfide	0
diphenyl sulfoxide	0
bis(4-bromophenyl) disulfide	0
bis(4-*tert*-butylphenyl) disulfide	0

Mechanism of the Polymerization. We studied the intermediate of this polymerization. Since diphenyl disulfide is rapidly polymerized to PPS, an intermediate for the polymerization was proposed by using nonpolymerizable dimethyl disulfide as a model compound.

For the reaction of dimethyl disulfide with $SbCl_5$, methylbis(methylthio)sulfonium antimony hexachloride (1) was isolated in dry atmosphere and was identified by spectroscopic data (see the Experimental Section). After the reaction, $SbCl_3$[23] was isolated as a reduction product of $SbCl_5$ from the reaction mixture. It is reasonable that methylbis(methylthio)sulfonium ion is formed by the oxidative reaction of disulfide with $SbCl_5$, as illustrated in eq 1.[24] This supports the idea that $SbCl_5$ does not act as a catalyst but as an oxidizing agent of the disulfides.



$$3\ CH_3\text{-}S\text{-}S\text{-}CH_3 + 3\ SbCl_5 \longrightarrow 2\ CH_3\text{-}\underset{\underset{CH_3}{|}}{\overset{+}{S}}\text{-}S\text{-}CH_3\ SbCl_6^- + SbCl_3 \quad (1)$$

1

^1H NMR spectra of dimethyl disulfide (0.1 mol) and $SbCl_5$ (0.1 mol) in dichloromethane at various temperatures are shown in Figure 2. The NMR spectrum at −50 °C shows two main signals at 3.0 and 3.6 ppm[25] with an intensity ratio of 1:2. The singlet peak is observed only at relatively high temperature, whose chemical shift depends on the temperature. This NMR spectral change is reversible with temperature. Thus, it is postulated that an exchange reaction between the methylbis(methylthio)sulfonium ion and dimethyl disulfide also occurs very rapidly (eq 2).[26]

Figure 3 shows the effect of the reaction temperature on the polymer yield. PPS is produced at 20–30 °C from dichloromethane solution in high yield and with relatively high molecular weight. However, the polymer yield

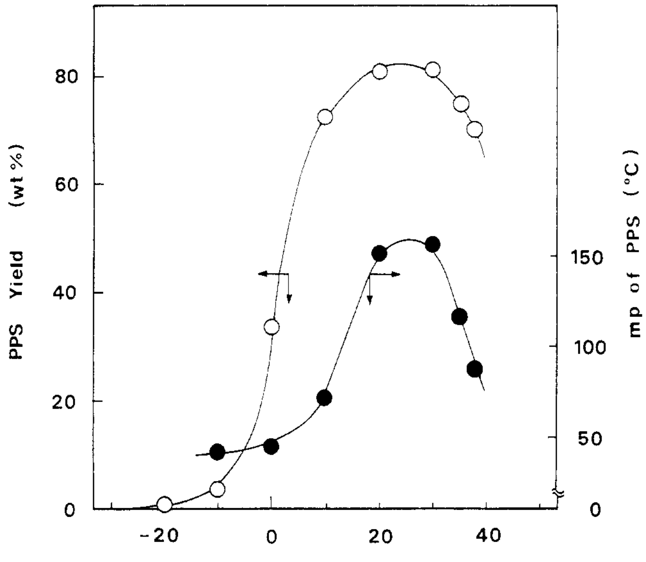
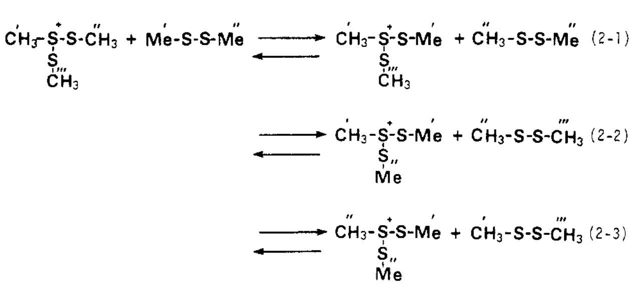


Figure 3. Effect of temperature on the polymerization of diphenyl disulfide with $SbCl_5$.



decreases above 30 °C. A similar temperature dependence of the PPS yield is observed in other solvents such as nitromethane and 1,1′,2,2′-tetrachloroethane. At the higher temperatures cationic species and/or $SbCl_5$ are assumed to be unstable. Polymer yield is also suppressed under 20 °C. Even at −20 °C the color of the mixture turned black as it did in the higher temperature. The ^{13}C NMR spectrum (Figure 4) of the reaction mixture at −40 °C shows four main signals, which are not assigned to diphenyl disulfide and the other sulfides[27] but to phenylbis(phenylthio)sulfonium cation (X).[28] The ESR signal ascribed to a radical species was not detected in the reaction mixture. These results suggest that phenylbis(phenylthio)sulfonium ion (X) is formed and is stable at low temperature.

The reaction mixture was stored at −50 °C for several hours, but the intermediate could not be isolated as a pure salt probably because the intermediate of diphenyl disulfide was more unstable than the methyl one. The mixture of diphenyl disulfide and the sulfonium cation (X)[29] was redissolved in dichloromethane solution containing an excess of diphenyl disulfide at −50 °C and allowed to stand for 20 h at room temperature in the absence of the additional $SbCl_5$. The black of the reaction mixture faded with time. The products of this reaction were trimer (Y), and monomer (Scheme II).[30] When an excess of diphenyl disulfide was added in the reaction mixture, only trimer (Y) was formed. An equimolar amount of addition of $SbCl_5$ to the dichloromethane solution of the isolated trimer yielded PPS. These results indicated that this polymerization proceeds through not a chain reaction but a stepwise one. Thus formed polymer or oligomer rereacts with $SbCl_5$ to form the cationic intermediate and to yield PPS.

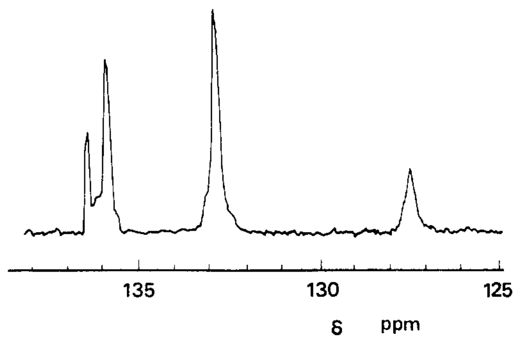


Figure 4. ^{13}C NMR spectra of a mixture of diphenyl disulfide and $SbCl_5$ in dichloromethane at −40 °C.

Scheme II

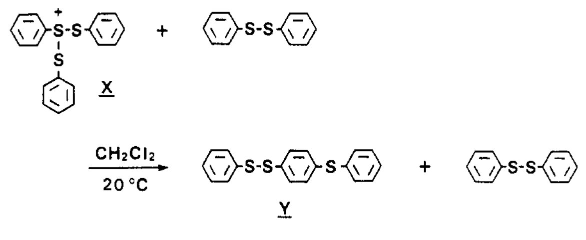
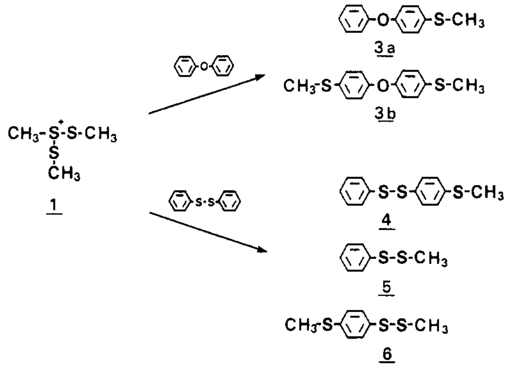


Table III
Electrophilic Reaction of Methybis(methylthio)sulfonium Antimony Hexachloride with Diphenyl Disulfide, Diphenyl Sulfide, and Diphenyl Ether

reactant	product	yield,[a] %
diphenyl sulfide	**2a**	42
	2b	51
diphenyl ether	**3a**	51
	3b	73
diphenyl disulfide	**4**	4
	5	61

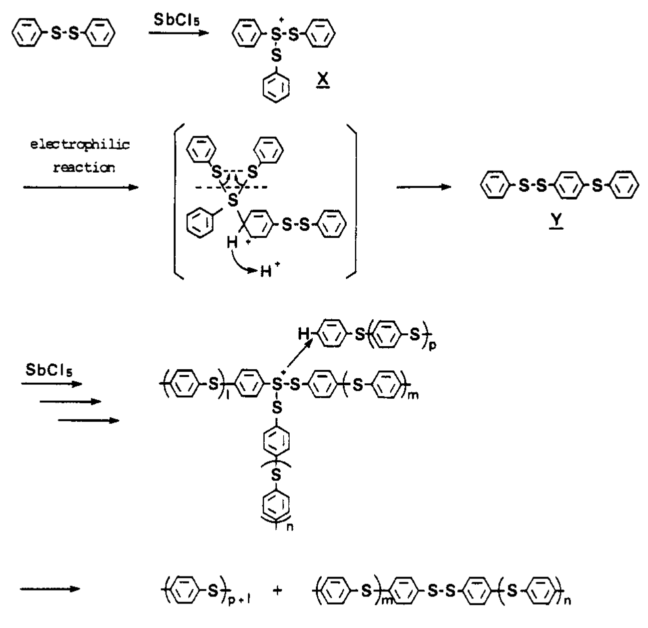
[a] Yield = [product in mol/L]/[reactant in mol/L] × 100.

Scheme III

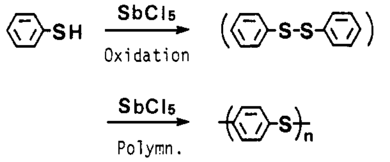


The reaction was studied by the control experiment using phenyl ether and phenyl sulfide. Methylbis(methylthio)sulfonium ion (1) as a model of phenylbis(phenylthio)sulfonium ion (X) is allowed to react with diphenyl disulfide, diphenyl sulfide, and diphenyl ether. The main products of the reactions are given in Table III. The reaction of the cation with diphenyl sulfide and diphenyl ether gives methylthio group(s) para-substituted compounds (**2a**,**b**, **3a**,**b**) and dimethyl disulfide in high yield (Scheme III). It is suggested that the para substitution of a methylthio group preferentially occurs by the electrophilic reaction of the sulfonium cation **1** on a phenyl ring. The acidity of the reaction mixture increased as

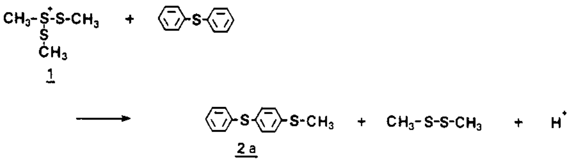
Scheme IV



Scheme V



the reaction proceeded. It is proposed that the cation reacts with the phenyl ring of the substrates to yield methylthio-substituted compounds and dimethyl disulfide accompanied by the elimination of a proton (eqs 3 and 4).



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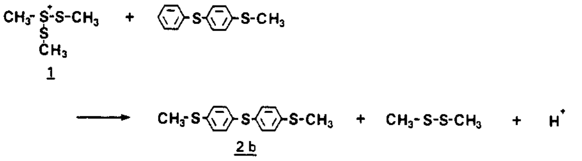

(4)

However, the reaction with diphenyl disulfide caused formation of a much larger amount of methyl phenyl disulfide (5) than 4-(methylthio)phenyl phenyl disulfide (4) (Table III). This means that the exchange reaction between the cation and disulfide (mentioned above in eq 2) occurs in the acidic atmosphere and suppresses the substitution reaction. The formation of other trace products such as (methylthio)phenyl methyl disulfide (6) was confirmed by gas mass spectroscopy; they were formed through the same exchange reaction. In this polymerization of diphenyl disulfide, once-formed 4-(phenylthio)phenyl phenyl disulfide (trimer) is electrophilically attacked by the sulfonium cation preferentially in the thiophenylene moiety.

The above-mentioned results suggest the following mechanism of this polymerization as shown in Scheme IV. Diphenyl disulfide is oxidized with $SbCl_5$ to phenylbis(phenylthio)sulfonium ion (X) quantitatively. $SbCl_5$ does not act as an initiator or a catalyst but as an oxidizing agent for the polymerization. The intermediate salt reacts electrophilically with the phenyl ring to form the trimer (Y). The S–S bond of the oligomer is similarly reoxidized to the intermediate cation. The propagation of this polymerization consists of the same electrophilic reaction of the corresponding phenylbis(phenylthio)sulfonium ion with the phenyl ring of the oligomer and gives PPS. This mechanism is not in conflict with the structure of the formed polymer containing a disulfide bond.

Polymerization of Thiophenol. When thiophenol is used as a starting material, the polymerization in the presence of 3 equiv of $SbCl_5$ also gives PPS at room temperature. Thiophenol is considered to be first oxidized to diphenyl disulfide and polymerized (Scheme V). These results support the idea that $SbCl_5$ acts as an oxidizing agent for the polymerization.

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(20) It has been reported that poly(thianthrylene sulfide) prepared by the polymerization of benzene and sulfur with aluminum trichloride at reflux is composed mainly of thianthrene units. The polymer prepared by us does not contain thianthrene units and has a linear structure. This is avoided in our preparation by conditions of room temperature.
(21) Koch, M.; Heitz, W. *Makromol. Chem.* **1983**, *184*, 779.
(22) Oae, S. In *Organic Chemistry of Sulfur*; Field, E., Ed.; Plenum: New York, 1977; Section 6.
(23) Antimony trichloride: orthorhombic, eliqquesc needle, mp 73 °C, recrystallized in carbon disulfide.
(24) A similar reaction has been proposed for the reaction mixture of dimethyl disulfide and methanesulfenyl chloride with boron trifluoride in sulfur dioxide. (a) Capozzi, G.; Lucchini, V.; Modena, G.; Rivetti, F. *J. Chem. Soc., Perkin Trans. 2* **1974**, 900. (b) Capozzi, G.; Lucchini, V.; Modena, G.; Rivetti, F. *J. Chem. Soc. Perkin Trans. 2* **1975**, 361.
(25) The chemical shifts of the methyl protons are situated at a lower magnetic field compared to dimethyl disulfide (2.5 ppm).

This means that there are two environments of the methyl protons influenced by a cationic charge in the molecule. (a) Smallcombe, S. H.; Casero, M. C. *J. Am. Chem. Soc.* **1971**, *3*, 5826. (b) Kice, J. L.; Favstritsky, N. A. *J. Am. Chem. Soc.* **1969**, *91*, 1751. (c) Perker, A. J.; Kharasch, N. *Chem. Rev.* **1959**, *59*, 583.

(26) This hypothesis is also consistent with the previously reported mechanism for acid-catalyzed exchange reactions of asymmetric disulfides.

(27) Diphenyl disulfide. ^{13}C NMR ($CDCl_3$, ppm): 128.9, 129.0, 130.7, 138.4. Diphenyl sulfide. ^{13}C NMR ($CDCl_3$, ppm): 126.9, 129.1, 131.1, 136.0. Thianthrene. ^{13}C NMR ($CDCl_3$, ppm): 127.5, 128.6, 135.5. Thiophenol. ^{13}C NMR ($CDCl_3$, ppm): 125.4, 128.9, 129.3, 130.7.

(28) The ^{13}C NMR data of the reaction mixture coincided with the previously reported data for phenylbis(phenylthio)sulfonium cation (X). The formation of even bis[(2,6-dimethylphenyl)thio]sulfonium cation, which is a sterically hindered cation in conparison with the phenyl one. Additionally, other sulfides have been reported to form the corresponding sulfonium cations. Gybin, A. S.; Smit, W. A.; Bogdanov, V. S. *Tetrahedron Lett.* **1980**, *21*, 383.

(29) We could isolate the mixture of the cation and diphenyl disulfide, from which $SbCl_5$ was completely removed through the selective extraction $SbCl_5$ with cool ether (this procedure should be carried out at low temperature). The NMR spectrum on the isolated mixture redissolved in dichloromethane indicated the existence of phenylbis(phenylthio)sulfonium cation.

(30) MS: *m/e* 217, 325. IR (KBr, cm^{-1}): 3075, 3090 (ν_{C-H}); 1445, 1480, 1580 ($\nu_{C=C}$); 825 (δ_{C-H}); 695, 745, 905, 1000, 1030, 1080, 1100, 1305, 1400.

Chiral Liquid Crystal Polymers. 10. Thermotropic Mesomorphism in Chiral Isomeric Polyesters

Emo Chiellini,* Giancarlo Galli, and Simona Carrozzino

Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56100 Pisa, Italy

Bernard Gallot

Laboratoire des Materiaux Organiques, CNRS, 69390 Vernaison, France.

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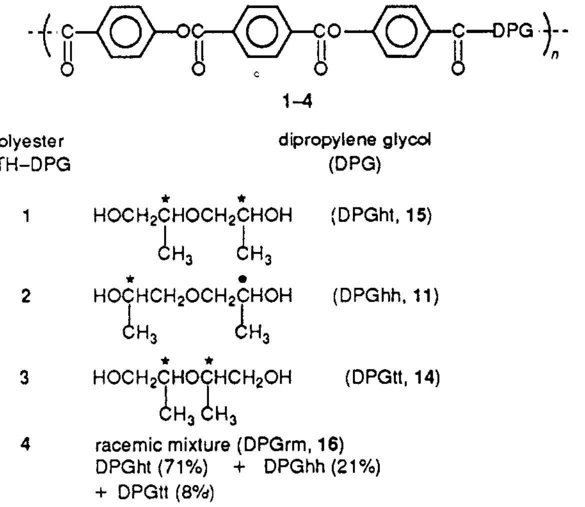
ABSTRACT: A series of four samples of chiral thermotropic polyesters 1–4 based on smectogenic 4,4′-(terephthaloyldioxy)dibenzoic (HTH) acid and the three optically active isomers of dipropylene glycol (DPG) and a commercially available mixture of the three racemic isomers was prepared. The thermotropic mesomorphism of the polymer samples was investigated with reference to the isomeric structure of the chiral spacer segment incorporated into the polyester backbone. The four polyesters display strikingly different thermal responses. The relative topology of the two methyl substituents, and hence of the two chiral centers, within the flexible segments, is effective in defining the onset, stability, and nature of the mesophases. The evolutions of the structures of the mesophases were followed as a function of temperature, and the occurrence of polymorphic sequences is proposed, which involve ordered smectic, disordered smectic, and nematic (or cholesteric) mesophases.

Introduction

Chiral liquid-crystalline polymers are attracting ever increasing attention in respect to their potential in optical and electrooptical applications, including the design and realization of both active and passive devices.[1–14]

In connection with this interest, we have been studying for a few years the structure-property correlations in series of different thermotropic liquid-crystalline polyesters comprised of chiral semiflexible segments as derived from diols and dithiols.[15,16] Depending upon the chemical and stereochemical structural features of the flexible chiral spacer and of the rigid aromatic core, a wide variety of new polymeric materials has been prepared and analyzed for their mesomorphic behavior in the melt and chiroptical properties in dilute solutions.[15,16]

In the present contribution we highlight the effect of structural isomerism in a series of polyesters, 1–4, prepared from a powerful mesogen, such as 4,4′-(terephthaloyldioxy)dibenzoic (HTH) acid, and the various dipropylene glycol (DPG) isomers. Namely, the head-to-tail (DPGht) isomer was used for sample 1, the head-to-head (DPGhh) isomer for sample 2, and the tail-to-tail (DPGtt) isomer for sample 3, in which the two chiral centers are located in the 1,4, 1,5, and 1,3 relative positions, respectively. A mixture of the three racemic isomers (DGPrm) was also used as the precursor of sample 4.



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