August, 1992] © 1992 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 65, 2029—2036 (1992) 2029

Synthesis of Soluble Poly(thio-2,6-dimethyl-1,4-phenylene) by Oxidative Polymerization of Bis(3,5-dimethylphenyl) Disulfide

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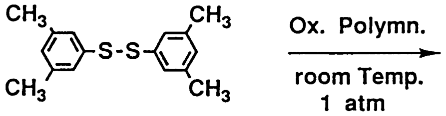
(Received March 13, 1992)

Poly(thio-2,6-dimethyl-1,4-phenylene) has been prepared by the oxidative polymerization of bis(3,5-dimethylphenyl) disulfide. The obtained polymer is amorphous and soluble in common organic solvents. The properties of the polymer are similar to those of poly(oxy-2,6-dimethyl-1,4-phenylene), rather than poly(thio-1,4-phenylene) (PPS). The polymer is obtained as a high molecular weight substance compared with other substituted or non-substituted PPS derivatives by the oxidative polymerization. The polymer containing a disulfide bond, whose structure was confirmed by the reduction of the polymer, acts as an initiator of radical polymerization.

Oxidative polymerization is an important method for preparing aromatic polymers. For example, poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO) is commercially produced by the oxidative polymerization of 2,6-dimethylphenol.[1] The polymerization proceeds homogeneously in solution at room temperature by the oxidation of 2,6-dimethylphenol with oxygen in the presence of a copper-amine complex as a catalyst. Oxygen oxidative polymerization provides a highly pure polymer without salt contamination. PPO, whose commercial name is Nolyl®, is used as an engineering plastic after a compound of polystyrene because of its excellent performances, such as thermal stability, high order of moldability, and electrical characteristics.[2] However 2,6-dimethylthiophenol, which is an analogous compound of 2,6-dimethylphenol, is not polymerized by the same method.

We have recently found that diphenyl disulfide is oxidatively polymerized to yield poly(thio-1,4-phenylene) (PPS) through oxidative polymerization.[3–5] The oxidative polymerization can be applicable to the synthesis of many substituted PPSs.[6,7] In this paper we describe the synthesis, characterization and properties of poly(thio-2,6-dimethyl-1,4-phenylene) by the oxidative polymerization of bis(3,5-dimethylphenyl) disulfide (Eq. 1). The polymer containing a disulfide bond in a chain is confirmed by reduction of the polymer, and acts as an initiator of radical polymerization. The polymerization factors are also examined in order to obtain a polymer of high molecular weight.

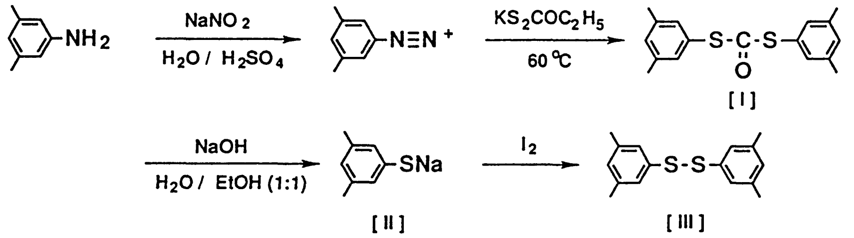


(1)

Experimental

Materials. Bis(3,5-dimethylphenyl) disulfide was prepared from 3,5-dimethylaniline. 3,5-Dimethylaniline was purified by distillation (60 °C/4 mmHg, 1 mmHg=133.322 Pa). A reagent-grade sodium nitrite and potassium *O*-ethyl dithiocarbonate were used without further purification. Oxidizing agents, such as vanadyl acetylacetonate and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), were also used without further purification. Lewis acids, antimony pentachloride, iron(III) chloride, aluminium chloride, and tin(IV) chloride, were used under a dry nitrogen atmosphere. Solvents, dichloromethane and tetrachloroethane, were purified by distillation in the usual manner. Olefins, styrene, methyl methacrylate, and acrylonitrile for radical polymerization, were also purified by distillation.

Preparation of Bis(3,5-dimethylphenyl) Disulfide (Scheme 1).[8] A solution of 3,5-dimethylaniline (85.0 g) in 600 cm^3 of water containing 50 cm^3 of sulfuric acid (sp. gr., 1.84) was diazotized below −5 °C by the dropwise addition of a cold solution of 53.8 g of sodium nitrite in 250 cm^3 of water. The resulting solution of the diazonium salt colored in yellow was neutralized to pH=ca. 5 by the addition of aqueous sodium carbonate (30 wt%) below −5 °C. The mixture was then poured into a solution, kept at 50—60 °C of 125 g of potassium *O*-ethyl dithiocarbonate in 600 cm^3 of water. Nitrogen



Scheme 1.

evolved smoothly and oil was separated. After completion of gas evolution at 60 °C, the mixture was cooled. The ether extract was washed with hydrochloric acid with 5 vol% (100 cm^3), aqueous sodium hydroxide with 5 wt% (200 cm^3) and finally with water until becoming neutral. After a column separation with hexane (R_f=0.25), *S,S*-bis(3,5-dimethylphenyl)dithiolcarbonate (**I**) was obtained. A mixture of **I** and 75.5 g of sodium hydroxide in 800 cm^3 of water–ethanol (1 : 1) was heated under reflux for 4 h to form a 3,5-dimethylphenyl sodium sulfide (**II**). A solution containing 55 g of iodine in ethanol was added to the mixture at room temperature. Yellow oil was separated and purified by column separation with hexane. Bis(3,5-dimethylphenyl) disulfide (**III**) was obtained after distillation (147 °C/0.5 mmHg). (Yield 25%): Mp 31 °C; IR(KBr) 2917, 2856, 1601, 1570, 1464, 1442, 1377, 1258, 1036, 995, 838, and 682 cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ=2.2 (12H, s, CH_3), 6.9 (2H, s, aromatic), 7.2 (4H, s, aromatic); ^{13}C NMR ($CDCl_3$, Me_4Si) δ=21.3 (CH_3), 125.3, 129.0, 136.9, 138.6 (aromatic); MS (*m*/*z*) 274, 137, 105. Found: C, 68.86; H, 6.67. Calcd for $C_{16}H_{18}S_2$: C, 69.02; H, 6.62%.

Polymerization Method. A typical experiment is as follows. Bis(3,5-dimethylphenyl) disulfide (0.01 mol) was dissolved in 50 cm^3 of dichloromethane, and then poured into the 50 cm^3 of a dichloromethane solution containing 0.01 mol of DDQ and 0.001 mol of trifluoromethanesulfonic acid. The mixture was stirred at 20 °C under a nitrogen atmosphere for 20 h. The reaction mixture was poured into 500 cm^3 of concd HCl–methanol (5/95 v/v). A white precipitate was collected and washed with methanol and an aqueous solution of potassium hydroxide (5 wt%) several times. The product was completely dissolved in hot tetrahydrofuran and reprecipitated in methanol. After filtration and washing with methanol, the product was dried in vacuo at 70 °C for 1 d to yield a white powder. IR(KBr) 2970, 2919, 1571, 1458, 1375, 1258, 1128, 1049, 994, 870, 854, 793, and 738 cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ=2.3 (6H, s, CH_3), 6.7 (1H, s, aromatic), 6.0, 6.2, 6.5, 6.9, 7.1, 7.3 (1H, s, aromatic); ^{13}C NMR ($CDCl_3$, Me_4Si) δ=22.0 (CH_3), 125.3, 126.1, 140.2, 144.4 (aromatic); MS (*m*/*z*) 408, 272, 137. Found: C, 69.83; H, 5.78%. Calcd for (C_8H_8S): C, 70.52; H, 5.92%.

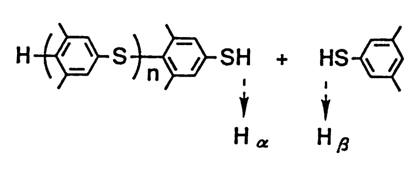
Detection and Determination of a Disulfide Bond in the Polymer. A typical experiment is as follows. The obtained polymer (0.5 g) was dissolved in dichloromethane (10 cm^3). A small amount of water (4 cm^3) was added to the solution. Triphenylphosphine (0.44 g) in dichloromethane (10 cm^3) was added dropwise to the mixture under a nitrogen atmosphere at room temperature in order to reduce the disulfide bond in a chain of the polymer. After 10 h, the mixture was evaporated and dried in vacuo with P_2O_5. IR(neat) 2563 cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ=3.3, 3.4 (1H, s, SH).

Radical Polymerization Initiated by Cleavage of a Disulfide Bond. A mixture of 10 cm^3 of olefin (styrene, methyl methacrylate, or acrylonitrile) and poly(thio-2,6-dimethyl-1,4-phenylene) (M_w=4500) was degassed by freezing three times and a sealed in a Pyrex tube. Radical polymerization was initiated by means of light irradiation with a wavelength longer than 300 nm by using a high-pressure mercury lamp. After 5 h, the mixture was poured into methanol to precipitate the polymer. The precipitation was collected by filtration, washed with methanol, and then dried in vacuo. IR(KBr) 3024, 2921, 2849, 1601, 1573, 1493, 1452, 1029, 906, 870, 855, 756, 698, and 539 cm^{-1}; ^{1}H NMR ($CDCl_3$, Me_4Si) δ=1.5 (2H, s, CH_2), 1.9 (1H, s, CH), 2.1—2.4 (6H, m, CH_3), 6.2—7.5 (6H, m, aromatic); ^{13}C NMR ($CDCl_3$, Me_4Si) δ=22.0 (CH_3), 40.3 (CH), 41.7, 42.7, 43.9, 46.0 (CH_2), 113.8, 125.0, 125.5, 125.6, 126.1, 127.9, 128.5, 136.8, 140.0, 144.4, 145.3 (aromatic).

Measurements. IR spectroscopy was carried out with a Perkin-Elmer FT-IR 1640 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz JEOL GSX-400. Mass spectra were measured using an ionization energy of 20 eV on a JMS-DX300 spectrometer. Differential scanning calorimetry (DSC) was carried out with a Seiko DSC220C thermal analyzer at a heating rate of 20 °C min^{-1}. Thermogravimetry (TG) and differential thermal analysis (DTA) was carried out simultaneously with a Rigaku thermal analysis station TAS 100 and thermoflex TG8110 at a heating rate of 20 °C min^{-1}. The determination of the molecular weight was carried out by GPC using a Shimadzu LC-9A system and Asahipac (GS 510H and 310H) columns. NMP was used as an eluent at 25 °C with flow rate of 1.0 cm^3 min^{-1}. The detector was a UV-vis spectrophotometer (Shimadzu SPD-6A, 265 nm). The GPC was calibrated by polystyrene standards. The inherent viscosity was calculated using a modified Ubellohde viscometer in chloroform at 20 °C.

Results and Discussion

The Polymer Structure. The polymer was prepared by the oxidative polymerization of bis(3,5-dimethylphenyl) disulfide and then isolated as a white powder (Eq. 1). The elemental analysis of the polymer supports the formation of poly(thio-2,6-dimethyl-1,4-phenylene) structure. The detailed structure was confirmed by spectroscopic measurements. The IR spectrum completely agrees with the poly(thio-2,6-dimethyl-1,4-phenylene) prepared by the polycondensation of 2,6-dimethylthiophenoxy copper salt. IR absorption bands between 800 and 900 cm^{-1} are significant for identifying the phenylene conjugation. The absorption bands at 870 and 854 cm^{-1} are observed in the IR spectrum. Those are attributed to an isolated C–H out-of-plain vibration of the benzene ring. The two bands are caused by different environments of the C–H bond.[9] In addition, four aromatic carbons were detected by ^{13}C NMR spectroscopy. ^{1}H NMR shows methyl and phenyl protons whose ratio is 6 to 2. The polymer was identified as being poly(thio-2,6-dimethyl-1,4-phenylene) containing a 1,4-linkage as the main structure.



(2)

The disulfide bond in a chain was confirmed by a reduction of the polymer (M_w=3000) with triphenylphosphine in the presence of water (Eq. 2). A new absorption band at 2563 cm^{-1}, which was assigned to

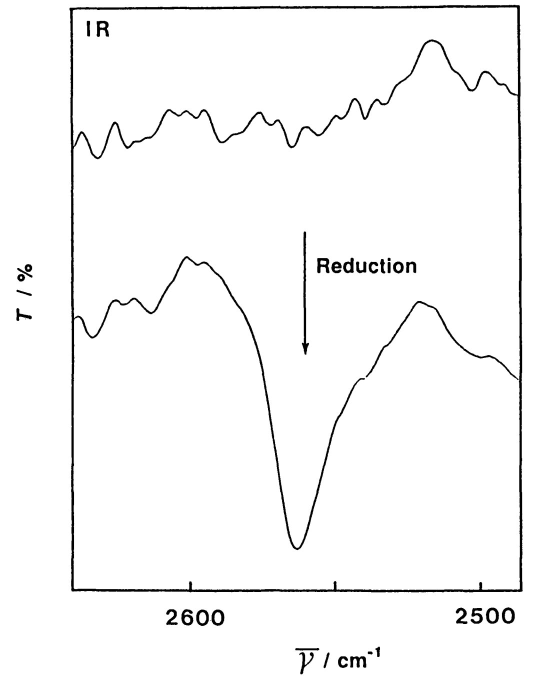


Fig. 1. SH stretching vibration of poly(thio-2,6-dimethyl-1,4-phenylene) after reduction.

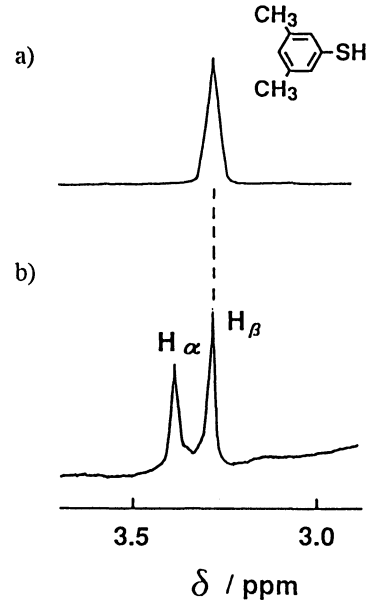
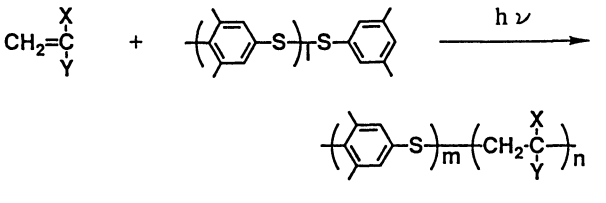


Fig. 2. ^{1}H NMR spectra of 3,5-dimethylthiophenol; (a), poly(thio-2,6-dimethyl-1,4,-phenylene) after reduction; (b).

the vibration of S–H, appears in the IR spectrum of the reduced polymer (Fig. 1). The ^{1}H NMR spectrum of the reaction mixture shows two peaks at 3.3 and 3.4 ppm after the reduction (Fig. 2). The peak at 3.3 and 3.4 ppm are attributed to mercaptoproton of 3,5-dimethyl thiophenol and that of the reduced polymer, respectively. These results indicate that a disulfide bond exists at the end of a chain in such polymer.

It is well-known that disulfide compounds act as an initiator of radical polymerization. In order to confirm the existence of a disulfide bond in the polymer, we carried out a control experiment, radical polymerization of the olefins by photo-irradiation in the presence of a small amount of poly(thio-2,6-dimethyl-1,4-phenylene) obtained by the oxidative polymerization (Eq. 3). Polystyrene and poly(methyl methacrylate) are only slightly formed without any initiators in the condition (experimental section) (Table 1). The yields of polystyrene and poly(methyl methacrylate) increase in the presence of poly(thio-2,6-dimethyl-1,4-phenylene). This means that poly(thio-2,6-dimethyl-1,4-phenylene) acts as an initiator for radical polymerization in terms of the cleavage of the disulfide bond. Polystyrene obtained by radical polymerization shows a single elution curve in GPC. That is, poly(thio-2,6-dimethyl-1,4-phenylene-co-styrene) is produced by the radical polymerization. The disulfide bond in poly(thio-2,6-dimethyl-1,4-phenylene) can be also considered as a functional group for organic reactions.



(3)

Sty: X=H, Y=Ph, MMA: X=CH$_3$, Y=COOCH$_3$, AN: X=H, Y=CN.

Table 1. Polymerization of Olefines with Poly(thio-2,6-dimethyl-1,4-phenylene) by UV Irradiation

Monomer	Yield/%	M_w	Mp/°C
Styrene	6.7 (0.2)$^{c)}$	15,000	110
MMA$^{a)}$	16.7 (2.2)$^{c)}$	—	140
AN$^{b)}$	0 (4.8)$^{c)}$	—	—

a) MMA: methyl methacrylate. b) AN: acrylonitrile. c) Polymerization without poly(thio-2,6-dimethyl-1,4-phenylene).

Properties of Poly(thio-2,6-dimethyl-1,4-phenylene). Poly(thio-2,6-dimethyl-1,4-phenylene) is soluble in many organic solvents such as chloroform, dichloromethane, tetrahydrofuran, and *N*-methyl-2-pyrrolidone, while PPS is completely insoluble at room temperature. The Mark–Houwink parameters, *K* and α, for poly(thio-2,6-dimethyl-1,4-phenylene) in chloroform at 20 °C were obtained by measuring the inherent viscosity of 9 samples determined M_w by GPC. The plots of log η versus log M_w leads to a good linear relationship (Fig. 3), given by

$$[\eta]=(0.92\times10^{-2})\,M_w^{0.75}.$$

This result suggests that the conformation of poly(thio-2,6-dimethyl-1,4-phenylene) is similar to that of PPO (K=4.8×10^{-2}/ml g^{-1}, α=0.64 at 25 °C).[10)]

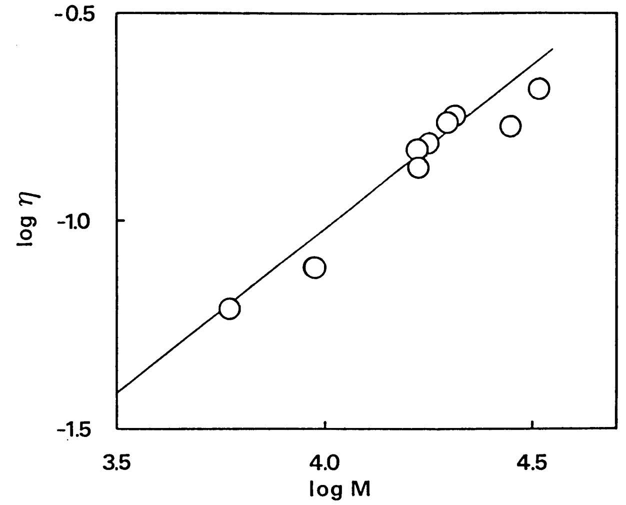


Fig. 3. Relationship between M_w and log η. (20 °C in $CHCl_3$).

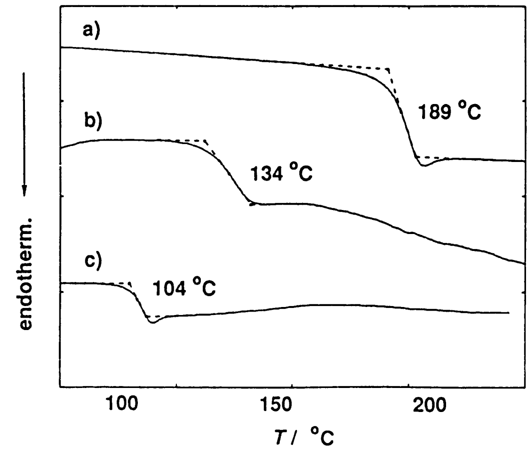
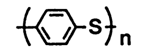
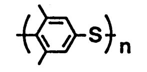
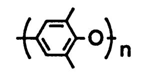


Fig. 4. DSC curves of poly(thio-2,6-dimethyl-1,4-phenylene); (a), blend polymer of poly(thio-2,6-dimethyl-1,4-phenylene) and polystyrene (1 : 1); (b), polystyrene; (c).

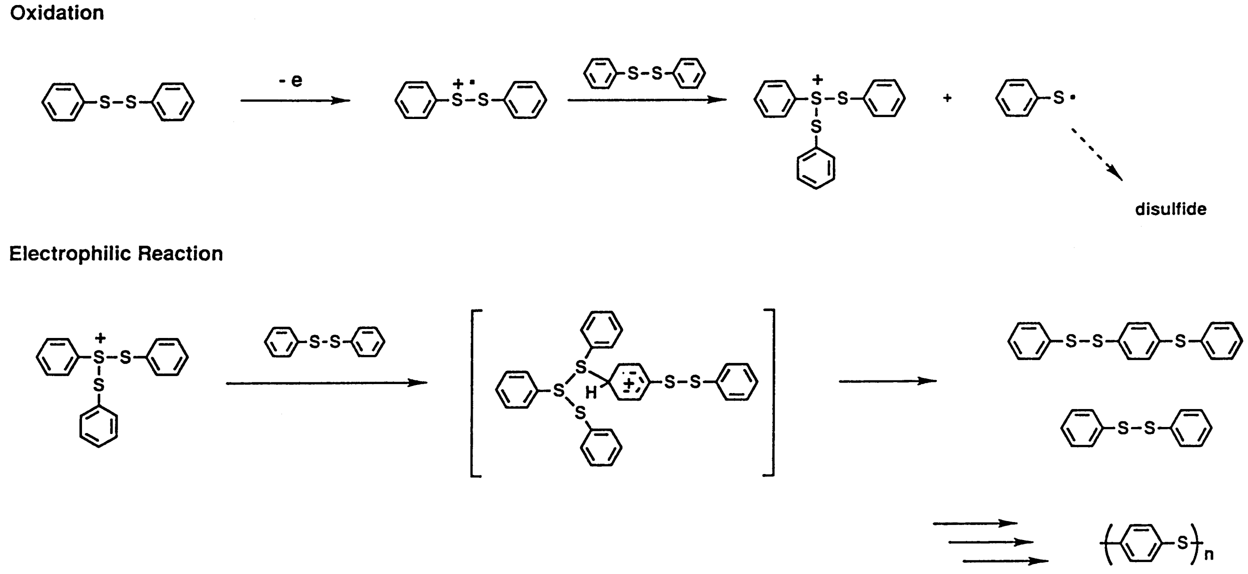
Table 2. Thermal Properties of Poly(arylene ether)s

Polymer	T_g/°C	T_m/°C	T_d/°C[a)]
	85	282	516
	189	—	418
	220	—	431

a) Temperature of 10% weight loss.

Thermal properties of poly(thio-2,6-dimethyl-1,4-phenylene) are listed in Table 2 with PPO and PPS. Poly(thio-2,6-dimethyl-1,4-phenylene) shows a glass transition at 189 °C and no melting point in DSC diagram. Though PPS is a crystalline polymer, poly(thio-2,6-dimethyl-1,4-phenylene) is an amorphous polymer that is similar to PPO. The introduction of disubstituents in the 2,6-position of the benzene ring results in a 90° rotation angle of the phenylene plane in the alternative benzene units, which causes the low crystallinity.

It is known that PPO is miscible with polystyrene in all regions of the composition.[11,12)] The blend polymer of poly(thio-2,6-dimethyl-1,4-phenylene) and polystyrene (1 : 1) shows a single glass transition at 134 °C, while the intrinsic glass transition of poly(thio-2,6-dimethyl-1,4-phenylene) (189 °C) and polystyrene (104 °C) have disappeared (Fig. 4). Each glass transition for the blend polymer with various compositions is always single. The variation curve of the glass transition temperature against the composition fits Couchman's equation (Fig. 5).[13)] This result indicates



Scheme 2.

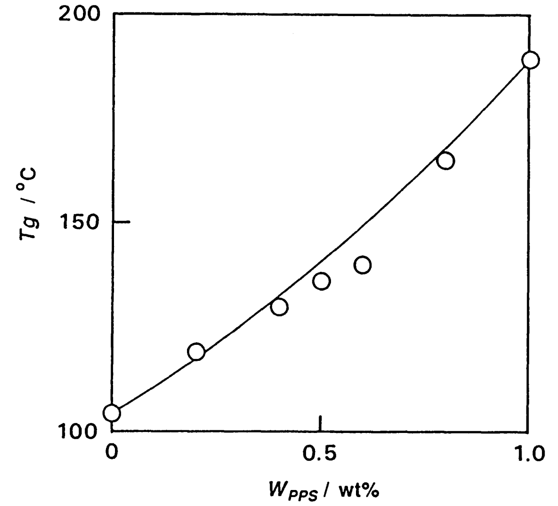


Fig. 5. Glass transition temperature for the blend polymer of poly(thio-2,6-dimethyl-1,4-phenylene) and polystyrene (W_{PPS}: weight fraction of poly(thio-2,6-dimethyl-1,4-phenylene)).

that poly(thio-2,6-dimethyl-1,4-phenylene) is completely miscible with polystyrene, similar to the case of PPO.

Polymerization Mechanism. We previously reported the polymerization mechanism for the oxidative polymerization of diphenyl disulfide (Scheme 2).[14] Diphenyl disulfide is oxidized to form the sulfonium cation as an active species of the polymerization. The cation electrophilically attacks a *p*-position of the benzene ring in diphenyl disulfide. These reactions occur repeatedly to yield PPS.

The molecular weight of poly(thio-2,6-dimethyl-1,4-phenylene) increases continuously after the polymer yield becomes constant. Especially, the polymer chain grows drastically during the end stage of polymerization (Fig. 6). Therefore, oxidative polymerization can be classified as being a kind of stepwise reaction. Figure 6 shows that the plots in the region of low conversion missed a theoretical curve on a stepwise reaction. The experimental molecular weight is larger than the theoretical one. This feature is caused by the polymerization mechanism.

The obtained polymer from the oxidative polymerization has a disulfide bond in a chain. The detection and determination of the disulfide bond at the end of a chain give information concerning the electrophilic reaction.

The content of the disulfide bond at the end of a chain can be estimated by the determination of 3,5-dimethylthiophenol formed after the reduction of the polymer (Fig. 7). A large amount of 3,5-dimethylthiophenol has been detected in the polymer obtained during the early stage of polymerization. This result indicates that the disulfide bond exists at the end group in a chain. Thus, the electrophilic substitution of the sulfonium cation to the phenyl ring occurs more preferentially at the side of the end phenyl ring binding with sulfide bond (**A**) than at the opposite end side (binding with disulfide bond) (**B**) (Scheme 3). This selectivity of the electrophilic attack of the sulfonium cation causes the gap between the experimental curve and the calculated one in Fig. 6. This polymerization can be classified as a reactive intermediate polycondensation, since the reactivity of the oligomer is higher than that of the monomer.

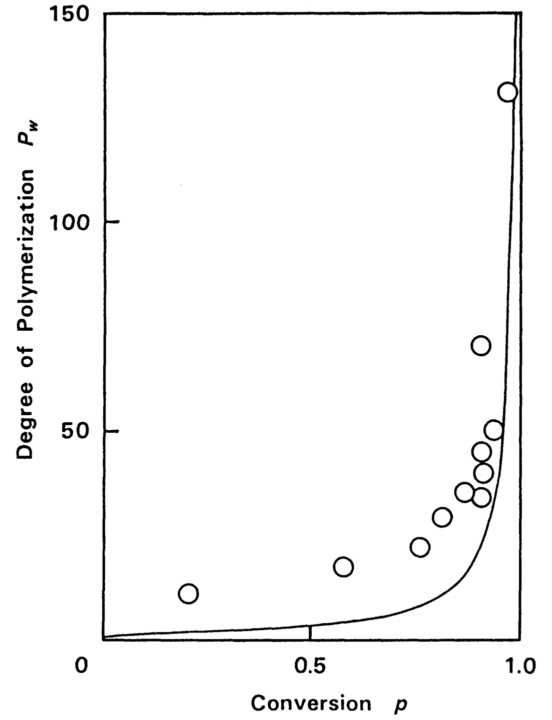


Fig. 6. Dependence of the degree of polymerization on the conversion. The line indicates the calculated curve of a stepwise polycondensation.

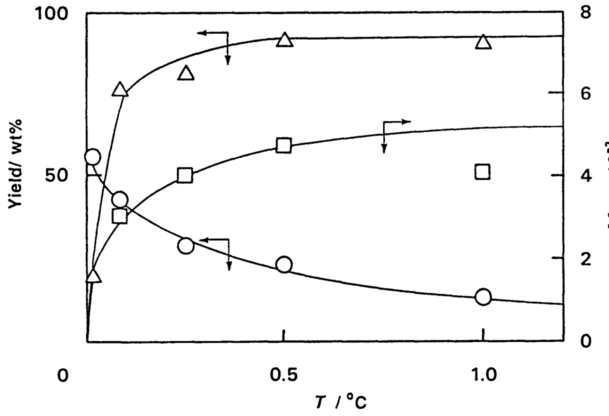
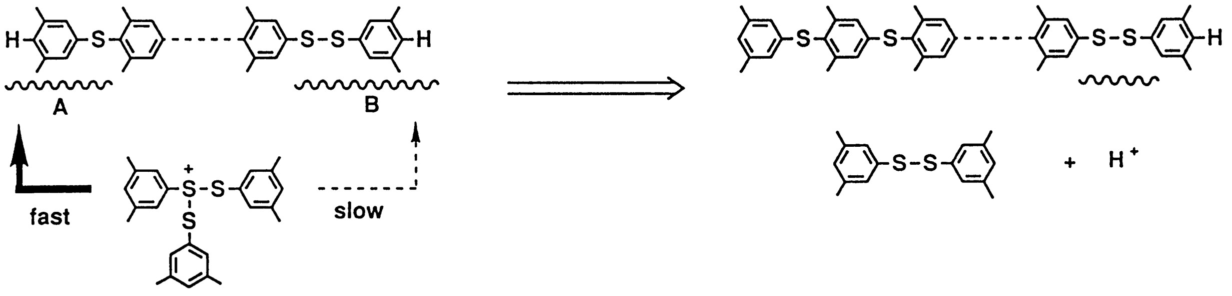
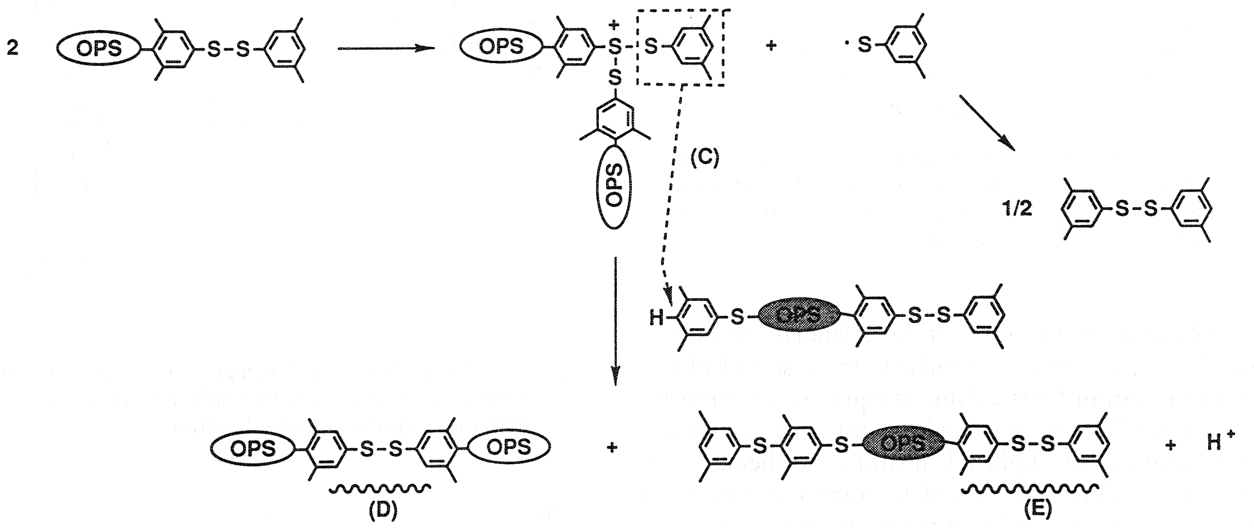


Fig. 7. Estimation of a disulfide bond in the polymer chain. 3,5-dimethylthiophenol; (○) polymer yield; (△), M_w; (□).

The yield of 3,5-dimethylthiophenol decreased with increasing molecular weight of the obtained polymer. After consumption of the monomer, the sulfonium cation arising from oligomers (**C**) is feasible to form by the oxidation (Scheme 4). Subsequently, (**C**) attacks



Scheme 3.



Scheme 4.

electrophilically to another oligomer to yield the polymer (**E**). The coupling of oligomers provides the polymer containing a disulfide bond at the middle of the chain (**D**).

Polymerization Behavior. We have reported that alkyl-substituted diphenyl disulfides are oxidatively polymerized to yield the corresponding PPS derivatives.[7] Introduction of electron donating substituents at a meta position of the phenyl ring results in the most efficient polymerization.[15] Polymerization of bis(3,5-dimethylphenyl) disulfide (0.1 mol dm^{-3}) proceeds much more rapidly than that of another substituted or non-substituted diphenyl disulfides, resulting in a 90% yield of poly(thio-2,6-dimethyl-1,4-phenylene) for 30 min in the presence of an equimolar amount of DDQ as an oxidizing agent. After 40 h, poly(thio-2,6-dimethyl-1,4-phenylene) with M_w of 10^4 is obtained in both polymerization methods by using DDQ and oxygen in the presence of vanadyl acetylacetonate (Fig. 8). Since poly(thio-2,6-dimethyl-1,4-phenylene) is soluble and the reaction proceeds homogeneously, the molecular weight of polymer formed is higher than that of insoluble non-substituted PPS.

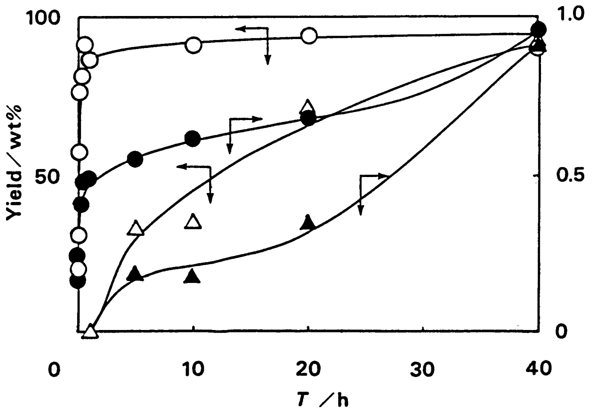


Fig. 8. Oxidative polymerization of bis(3,5-dimethylphenyl) disulfide with DDQ; polymer yield: (○), M_w: (●), with O_2 in the presence of $VO(acac)_2$; polymer yield: (△), M_w: (▲).

Oxidative polymerization of bis(3,5-dimethylphenyl) disulfide was carried out with various oxidizing agents such as quinones, Lewis acids, and oxygen in the presence of vanadyl acetylacetonate (Table 3). These oxidizing agents are able to yield the polymer in oxidative polymerization. The polymerization with DDQ, or oxygen provides ultra-pure poly(thio-2,6-dimethyl-1,4-phenylene) without salt contamination. Oxidizing agents such as benzoquinone and tin(IV) chloride do not act as an oxidizing agent for the polymerization because

Table 3. Polymerization[a] of Bis(3,5-dimethylphenyl) Disulfide with Various Oxidizing Agents

Oxidizing agent	Acid	Concn[b]	Yield	M_w[c]
		mol dm^{-3}	wt%	
VO(acac)$_2$/O$_2$	CF$_3$COOH	1.0	93	9200
VO(acac)$_2$/O$_2$	CF$_3$SO$_3$H	0.01	96	5600
DDQ	CF$_3$COOH	0.1	100	3400
DDQ	CF$_3$COOH	1.0	91	9600
DDQ	CF$_3$SO$_3$H	0.005	86	3500
DDQ	CF$_3$SO$_3$H	0.01	87	2400
Benzoquinone	CF$_3$COOH	1.0	0	—
Benzoquinone	CF$_3$SO$_3$H	0.01	0	—
SbCl$_5$	—	—	74	3800
FeCl$_3$	—	—	Trace	—
SnCl$_4$	—	—	0	—

a) Monomer: 0.1/mol dm^{-3}, in dichloromethane at 25 °C. b) Concentration of the acid. c) Measured by GPC standerded by polystyrene.

Table 4. Polymerization of Bis(3,5-dimethylphenyl) Disulfide in Various Solvents

Solvent	Donor number	Yield/wt%	M_w
CH$_2$Cl$_2$	0	94	6800
(CHCl$_2$)$_2$	0	96	4300
CHCl$_3$		91	3700
C$_6$H$_6$		89	1900
CH$_3$NO$_2$	2.7	84	1000
C$_6$H$_5$NO$_2$	4.4	81	7200
CH$_3$CN	14.1	0	
PC[a]	15.1	0	
THF[b]	20.0	0	
DMF[c]	26.6	0	
NMP[d]	27.3	0	

a) Propylene carbonate. b) Tetrahydrofuran. c) *N,N*-Dimethylformamide. d) *N*-Methyl-2-pyrrolidone.

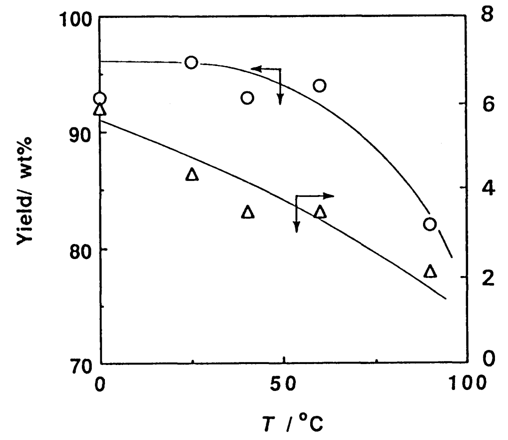


Fig. 9. Effect of the temperature on the oxidative polymerization of bis(3,5-dimethylphenyl) disulfide. polymer yield: (○), M_w: (△).

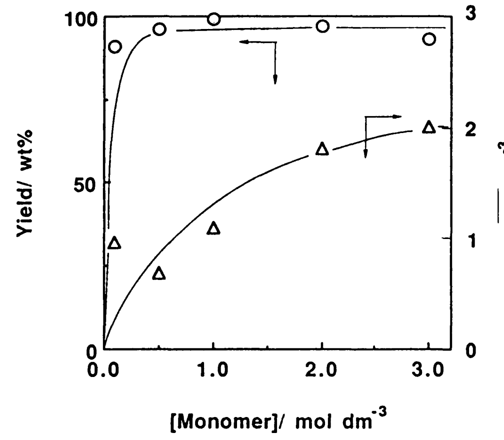


Fig. 10. Dependence of the feed concentration of the monomer on the molecular weight of the obtained polymer in the oxidative polymerization with equimolar amount of DDQ. Polymer yield: (○), M_w: (△).

of the low oxidizing ability.

A strong acid is essential for polymerization. The acid suppresses the deactivation of the sulfonium cation by nucleophilic agents. The polymerization proceeds efficiently under 1.0 mol dm^{-3} of trifluoroacetic acid. Using trifluoromethanesulfonic acid results in the formation of a polymer of low molecular weight. Since trifluoromethane sulfonic acid is known to be a strong acid ($H^{\circ}=-14.6$), the sulfonium cation may be stabilized by the acid. That is, trifluoromethanesulfonic acid also acts as an inhibitor for the electrophilic reaction.

Polymerization was carried out in various solvents (Table 4). Low-basic solvents, such as dichloromethane and 1,1,2,2-tetrachloroethane, are suitable for polymerization. Polymerization, however, does not proceed in large donor number solvents, such as dimethylformamide and *N*-methyl-2-pyrrolidone. These results support the idea that polymerization proceeds via a cationic mechanism. The polarity of the solvent also affects the polymerization rate. Nitrobenzene is a good solvent from the view point of its large polymerization rate. The polymerization proceeds more rapidly in a polar solvent than in a nonpolar solvent. The solvent effect is similar to that of a cationic polymerization of olefins. These results also indicate that the polymerization proceeds through the reaction of a cation.

Figure 9 shows the effect of temperature on polymerization. Polymerization was carried out in tetrachloroethane for 20 h. The polymer was isolated in 90% yield below 60 °C. The yield and molecular weight of the polymer decreased at high temperature (90 °C) and the structure of the polymer changed, which could be confirmed by IR (shoulder peak at 848 cm^{-1}). These are the same in the polymerization of diphenyl disulfide at high temperature, which contains a thianthrene structure.[14] Polymerization at low temperature prefers to obtain a polymer of high molecular weight with high yield.

Polymerization in a high feed concentration of the monomer in the presence of an equimolar amount of DDQ was carried out in order to obtain a polymer of high molecular weight (Fig. 10). The molecular weight of the obtained polymer increases with the concentration of the monomer. Since the concentration of the active center and sulfonium cation of the polymer chain are low during the end stage of polymerization, a high monomer concentration is apparently effective for electrophilic substitution. That results in the formation of a polymer of high molecular weight. Therefore, poly(thio-2,6-dimethyl-1,4-phenylene) with 28000 of molecular weight is obtained by polymerization with 2.0 mol dm^{-3} of the monomer after 120 h.

This work was partially supported by The Asahi Glass Foundation and a Grant-in-Aid for Developmental Scientific Research Nos. 04555223, 04750707, and 040869 from the Ministry of Education, Science and Culture.

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