November, 1989] © 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 3655—3660 (1989) 3655

Preparation of Poly(phenylene sulfide)s: Polymerization of Aromatic Disulfides with Lewis Acids

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(Received July 7, 1989)

Poly(*p*-phenylene sulfide) is prepared through the polymerization of diphenyl disulfide with various Lewis acids, such as $AlCl_3$ and $SbCl_5$. Thiophenol also yield poly(*p*-phenylene sulfide) through its oxidation to diphenyl disulfide in the presence of an oxidizing agent or electrolysis during polymerization. Alkyl-substituted diphenyl disulfides are polymerized with a Lewis acid to efficiently yield alkyl-substituted poly(*p*-phenylene sulfide)s such as poly(2-methyl-, 2,6-dimethyl-, and 2,6-diethylphenylene sulfide)s, with high molecular weight and solubility in common solvents.

Poly(*p*-phenylene sulfide)(PPS) has been increasingly used owing to its excellent chemical, thermal, and mechanical properties.[1-6] A commercially important preparation procedure of PPS involves the polycondensation of 1,4-dichlorobenzene and sodium sulfide in a polar solvent, such as *N*-methylpyrrolidone, at high temperature and pressure.[7-9] Much effort has been consumed in the modification of the synthetic routs for PPS. It has been reported that PPS can also be prepared by the polycondensation of metal *p*-halobenzenethiolate at ca. 350 °C.[10-15] High-temperature conditions are required to increase the reactivity of the monomer in the formation of high-molecular PPS. However, the polycondensation of alkyl-substituted monomers does not provide PPSs with high molecular weight, even at high temperatures. Few papers have reported on the preparation of substituted poly(phenylene sulfide)s.[16,17]

We have reported that diphenyl disulfide as a monomer reacts with Lewis acid to cleave its S–S bond and is easily polymerized to a linear PPS at room temperature and atmospheric pressure.[18-20] In this study, alkyl-substituted diphenyl disulfides were applied for this polymerization in order to prepare the corresponding poly(alkylsubstituted phenylene sulfide)s with high molecular weight. The polymerization behavior of the diphenyl disulfides with Lewis acids and the structure of the formed polymers are described.

Experimental

Materials. Diphenyl disulfide was purified by two recrystallization processes from ethanol-water and dried in vacuo for 1 day at 30 °C, producing a white needles: mp 59 °C. Thiophenol was distilled twice under reduced pressure and stored under nitrogen atmosphere. Bis(2-methylphenyl) disulfide, bis(2-methoxyphenyl) disulfide, bis(2,6-dichlorophenyl) disulfide, bis(4-methylphenyl) disulfide, di(2-naphthyl) disulfide, and dibenzyl disulfide were prepared through the oxidation of the corresponding thiophenols with I_2 in alkaline methanol and used through recrystalized twice before use. Bis(2,6-dimethylphenyl) disulfide and bis(2,6-diethylphenyl) disulfide were prepared by a Leuckart reaction from 2,6-dimethylaniline and 2,6-diethylaniline, as the starting material, respectively.[21] Bis(2,6-dimethoxyphenyl) disulfide was obtained by the oxidation of 2,6-dimethoxythiophenol prepared through the reported method from *m*-dimethoxybenzene.[22] The prepared diphenyl disulfides were recrystallized with analytical purity. Bis(2,6-dimethylphenyl) disulfide: ^{13}C NMR ($CDCl_3$), δ=21 (methyl C); 128, 129, 131, 143 (phenyl C). ^1H NMR ($CDCl_3$), δ=2.2 (methyl 6H); 7.0 (phenyl 3H). IR (KBr, cm^{-1}) 2900, 2960, 3040 (ν_{C-H}); 1460 ($\nu_{C=C}$); 760 (δ_{C-H}). Bis(2,6-diethylphenyl) disulfide: ^{13}C NMR ($CDCl_3$) δ=15, 28 (ethyl C); 126, 130, 134, 150 (phenyl C). ^1H NMR ($CDCl_3$) δ=1.1, 2.8 (ethyl 10H); 7.1 (phenyl 3H). IR (KBr, cm^{-1}), 2960, 3050 (ν_{C-H}); 1460 ($\nu_{C=C}$); 750 (δ_{C-H}). Bis(2-methyl-6-chlorophenyl) disulfide: ^{13}C NMR ($CDCl_3$), δ=22 (methyl C); 128.7, 128.7, 130.3, 134.3, 140.7, 145.2 (phenyl C). IR (KBr, cm^{-1}) 2926, 2962 (ν_{C-H}); 1400, 1500 ($\nu_{C=C}$); 745, 860 (δ_{C-H}). 2,6-Dimethoxythiophenol: white needle-like solid, ^{13}C NMR ($CDCl_3$) δ=57 (methoxy C); 125, 131, 133, 162 (phenyl C). ^1H NMR ($CDCl_3$) δ=6.8 (phenyl 3H); 3.9 (methoxyl 6H); 3.7 (mercapto H). IR (KBr, cm^{-1}) 2960, 3040 (ν_{C-H}); 2592 (ν_{S-H}); 1460 ($\nu_{C=C}$); 740 (δ_{C-H}).

Guaranteed reagents of Lewis acids and oxidizing agents were used without further purification and under a dry nitrogen atmosphere. Dichloromethane, 1,1,2,2-tetrachloroethane, nitromethane, and nitrobenzene as the polymerization solvents were purified by distillation in the usual manner.

Measurements. ^1H NMR and ^{13}C NMR spectra were measured of a 90-MHz JEOL FX-100. IR spectroscopy was carried out on a JAS IR-810 model spectrometer. Mass spectra were measured on a JMS-DX300 model spectrometer at an ionization energy of 20 eV.[23] Melting points were determined on the stage of a microscope at a heating rate of 2 °C min^{-1}. DSC measurements were carried out on a SEIKO thermal analyzed model SSC/500 with a heating rate of 20 °C min^{-1}. The molecular weight of the benzene-soluble part of PPS was measured by vapor pressure osmometry.

Polymerization Method. The typical experiment can be described as follows: 0.1 mol l^{-1} of diphenyl disulfide was dissolved in 50 ml of nitromethane and was poured into 50 ml of nitromethane containing Lewis acid kept at 20 °C under nitrogen atmosphere for 20 h. The reaction mixture color changed to deep black from yellow. After the polymerization, the reaction mixture was poured into 500 ml of methanol with 5% hydrogen chloride to precipitate a polymeric material. The polymer was purified according to the previously reported procedure.[18-20] The purified polymer was not mixed with Lewis acid metal of more than 200 ppm according to an analysis by inductively coupled plasma emission spectroscopy. Polymerization of thiophenol (0.2 mol l^{-1}) was similarly carried out in the coexistence of an oxidizing agent (0.1 mol l^{-1}).

Electrolysis. A pair of platinum plates (2×5 cm) was placed in the cell with a 1 cm spacing as the working and auxiliary electrodes. The reference electrode was Ag/AgCl. A nitromethane solution of thiophenol (0.1 mol l^{-1}) contained Lewis acid and was kept at 20 °C under a nitrogen atmosphere. The preparative electrolysis was carried out under a controlled potential at 1.5 V with a NIKKO KEISOKU NPGS-301 potentiogarvanostat. The electrolysis was turned off at 5 F mol^{-1}.

Spectroscopic Data of the Formed Polymers. Poly(*p*-phenylene sulfide): Calcd for (C_6H_4S): C, 66.67; H, 3.7; S, 29.63%. Found: C, 66.51; H, 3.81; S, 29.44%. IR(KBr, cm^{-1}) 3025($\nu_{C\text{-}H}$); 1395, 1480, 1580($\nu_{C=C}$); 820($\delta_{C\text{-}H}$); 480, 560, 740, 1015, 1080, 1110. MS (*m/z*) 756, 684, 540, 434. X-Ray diffraction pattern 2θ=19, 21.

Poly(2-methylphenylene sulfide): Calcd for (C_7H_6S): C, 68.85; H, 4.92; S, 26.23%. Found: C, 68.50; H, 4.77; S, 25.92%. IR (KBr, cm^{-1}) 2920, 2950, 2980, 3050 ($\nu_{C\text{-}H}$); 1440, 1460, 1580 ($\nu_{C=C}$); 820, 880 ($\delta_{C\text{-}H}$); 760, 1050, 1100, 1200, 1380. ^1H NMR ($CDCl_3$), δ=2.3 (methyl 3H); 7.1 (phenyl 3H). ^{13}C NMR ($CDCl_3$), δ=21 (methyl C); 127, 130, 131, 134, 136, 141 (phenyl C). NMR signals of methylene proton and carbon were not detected at δ=3.6 and 60, respectively. MS (*m/z*) 612, 490, 368.

Poly(2,6-dimethylphenylene sulfide): Calcd for (C_8H_8S): C, 70.54; H, 5.92; S, 23.54%. Found: C, 70.06; H, 5.97; S, 23.21%. IR and ^{13}C NMR spectra were shown in Figs. 1 and 2. ^1H NMR ($CDCl_3$), δ=2.3 (methyl 6H); 7.1 (phenyl 2H). MS (*m/z*) 682, 544, 408.

Poly(2,6-diethylphenylene sulfide): Calcd for ($C_{10}H_{12}S$): C, 73.12; H, 7.36; S, 19.52%. Found: C, 73.05; H, 7.41; S, 19.46%. IR (KBr, cm^{-1}) 2950, 2980, 3050 ($\nu_{C\text{-}H}$); 1460, 1560 ($\nu_{C=C}$); 800, 860 ($\delta_{C\text{-}H}$); 1020, 1060, 1160, 1320, 1370. ^1H NMR ($CDCl_3$), δ=1.25 (methyl 6H); 2.7 (methylene 4H); 7.0 (phenyl 2H). ^{13}C NMR ($CDCl_3$), δ=16 (methyl C); 28 (methylene C); 127, 131, 143, 150 (phenyl C). NMR signals of methylene proton and carbon were not detected at δ=3.6 and 60, respectively. MS (*m/z*) 658, 492.

Poly(2-methoxyphenylene sulfide): Calcd for (C_7H_6SO): C, 60.87; H, 4.35%. Found: C, 60.02; H, 4.62%. IR (KBr, cm^{-1}) 2880 ($\nu_{C\text{-}H}$); 1420, 1480, 1580, 1600 ($\nu_{C=C}$); 1180 ($\nu_{C\text{-}O\text{-}C}$); 840, 880 ($\delta_{C\text{-}H}$); 720, 1030, 1070, 1270.

Poly(2,6-dimethoxyphenylene sulfide): Calcd for ($C_8H_8SO_2$): C, 54.14; H, 4.76%. Found: C, 55.23; H, 4.86%. IR (KBr, cm^{-1}) 2870 ($\nu_{C\text{-}H}$); 1370, 1470, 1600 ($\nu_{C=C}$); 1180 ($\nu_{C\text{-}O\text{-}C}$); 820 ($\delta_{C\text{-}H}$); 480, 1040, 1210, 1280.

Poly(2-methyl-6-chlorophenylene sulfide): Calcd for (C_7H_5SCl): C, 53.67; H, 3.19%. Found: C, 53.25; H, 3.21%. IR (KBr, cm^{-1}) 2870 ($\nu_{C\text{-}H}$); 1440, 1560, 1580 ($\nu_{C=C}$); 820, 860 ($\delta_{C\text{-}H}$); 720, 740, 780, 1000, 1100, 1180, 1380. ^{13}C NMR ($CDCl_3$), δ=22.0 (methyl C); 122.8, 128.3, 129.2, 130.4, 137.3, 145.7 (phenyl C).

Poly(thiomethylene phenylene): Calcd for (C_7H_6S): C, 68.85; H, 4.92; S, 26.23%. Found: C, 67.81; H, 5.10; S, 25.98%. IR (KBr, cm^{-1}) 3100 ($\nu_{C\text{-}H}$); 1410, 1440, 1450, 1500, 1600 ($\nu_{C=C}$); 810 ($\delta_{C\text{-}H}$); 465, 700, 760, 900, 1020, 1080, 1260, 1350.

Poly(naphthylene sulfide): Calcd for ($C_{10}H_6S$): C, 75.95; H, 3.80; S, 20.25%. Found: C, 76.12; H, 3.51: S, 19.34%. IR (KBr, cm^{-1}) 1500, 1550, 1580, 1620 ($\nu_{C=C}$); 820, 870 ($\delta_{C\text{-}H}$); 480, 540, 740, 780, 960, 1080, 1120, 1260, 1320, 1350.

Isolation of Thianthrene. The reaction mixture was poured into methanol. The methanol solution was evaporated to dryness after the precipitate was separated out. The product was extracted with chloroform from the residue. The thianthrene formation was confirmed by gass cromatography and ^{13}C NMR spectroscopy. ^{13}C NMR ($CDCl_3$), δ=127.4, 128.6, 135.5. IR (KBr, cm^{-1}) 3050 ($\nu_{C\text{-}H}$); 1430, 1550 ($\nu_{C=C}$); 760 ($\delta_{C\text{-}H}$); 460, 660, 1250, 1100. MS (*m/z*) 108, 139, 171, 184, 216.

^{13}C NMR Spectrum of the Reaction Mixture. The ^{13}C NMR spectra of disulfides with $SbCl_5$ were measured at −30 °C in double compartment cell probes of which internal and standard sample was CD_3OD/tetramethylsilane. ^{13}C NMR (CH_2Cl_2, phenyl carbon); the reaction mixture of diphenyl disulfide: δ=127.4, 132.8, 135.9, 136.4. Diphenyl disulfide: δ=128.4, 128.8, 130. 9, 138.1. The reaction mixture of bis(2-methylphenyl) disulfide: δ=129.2, 131.4, 131.7, 132.3, 132.9, 140.7. Bis(2-methylphenyl) disulfide: δ=127.9, 128.4, 128.5, 132.0, 136.3, 132.0. The reaction mixture of bis(2,6-dimethylphenyl) disulfide: δ=131.1, 131.4, 134.3, 145.8. Bis(2,6-dimethylphenyl) disulfide: δ=129.6, 131.0, 135.9, 144.9.

Results and Discussion

Polymerization of Diphenyl Disulfides. Diphenyl disulfide was allowed to react with aluminum trichloride at room temperature in nitromethane. The

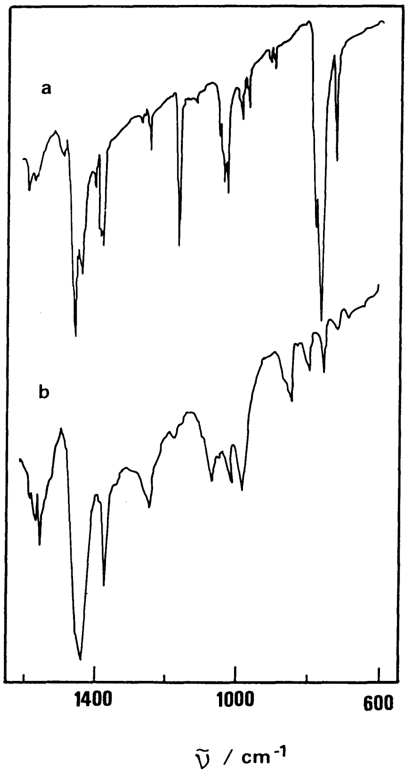
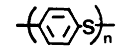
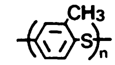
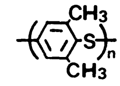
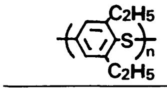
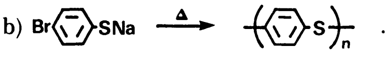
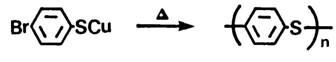


Fig. 1. IR spectra of bis(2,6-dimethylphenyl) disulfide (a) and the formed polymer through the polymerization of *bis(2,6-dimethylphenyl) disulfide* (b).

Table 1. Polymerization[a] of Diphenyl Disulfides with $AlCl_3$

Polymer	Polymer yield	$CHCl_3$-insoluble Mp	$CHCl_3$-soluble Mp	M_n	Lenz's method[b] Mp	M_w	Port's method[c] Mp	M_w
	wt%	°C	°C		°C		°C	
	51	213	90	450	250—280	3000	280—285	—
	35	240	140	3800	60—120	1550	140—150	5400
	81	245	170	4300	140—180	2500	218	8270
	86		195	10000	—	—	—	—

a) 100 h. b)  . c)  .

polymer was formed as a white powder having an empirical formula C_6H_4S and was soluble in hot *N*-methylpyrrolidone. The spectroscopic data agreed with that of a commercially available product. Polymerization of bis(2-methylphenyl) disulfide with $AlCl_3$ gave a polymer whose IR spectrum and other spectroscopic data agreed with the prepared poly(2-methyl-1,4-phenylene sulfide) by the polycondensation of sodium 4-bromo-2-methylbenzenethiolate.

The absorption bands at 820 and 880 cm^{-1} were attributed to the adjacent 2H of the C–H out-of-plane vibration and to the isolated 1H, respectively, which supports the 1,4-conjugated thiophenylene. Bis(2,6-dimethylphenyl) disulfide was also polymerized to give the polymer. The formed polymer also showed absorption bands at 860 and 820 cm^{-1}, which supported the belief that the polymer does not only contain the 1,4-conjugated thiophenylene structure, but 1,3-conjugated as well (Fig. 1). Bis(2,6-diethylphenyl) disulfide was also polymerized to form a polymer with a molecular weight of 4×10^4—1×10^3. The elemental analysis data of the formed polymer agreed with the calculated values for poly(2,6-diethylphenylene sulfide). The IR spectrum of the polymer supported the structure of poly(2,6-diethylphenylene sulfide). The complete polymerization of bis(2,6-diethylphenyl) disulfide was also indicated by a decrease in the absorption band at 760 cm^{-1} attributed of an adjacent 3H C–H out-of-plane vibration on the monomer. NMR spectra also supported the idea that the formed polymer dose not combine through a thiomethylene moiety but, through a thiophenylene moiety (Fig. 2).

These polymers were quite soluble in chloroform, benzene, *N*-methylpyrrolidone, *N,N*-dimethylformamide. The substituent groups on the phenylene ring of PPS greatly increased the solubility of PPS and expanded its application potential. The melting points of polymers were much higher than those of polymers prepared by the conventional polycondensation (Table 1). The substituent alkyl groups drastically increased the solubility of the polymer providing the polymer with a high molecular weight.

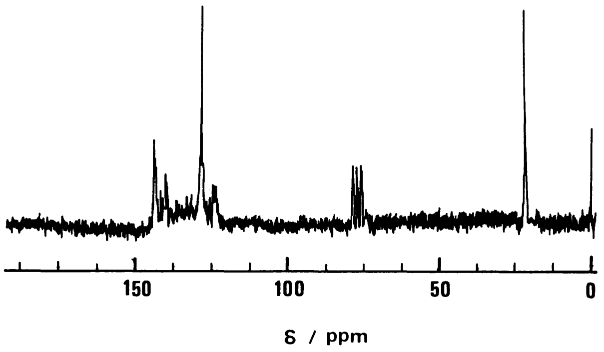
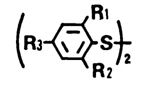


Fig. 2. ^{13}C NMR spectra of the chloroform-soluble part of the formed polymer through the polymerization of bis(2,6-dimethylphenyl) disulfide.

Table 2. Polymerization of Various Aromatic Disulfides with $AlCl_3$

Sulfide monomer[a] R1	R2	R3	Yield wt%	Mp °C
$-OCH_3$	-H	-H	46	270
$-OCH_3$	$-OCH_3$	-H	8	113
$-CH_3$	-Cl	-H	73	214
-Cl	-Cl	-H	0	—
-H	-H	$-CH_3$	0	—
-H	-H	$-C(CH_3)_3$	0	—
Dibenzyl disulfide			89	253
Dinaphthyl disulfide			91	188

a)  .

Various diphenyl disulfide derivatives such as dibenzyl disulfide, bis(2-methoxyphenyl) disulfide, and di(2-naphthyl) disulfide were also polymerized with aluminum chloride to yield the corresponding

PPS derivatives in high yield (Table 2). Alkylsubsituted PPSs were also efficiently produced by polymerization. Thus, the polymerization route of diphenyl disulfides with Lewis acid is a convenient procedure for the preparation of PPS and poly(aromatic sulfide)s. However, *p*-substituted and bis(2,6-dichlorophenyl) disulfide were not allowed to give the corresponding polymers. Electron-withdrawing substituents and the positions of substituents influenced the polymerization.

Polymerization Mchanism. In previous papers[18,20] we concluded that the sulfonium cation is the active species for the polymerization of diphenyl disulfide, based on ^{13}C NMR and the isolation of the sulfonium cation as a salt. The ^{13}C NMR spectrum of the reaction mixture of bis(2-methylphenyl) disulfide and bis(2,6-dimethylphenyl) disulfide at −30 °C shows signals which were not assigned to the corresponding disulfides and the other sulfides (Experimental section). In this experiment the phenylbis(phenylthio)sulfonium cation was formed with the Lewis acid.

Figure 3 shows polymerization curves for the diphenyl disulfides. The melting point which corresponds to the molecular weight of the polymer, increased after the polymer yield became constant. The formed polymer or oligomer re-reacted with Lewis acid to form PPS. This means that the polymerization proceeds in a stepwise fashion to yield PPS. It is considered that the cation electrophilically reacts with diphenyl disulfide to form the trimer. The polymerization mechanism of diphenyl disulfide is illustrated in Eq. 1. Poly(methyl-substituted phenylene sulfide)s were rapidly formed on the polymerization in comparison with PPS because of the electron-donating substituents. The results also supported the cationic mechanism.

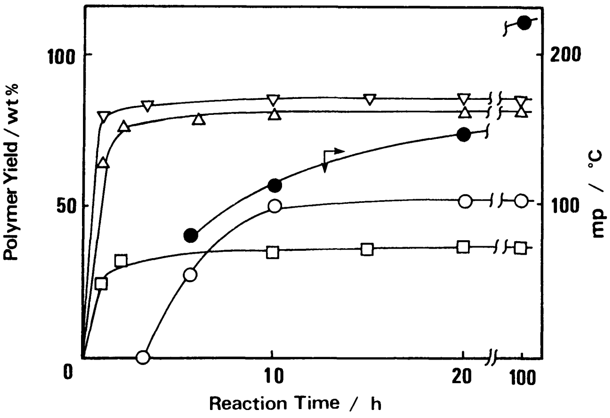
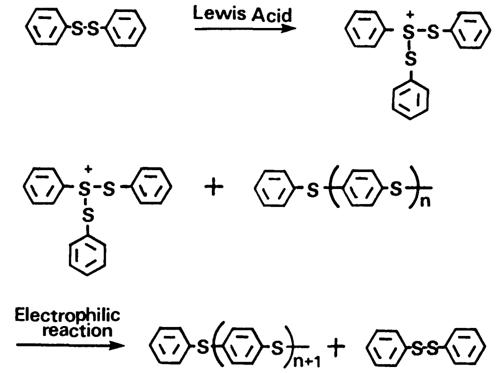


Fig. 3. Polymerization curves of bis(2-methylphenyl) disulfide (□), bis(2,6-dimethylphenyl) disulfide (△), bis(2,6-diethylphenyl) disulfide (▽), and diphenyl disulfide (○); melting point of the formed polymer from diphenyl disulfide (●).



(1)

Polymerization with Various Lewis Acids. Polymerization proceeded with various Lewis acids such as $SbCl_5$, $MoCl_5$, and $TiCl_4$, although the PPS yield and/or molecular weight were influenced by Lewis acid and the solvent species (Table 3).

The PPS yield remained at about 50% for the polymerization of diphenyl disulfide, and decreased with an increase in the temperature (Fig. 4). Gaseous mass spectroscopy of the reaction mixture indicated the formation of thianthrene. Thianthrene was isolated and confirmed by the results of NMR and IR spectroscopy (Experimental section). Thianthrene was formed as a by-product during polymerization. In contrast, the polymerization of bis(2,6-substituted phenyl) disulfides gave their polymers with relatively high yield in comparison with those of bis(mono- and unsubstituted phenyl) disulfides (Fig. 4). 2,6-Dialkyl-substituents does not only increased the solubility of the formed polymer, but also strongly suppressed the formation of thianthrene by the side reaction, and gave a polymer with high molecular weight and high yield. These results suggested that the temperature influenced the reaction of diphenyl disulfide with $AlCl_3$. That is, the high temperature resulted in the forma-

Table 3. Polymerization[a)] of Diphenyl Disulfide with Lewis Acids

Solvent		$AlCl_3$	$TiCl_4$	$FeCl_3$	$MoCl_5$	$SbCl_5$	$BF_3\cdot O(C_2H_5)_2$	$SnCl_4$
$C_6H_5NO_2$	Yield/wt%[b)]	31	96	60	29	28	0	0
	Mp/°C	180	183	150	207	194	—	—
CH_3NO_2	Yield/wt%	50	67	93	9	89	59	0
	Mp/°C	135	139	139	108	191	119	—
$(CHCl_2)_2$	Yield/wt%	36	0	42	60	67	0	0
	Mp/°C	124	—	104	115	140	—	—

a) 20 °C, 20 h, [Monomer]=0.1 mol l^{-1}, [Lewis Acid]=0.1 mol l^{-1} ($SbCl_5$, $MoCl_5$, $FeCl_3$), 1.0 mol l^{-1} (other Lewis acids). b) PPS yield.

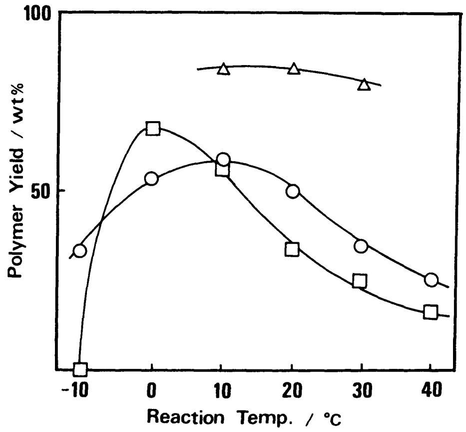


Fig. 4. Effect of the temperature on the polymerization of bis(2-methylphenyl) disulfide (□), bis(2,6-dimethylphenyl) disulfide (△), and diphenyl disulfide (○).

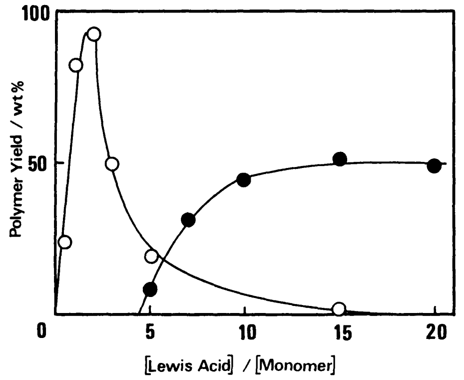


Fig. 5. Effect of the concentration of Lewis acid on the polymerization of diphenyl disulfide. $AlCl_3$ (●), $SbCl_5$ (○).

tion of thianthrene, the result of which was corresponded to the previously reported polymerization.[24–28]

The optimum concentration of $SbCl_5$, $MoCl_5$, and $FeCl_3$ is two times equimolar of diphenyl disulfide in this polymerization. In contrast, $AlCl_3$, $TiCl_4$, and $BF_3 \cdot O(C_2H_5)_2$ required more than ten times equimolar of the monomer for an efficient formation of PPS (Fig. 5). These results support the difference in the initiation mechanism of the polymerization or initiation efficiency, which was based on the difference of the oxidation ability between $AlCl_3$ and $SbCl_5$.[29,30] The melting point of the polymer increased during polymerization with $AlCl_3$ in nitromethane after the polymer yield became constant. This means that the polymerization proceeds in a stepwise manner to grow the polymer. It is considered that an increase in the molecular weight of the polymer caused by an increase in the polymer solubility on the basis of the formation of a polymer complex with $AlCl_3$ in the presence of excess $AlCl_3$.[31]

Polymerization of Thiophenol. It is well-known that thiophenol is quantitatively oxidized to diphenyl disulfide with oxidizing agents.[32,33] The polymerization of thiophenol as a starting material was carried out in the coexistence of an oxidizing agent and $AlCl_3$ to also give PPS (Table 4). This suggests that thiophenol is preferentially oxidized to diphenyl disulfide and polymerized with $AlCl_3$ without any retardation by oxidizing agents. Electrolysis was applied to the oxidation process on the polymerization instead of oxidizing agents. PPS was also precipitated in the electrolysis cell and on the electrode.

Table 4. Polymerization[a] of Thiophenol with Lewis Acid through the Oxidation

Oxidizing agent	Solvent	Polymer yield	Mp
		wt%	°C
I_2	CH_3NO_2	85	142
	$C_6H_5NO_2$	48	192
$CuCl_2$	CH_3NO_2	70	164
	$C_6H_5NO_2$	52	169
Chloramine B[b]	CH_3NO_2	35	178
	$C_6H_5NO_2$	Trace	—
$SOCl_2$	CH_3NO_2	88	189
	$C_6H_5NO_2$	Trace	—
Electrolysis	CH_3NO_2	87	193

a) 20 h. b) $C_6H_5SO_2NNaCl$.

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area of "Macromolecular Complexs" from the Ministry of Education, Science and Culture.

References

1) R. T. Howkins, *Macromolecules*, **9**, 189 (1976).
2) G. F. Ehlers, K. R. Fisch, and W. R. Powell, *J. Polym. Sci. Part A-1*, **7**, 2955 (1969).
3) D. G. Brady, *J. Appl. Polym. Sci.*, **36**, 231 (1981).
4) R. L. Elsenbaumer, L. W. Shacklette, J. W. Sowa, and R. H. Baughmam, *Mol. Cryst. Liq. Cryst.*, **83**, 229 (1982).
5) L. W. Shacklette, R. L. Elsenbaumer, R. R. Chance, H. Eckhardt, J. E. Formmer, and R. H. Baughman, *J. Phys. Chem.*, **75**, 1919 (1981).
6) F. Bertinelli, P. C. Bizzarri, C. D. Casa, and S. J. Saltini, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 2197 (1986).
7) J. T. Edomonds Jr. and H. W. Hill Jr., U.S. Patent, **1967**, 3354129; *Chem. Abstr.*, **68**, 13598 (1968).
8) R. W. Cambell and J. T. Edmonds, U.S. Patent, **1975**, 4038259; *Chem. Abstr.*, **87**, 10285v (1977).
9) M. Koch and W. Heitz, *Makromol. Chem.*, **184**, 779 (1983).
10) R. W. Lenz, C. E. Handlovits, and W. K. Carrington, *J. Polym. Sci.*, **43**, 333 (1959).
11) R. W. Lenz and C. E. Handlovits, *J. Polym. Sci.*, **43**, 167 (1960).
12) R. W. Lenz, C. E. Handlovit, and H. A. Smith, *J. Polym. Sci.*, **58**, 351 (1962).
13) C. E. Handlovit, *Macromol. Synth.*, **3**, 131 (1968—1969).
14) H. A. Smith, C. E. Handlovit, "Phenylene Sulfide Polymers," ASD-TDR 62-322", Part, I II, (1962).

15) A. D. Macallum, *J. Org. Chem.*, **13**, 154 (1949).

16) A. B. Port and R. H. Still, *J. Appl. Polym. Sci.*, **24**, 1145 (1979).

17) S. Tsunawaki and C. C. Price, *J. Polym. Sci., Part A*, **2**, 1511 (1964).

18) E. Tsuchida, K. Yamamoto, H. Nishide, and S. Yoshida, *Macromolecules*, **20**, 2030 (1987).

19) E. Tsuchida, H. Nishide, K. Yamamoto, and S. Yoshida, *Macromolecules*, **20**, 2315 (1987).

20) E. Tsuchida, K. Yamamoto, H. Nishide, S. Yoshida, and M. Jikei, *Macromolecules*, **23**, 1136 (1990).

21) J. R. Cox, Jr., C. L. Gladys, L. Field, and D. E. Pearson, *J. Org. Chem.*, **25**, 1083 (1960).

22) B. M. Trost and L. N. Jungheim, *J. Am. Chem. Soc.*, **102**, 7910 (1980).

23) G. Montaudo, C. Puglish, E. Scamporrino, and Vitalini, *Macromolecules*, **19**, 2157 (1986).

24) M. Wejchan-Judek, E. Pogalond, and A. Zuk, *Polymer*, **22**, 845 (1981).

25) M. Wejchan-Judek and E. Rogal, *Polymer*, **25**, 53 (1984).

26) A. Zuk, M. Wejchan-Judek, and E. Rogal, *Polymer*, **19**, 438 (1978).

27) V. A Sergeyev and V. I. Nedelkin, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 3153 (1986).

28) J. W. Cleary, *Polym. Sci. Technol.* (Plenum) **1985**, 159.

29) G. A. Olah, "Friedel-Crafts and Related Reaction," Interscience (1964).

30) S. Santini, G. Reichenbach, and V. Mazzucato, *J. Chem. Soc., Perkin Trans. 2*, **1974**, 494.

31) J. E. Frommer, *Acc. Chem. Rev.*, **19**, 2 (1986).

32) F. Magno, G. Bontompelli, and G. Pillon, *J. Electroanal. Chem.*, **30**, 357 (1971).

33) J. T. Wallance and A. Schriesheim, *Tetrahedron*, **21**, 2271 (1965).