Table I
Polymerization of BEMI[a]

run	initiator (mol %)	cocatalyst (mol %)	solvent	yield, %	η_{inh}
1	NaH (6)	Ac_2O (3)	CH_3CN[b]	77	
2	NaH (6)	Ac_2O (3)	DMSO	38	
3	KH[c]	PhNCO (3)		100	0.07
4	KO-*t*-Bu (2.5)			58	0.37

[a] Under argon atmosphere at 28 °C for 20 h. [b] Heterogeneous. [c] Could not be weighed accurately.

and the reaction mixture was stirred for an additional 2 h. After the toluene had been evaporated, the residue was added to 60 mL of water, containing 5.2 g (62 mmol) of $NaHCO_3$. The heterogeneous reaction mixture was stirred overnight. The mixture was extracted with 25 mL of ether. After acidification of the aqueous layer with 2 N HCl, it was again extracted with 15 mL of ether. The ether extracts were combined, washed with water, dried over Na_2SO_4, and filtered and the ether was evaporated. The residue was distilled by using a short-path distillation head; bp 103–110 °C (0.7 mmHg). A clear colorless liquid was obtained; yield, 7.15 g (68%). The product was distilled a second time and the fraction between 92 and 95 °C (0.2 mmHg) was collected. Only one spot was obtained on TLC for this fraction ($R_f = 0.76$ in Et_2O; $R_f = 0.63$ in $CHCl_3$). ^1H NMR ($CDCl_3$) δ 0.905 (t, 3 H), 1.025 (t, 3 H), 1.36 (m, 4 H), 1.70 (m, 2 H), 1.760 (g, 2 H), 8.54 (br s, NH); ^{13}C NMR ($CDCl_3$) δ 8.81 (CH_3 of Bu), 13.51 (CH_3 of Et), 22.55, 23.42, 26.63 ($3CH_2$ of Bu), 29.75 (CH_2 of Et), 69.15 (C_{quart}), 173.78 (C═O); IR (KBr) 3574, 3245 (br, NH), 2962, 2935, 2876, 1736 (vs), 1460, 1383, 1347, 1274, 1158, 1096, 967 cm^{-1}; MS (EI probe) *m*/*e* 169 (M^+, 0.4%), 141 (–CO), 127 (–CON), 126 (26%, –CONH), 98 (60%), 83 (73%), 55 (100%, $CH_3CH_2C^+CH_2$ or $CH_3C^+{=}C{=}O$). Anal. Calcd: 63.88, C; 8.93, H; 8.28, N. Found: 63.81, C; 9.17, H; 8.18, N.

Polymerization Procedure. All polymerizations were run for 20 h at room temperature under argon atmosphere. The polymers were dissolved in chloroform, preciptated in ether, filtered, dried, and weighed. The inherent viscosities were determined in chloroform at 30 °C (concentration 50 mg/10 mL). Mp 240 °C (no tg); ^1H NMR ($CDCl_3$) 3 broad peaks, δ 2.1, 1.3, 0.9; ^{13}C NMR ($CDCl_3$) δ 9.57 (CH_3 of Bu), 13.68 (CH_3CH_2), 22.50, 32.20, 38.97 (CH_2 of Bu), 38.97 (CH_3CH_2), 61.19 (C_{quart}), 170.5, 171.0, 174.8, 175.8 (C═O); IR (KBr) 3200 (br), 2960, 1760, 1470, 1420, 1205, 1145, 965, 902, 780, 631 cm^{-1}. Anal. Calcd: 63.88, C; 8.93, H; 8.28, N. Found: 63.63, C; 8.88, H; 8.29, N.

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Electrooxidative Polymerization of Thiophenol To Yield Poly(*p*-phenylene sulfide)

There is currently a great interest in coating electrodes with thin polymer films by electrooxidative polymerization of aromatics such as pyrrole,[1] thiophene,[2] aniline,[3] phenol,[4] and benzene.[5] However, electrooxidative polymerization of thiophenol has not been reported; anodic oxidation of thiophenol merely yields diphenyl disulfide. Poly(*p*-phenylene sulfide) (PPS) is commercially produced by the polycondensation of *p*-dichlorobenzene and sodium sulfide at high pressure and temperature.[6] This paper describes the electrooxidative polymerization of thiophenol in the presence of an acid to yield pure PPS efficiently at room temperature. A polymerization mechanism is also described based on electrochemical measurement.

Thiophenol was dissolved in dry nitromethane containing 1.5 M trifluoroacetic acid and kept under dry atmosphere in a one-compartment cell with a pair of platinum plates as a working and an auxiliary electrode. The electrolysis was carried out with controlled potential at 2.0 V (vs Ag/AgCl). During the electrolysis the solution around the working electrode was colored brown and white polymer was precipitated. After the electrolysis (2 F/mol) the polymer was isolated by simple filtration in a 77% yield as white powder having an empirical formula $C_6H_4S_1$. Atomic absorption analysis with the sensitivity of 10^{-3}% of the polymer sample revealed no salts such as sodium chloride with which a commercial PPS is often contaminated. The structure including the 1,4-phenylene unit was confirmed by IR spectrum.[7] The polymer was soluble in hot *N*-methylpyrrolidone and its melting point at 180–190 °C suggested a molecular weight of more than 10^3.

The polymerization also proceeded in the presence of other acids such as sulfuric acid and stannic chloride, although the polymer yield and molecular weight were influenced by the added acid and solvent species. The polymerization was inhibited by basic solvents such as methanol and *N*,*N*-dimethylformamide and by water.

The cyclic voltammogram of thiophenol in the presence of trifluoroacetic acid was measured. The first oxidation peak was observed at 1.6 V, which has been attributed[8] to the oxidation of thiophenol to yield diphenyl disulfide. The second peak current was measured at 1.8 V, which has been attributed to the oxidation of diphenyl disulfide to its cation radical, the product of which has been allowed to react nucleophilically and irreversibly with basic species such as acetonitrile as in previous work.[8] In the strongly acidic atmosphere of this experiment, it is considered that this cationic species formed by the oxidation at 1.8 V leads to the PPS formation.

The reaction mixture had a brown color during the electrolysis, which disappeared by the addition of bases. This visible absorption is enhanced in the presence of the acid. From these results, the polymerization mechanism is illustrated in Scheme I: the cation which is produced by oxidation of diphenyl disulfide is assumed to be an

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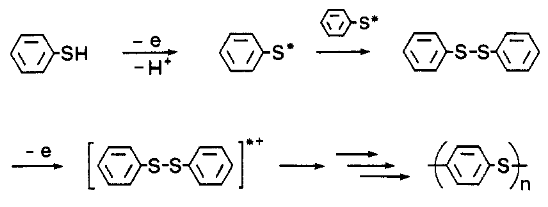
Scheme I



active species of this polymerization.

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Registry No. Thiophenol, 108-98-5; thiophenol (homopolymer), 33411-63-1; thiophenol (SRU), 25212-74-2.

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(7) Poly(p-phenylene sulfide): IR (KBr) (cm^{-1}) 3000, 3050 (ν_{C-H}); 1380, 1460, 1560 ($\nu_{C=C}$); 820 (δ_{C-H}); 480, 550, 700, 740, 1050, 1080, 1090. The absorption attributed to 1,4-substituted phenylene indicates a linear or 1,4-conjugated phenylene sulfide structure. No typical absorption in the range between 800 and 900 cm^{-1} excludes a branching and cross-linking structure.
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Photoinitiated Anionic Coordination Polymerization of Epoxides, a Novel Polymerization Process[1]

Much attention has recently been paid to the photoinitiated cationic polymerization of epoxides for its potential application in industry.[2] However, no works on the anionic counterpart appear to have been reported. Strohmeier and Barbeau[3] previously described the polymerization of propylene oxide with dimanganese decacarbonyl under UV irradiation, but the polymerization mechanism remains equivocal. We wish to report herein the first unambiguous example of photoinduced anionic coordination polymerization of epoxides.

Quite recently we have communicated a new catalyst system comprised of titanium tetraisopropoxide and phenol or its derivatives, which is highly effective for the anionic coordination polymerization of cyclohexene oxide.[1]

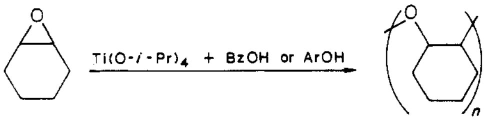
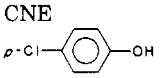
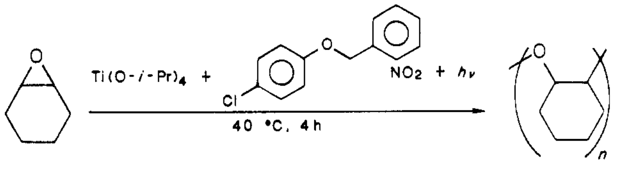


Table I
Photoinitiated Polymerization[a]

no.	catalyst	UV	ratio	yield
1	Ti(O-i-Pr)$_4$ + CNE	+	1:1	19
2	Ti(O-i-Pr)$_4$ + CNE	+	1:2	35
3	Ti(O-i-Pr)$_4$ + CNE	+	1:4	54
4	Ti(O-i-Pr)$_4$ + CNE	+	1:6	57
5	Ti(O-i-Pr)$_4$ + CNE	–	1:2	1
ref	Ti(O-i-Pr)$_4$ + 	–	1:2	88

[a] CNE = p-chlorophenyl o-nitrobenzyl ether; cyclohexene oxide, 20 mmol; Ti(O-i-Pr)$_4$ 0.02 mmol; UV irradiation, 4 h; temperature 40 °C; time, 4 h.

It was noticed that, while the ring-opening reaction itself is initiated by an isopropoxy group, the addition of phenolic derivatives is a prerequisite to control the electronic state of the titanium center for the coordination of epoxides. This fact prompted us to design those compounds that can generate phenol or its derivatives under UV irradiation. Photogeneration of alcohol[4] or silanol[2o,p] from o-nitrobenzyl derivatives was reported, so that p-chlorophenyl o-nitrobenzyl ether was prepared, which afforded p-chlorophenol quantitatively after irradiation of UV light for 4 h at 40 °C.



A representative procedure for the photoinitiated polymerization is as follows. To a mixture of titanium tetraisopropoxide (5.7 mg, 0.02 mmol) and o-nitrobenzyl p-chlorophenyl ether (21.1 mg, 0.08 mmol) was added cyclohexene oxide (1.96 g, 20 mmol) at room temperature. The mixture was stirred for 4 h at 40 °C under irradiation of ultraviolet rays. (500-W USHIO high-pressure mercury lamp, USH-500D, without filter). The polymer was obtained in 54% yield after removal of unreacted monomer. Without UV irradiation no polymer was obtained.

The yield increased with increase of the ratio of p-chlorophenyl o-nitrobenzyl ether to titanium tetraisopropoxide, but no further significant increase in the yield was observed at the ratio higher than 4 (6:1, 57%) as shown in Table I. These results are inconsistent with the fact that the yield was as high as 83% at the 2:1 ratio of p-chlorophenol to titanium tetraisopropoxide under the same conditions without UV lights. This is not only because an excess of p-chlorophenol formed during the reaction occupies the coordination sphere of the titanium metal center to inhibit the access of cyclohexene oxide to it but because the by-products formed concomitant with p-chlorophenol in the photodecomposition reaction may somehow retard the polymerization. In fact, the yield of polymer decreased when an excess of phenol was added to the system. Furthermore, the use of a photodegradated mixture of o-nitrobenzyl p-chlorophenyl ether in cyclohexane oxide involving p-chlorophenol and other components, in place of the pure p-chlorophenol, gave a polymer in a low yield under similar conditions (the ratio of p-chlorophenol formed to titanium was 4:1). Further investigations are now in progress to elucidate these factors and to explore new catalyst systems using other transition metals for photoinitiated anionic polymerization of epoxides.

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