Novel Synthesis of Poly(thioarylene)s *via* Reaction between Arenethiols and Bromo Compounds with a Free Radical Initiator

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Received March 21, 1997; Revised Manuscript Received June 30, 1997[⊗]

ABSTRACT: Poly(*p*-phenylene sulfide) (PPS) was obtained by polymerization of 4-bromobenzenethiol in the presence of a free radical initiator, which can be any aryl disulfide, although bis(4-bromophenyl) disulfide (**1**) is recommended. The PPS polymer obtained has a weight average molecular weight of 19 600 (PD = 2.8), as determined by high-temperature GPC when 1.0 mol % of **1** is used as the initiator after 96 h of reaction. Its molecular weight and structural information have also been studied by thermal analyses, elemental analyses, and a FT-IR study. Other poly(thioarylene)s were prepared by copolymerization of arenedithiols and dibromo aromatic compounds in the presence of a catalytic amount of **1** as initiator. A mechanism for the polymerizations is proposed.

Introduction

The commercial process for the manufacture of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO resin), an important engineering plastic, is based on an oxidative polymerization reaction.[1−3] The polymerization of 2,6-dimethylphenol is realized at room temperature with a copper−amine catalyst in the presence of oxygen. When the same reaction conditions were applied to benzenethiol, only diphenyl disulfide was formed.[4,5] PPO can also be prepared from the sodium salt of 4-bromo-2,6-dimethylphenol by the addition of a catalytic amount of a free radical initiator at room temperature.[6] Much more stringent conditions are required to prepare the homopolymer of benzenethiol, poly(*p*-phenylene sulfide) (PPS), compared to the preparation of PPO. PPS is commercially manufactured by a condensation reaction between 1,4-dichlorobenzene and sodium sulfide in a polar solvent, such as *N*-methylpyrrolidinone at 200−280 °C under high pressure.[7,8] Because of its outstanding thermal, oxidative, and chemical resistance, the synthesis of PPS has been extensively studied. At least four different methods have been reported for the preparation of PPS. The industrial process proceeds through a nucleophilic substitution reaction.[7] Melt copolymerization of 1,4-diiodobenzene and sulfur,[9,10] thermal polymerization of bis(4-iodophenyl) disulfide,[11] and copolymerization of cyclic(arylene disulfide) oligomers with dihaloaromatic compounds[12,13] have been described as proceeding by free radical mechanisms. The polymerization of salts of 4-bromobenzenethiol is believed to be a single-electron transfer process.[14,15] Electrophilic substitution reactions have been extensively studied by Tsuchida.[16−19]

There are two reports related to the use of a catalytic process or an initiator for the preparation of PPS. Tsuchida *et al.* reported that high molecular weight PPS was obtained via a soluble precursor by catalytic oxidative polymerization of methyl phenyl sulfide with oxygen in the presence of cerium ammonium nitrate (CAN) catalyst in the presence of strong acid.[20] The major drawbacks of this process are the need for large amounts of strong acids and the necessity for maintaining anhydrous conditions. In 1986, Novi *et al.* reported that polymerization of 4-bromobenzenethiolate was achieved in DMSO by the employment of catalytic amounts of a diazonium salt *via* a radical-anion chain pathway.[21] Because the polymerizations were carried out at room temperature and PPS is highly insoluble, it is not surprising that only oligomeric PPS was obtained with repeating units around 9 based on the elemental analyses.

In a previous communication, we briefly described a novel process for synthesis of PPS *via* self-polymerization of 4-bromobenzenethiol in the presence of a free radical initiator.[22] Herein, we further describe this novel polymerization reaction as well as the synthesis of other poly(thioarylene)s *via* a reaction between arene thiols and aromatic bromo compounds with a free radical initiator. This novel process provides PPS and poly(thioarylene)s without formation of any salt. HBr is formed as the sole side product.

Results and Discussion

Homopolymerization of 4-Bromobenzenethiol with a Free Radical Initiator. The polymerization of 4-bromobenzenethiol was achieved when a catalytic amount of free radical initiator was present in the reaction mixture (Scheme 1). The polymerization reaction was carried out in *m*-terphenyl solution at 270 °C. *m*-Terphenyl is a high-boiling solvent (bp 365 °C) that is unreactive to the thiyl radical. It can be easily removed from the products since it is very soluble in hot methanol. The purpose of using a high-boiling point solvent is to hold the monomer in solution, since the boiling point of 4-bromobenzenethiol is only 230 °C. Different initiators were used to effect the polymerization reaction, such as bis(4-bromophenyl) disulfide, cyclic disulfide oligomer **2**, diphenyl disulfide, 2,2′-dithiobis(benzothiazole), and elemental sulfur. Since 4-bromobenzenethiol can be easily transformed to bis(4-bromophenyl) disulfide by oxidants, it is conceivable that catalytic amounts of other oxidants would also be effective initiators for the polymerization reaction.

Bis(4-bromophenyl) disulfide was used as an initiator to determine suitable conditions for the polymerization of 4-bromobenzenethiol. The effect of different conditions on the polymerization are shown in Table 1. When 1 mol % of bis(4-bromophenyl) disulfide was used, the molecular weight of the PPS increased as the reaction time increased, based on the increasing glass transition temperatures (T_g) and crystallization temperatures (T_c)

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1997.

S0024-9297(97)00395-1 CCC: $14.00

Scheme 1. Polymerization of 4-Bromobenzenethiol with Different Initiators

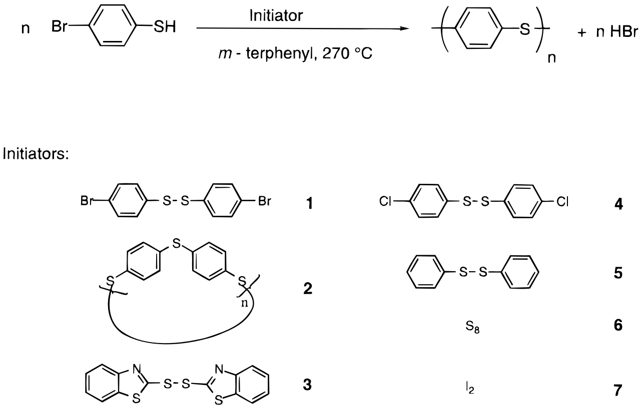


Table 1. Polymerization of 4-Bromobenzenethiol Initiated by Bis(4-bromophenyl) Disulfide[a]

no.	cat. % (mol)	time (h)	yield (%)	T_g (°C)	T_c (°C)	T_m (°C)
1	1.0	24	93	68	117	259
2	1.0	48	96	75	121	282
3	1.0	72	96	83	133	283
4	1.0	96	95	92	145	285
5	0.5	96	61	79	121	282
6	2.0	96	100	85	138	278
7	3.0	96	96	63	110	261

[a] Thermal properties were obtained by DSC at a heating rate of 20 °C/min. Samples were quenched from 350 °C on a cold metal block.

Table 2. Polymerization of 4-Bromobenzenethiol with Different Initiators

catalyst[a]	yield (%)	T_g (°C)	T_c (°C)	T_m (°C)
1	96	92	146	285
2	96	87	133	284
3	89	89	142	278
4	93	89	143	281
5	96	82	126	277
6	89	87	137	280
7	70			250

[a] The amount of initiator used was 1 mol %. The structures of the initiators are shown in Scheme 1. [b] Thermal properties were obtained by DSC at a heating rate of 20 °C/min. Samples were quenched from 350 °C on a cold metal block.

for the products obtained as measured by differential scanning calorimetry (DSC). Fagerburg *et al.* have established that T_c linearly increases with the logarithm of the degree of polymerization.[23] Although this relationship cannot be rigorously applied to PPS polymers prepared by other methods, the trend should be the same. When different amounts of initiator were used for the polymerization carried out for 96 h, 1 mol % of initiator gave the best result based on both T_g and T_c of the polymer formed. Using 0.5 mol % of initiator, a relatively high molecular weight PPS was isolated although the yield was only 61%. This is the same phenomena observed for the polymerization of salts of 4-bromobenzenethiol,[24,25] which was termed "preferential polymer formation".[24] As the amounts of initiator were increased, molecular weights of the resulting polymers were lower.

The effects of different initiators on the properties of polymers, obtained by using 1 mol % initiator and 96 h reaction time, are listed in Table 2. Several aryl disulfides were used as effective initiators for the polymerization of 4-bromobenenethiol. In all cases, flexible PPS films were obtained by the following simple technique. PPS powder (200 mg) was put on a piece of aluminum foil and the foil was folded into a rectangle around 1 × 2.5 cm. The rectangle was put on the surface of a hot plate preheated to 330 °C for 5 min and pressed with a piece of glass, then quenched immediately by dipping into cold water. After removing the aluminum foil, a flexible PPS film was obtained. However, if the sample was cooled slowly to allow the polymer to crystallize, the film appeared to be brittle, which is an indication that the polymer has a M_w less than 20 000.[26]

Table 3. Elemental Analyses and High-Temperature GPCs for PPS Polymers

		elemental analysis				GPC[a]	
PPS	initiator	C	H	S	Br	M_w	M_n
1	**1**	66.21	3.85	29.59	1.46	19 600	6900
2	**2**	66.83	3.98	30.47	1.60	15 200	5200

[a] The eluent was 1-chloronaphthalene. Polystyrenes were used as calibration standards.

Based on the T_g and T_c of the products, bis(4-bromophenyl) disulfide as an initiator gave the best results. Bis(4-bromophenyl) disulfide itself is a monomer for PPS under the conditions applied here; hence it would not act as a termination agent.

Elemental analyses for polymers from polymerization reactions initiated by bis(4-bromophenyl) disulfide and cyclic aryl disulfide oligomers **2** are listed in Table 3. By assuming both of the end groups are bromine atoms, the calculated repeating units for PPS formed by initiation with bis(4-bromophenyl) disulfide is 101 and for PPS initiated by **2** is 92. The weight average molecular weight ($M_w = 19\,600$) and number average molecular weight ($M_n = 6900$) were obtained from high temperature GPC for PPS initiated by **1**. For PPS initiated by **2**, $M_w = 15\,200$ and $M_n = 5200$ were obtained.

The empirical formula for PPS **1** is $C_{6.0}H_{4.1}SBr_{0.02}$ and for PPS **2** is $C_{5.9}H_{4.2}SBr_{0.02}$. These empirical formulas indicate that PPS obtained from polymerization of 4-bromobenzenethiol initiated by bis(4-bromophenyl) disulfide does not contain any significant amount of disulfide linkages. However, PPS initiated by cyclic aryl disulfide oligomers may contain small amounts of disulfide linkages.[27] Therefore, bis(4-bromophenyl) disulfide is strongly recommended as the initiator of choice for the polymerization of 4-bromobenzenethiol. When iodine was used as an initiator, only very low molecular weight oligomers were obtained. This is presumably due to the high reducing capability of HI, which would terminate the chain reaction.

The polymers obtained from polymerization of 4-bromobenzenethiol have been analyzed by FT-IR. All of the polymers obtained show IR spectra identical to those of PPS obtained by other methods.[9,28]

Polymerization reactions were also attempted with 4-chlorobenzenethiol. When 1.0 mol % of **2** was used as an initiator, only low molecular weight PPS oligomers with T_g of 55 °C, T_c of 97 °C, and T_m of 270 °C were obtained. This low efficacy of the polymerization compared to 4-bromobenzenethiol is due to the low reactivity of the aryl chloride and the very high reactivity of chlorine radical intermediates.

Copolymerization of Arenedithiols with Dibromoarylenes. 4-Bromobenzenethiol is an AB type monomer. This free radical initiated polymerization can also be extended to AA, BB type monomers. 4,4′-Thiobis(benzenethiol), was chosen to demonstrate the polymerization reaction. 1,4-Dibromobenzene, bis(4-

Scheme 2. Copolymerization Reactions between Arenedithiol 8 and Dibromo Compounds

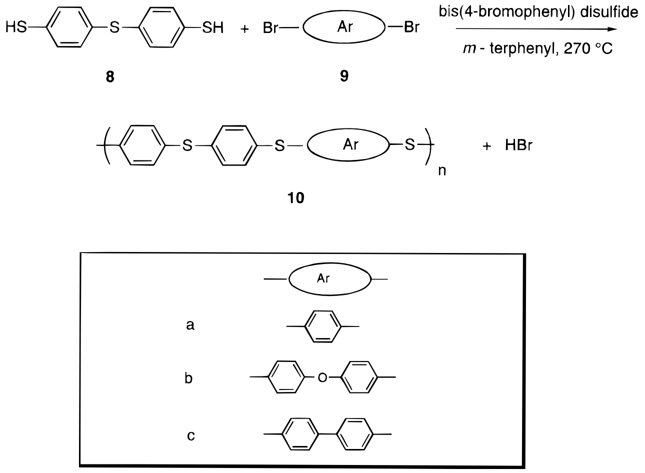


Table 4. Copolymerizations of 4,4′-Thiobis(benzenethiol) with Dibromo Compounds Initiated with Bis(4-bromophenyl) Disulfide

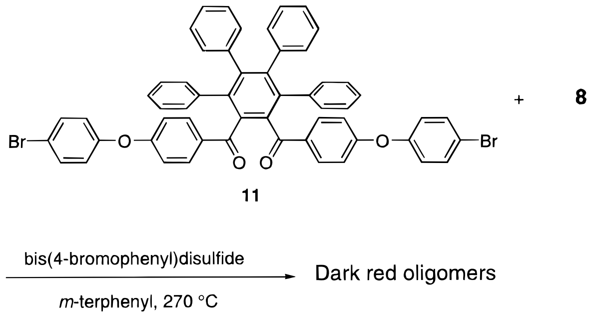
polymer	yield (%)	T_g (°C)	T_c (°C)	T_m (°C)
10a	90	92	137	271
10b	90	83	155	223
10c	97	113		

[a] Thermal properties were obtained by DSC at a heating rate of 20 °C/min. The samples were quenched from 350 °C on a cold metal block.

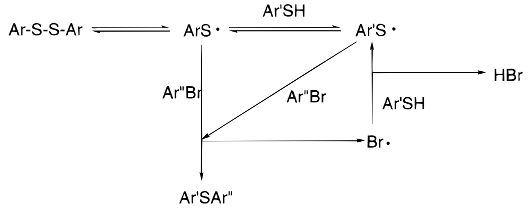
bromophenyl) ether, and 4,4′-dibromobiphenyl were used as comonomers. The polymerization reaction is shown in Scheme 2. The amount of initiator used was 2.0 mol % based on the amount of one monomer, and the reaction time was 96 h. The polymerization temperature was 270 °C. These polymerization conditions were not optimized. Since each monomer contained 2 equiv of mercapto groups, we used 2 mol % of initiator based on the amount of one monomer to compare with the polymerization conditions for 4-bromobenzenethiol. The polymers obtained were characterized by DSC, and the thermal properties are listed in Table 4. All of the polymers are insoluble in common organic solvents, but all are soluble in 1-chloronaphthalene at 200 °C. PPS obtained via this copolymerization reaction has a very high T_g (92 °C), which indicates the polymer has a relatively high molecular weight. Polymer **10b** has a T_g of 83 °C, which is comparable to that of polymer prepared from cyclic arylene disulfide oligomers **2** and bis(4-bromophenyl) ether.[13] The FT-IR (KBr) spectrum of this polymer shows a strong absorption at 1234 cm^{-1}, which is attributed to stretching of $-C-O-C-$ bonds. Polymer **10c** has a T_g of 113 °C, which is higher than that reported by Park *et al.*,[29,30] while it is comparable to that of polymer prepared from cyclic disulfide and 4,4′-dibromobiphenyl.[13]

Attempts to copolymerize 4,4′-thiobis(benzenethiol) with **11** were unsuccessful (Scheme 3), although the intended polymer was previously obtained from copolymerization of cyclic disulfide oligomers **2** and **11**.[13] In this case, dark red oligomers were isolated. Apparently, there are some side reactions between the dithiol and ketone groups in **11**, which prevents the formation of polymer.

Scheme 3. Attempted Polymerization between an Arenedithiol and a Ketone-Containing Monomer



Scheme 4. Proposed Mechanism for Polymerization between Arenethiols and Bromo Compounds



Polymerization Mechanism. One of the earliest methods used to prepare PPS was the polymerization of salts of 4-bromobenzenethiol.[24] This polymerization reaction has been described as a single-electron transfer process.[14,15] We have previously reported that bis(4-iodophenyl) disulfide on heating above 220 °C yields linear high molecular weight PPS along with elemental iodine.[11] This reaction is believed to operate by a free radical *ipso*-substitution mechanism.[11,31,32] When bis(4-bromophenyl) disulfide is heated, bromination of the solvent or oligomers occurs. Therefore, it is not suprising that the attempted polymerization of bis(4-bromophenyl) disulfide itself gave either no polymerization[33] or very low molecular weight products.[11] However, high molecular weight polymers are formed if iodide ion is added to reduce the bromine radicals. By analogy, it appears that bromine radicals generated from reaction of bis(4-bromophenyl) disulfide would react with the thiol group to generate HBr and thiyl radical. The chain reaction then continues, and high molecular weight polymers are formed. The bromine radical plays a key role here (Scheme 4) by oxidation of the arenethiol to form a new thiyl radical with evolution of HBr.

Experimental Section

Measurements. DSC analyses were conducted on a Seiko 220 DSC instrument at a heating rate of 20 °C/min in a nitrogen atmosphere (160 mL/min). Elemental analyses (C, H, S, and Br) were performed by Galbraith Laboratories, Inc. (Knoxville, TN). FT-IR spectra were measured with an Analect AQS-18 FTIR spectrometer and data were recorded with an Analect MAP-67 data system. High-temperature GPC analyses were carried out on a Senshu Kagaku Model VHT-GPC SSC-7000 with a Soma Optics S-3750 UV/vis absorption detector set at 360 nm. Two Shodex AT80M/A columns and an AT-800P column from Showa Denko were installed. 1-Chloronaphthalene was used as the eluent, and the flow rate was 1 mL/min. The temperatures of the column oven, the transfer line, and the flow cell were regulated at 210 °C. Polystyrene standards substituted by a fluorescent pyrene group were used as calibrating references.

Materials. 4-Bromobenzenethiol was purchased from Lancaster Synthesis Inc. and recrystallized from chloroform under a N_2 atmosphere. *m*-Terphenyl, 1,4-dibromobenzene, sublimed sulfur, sublimed iodine, and bis(4-bromophenyl) ether were purchased from Aldrich Chemical Inc. and used as received. 4,4′-Dibromobiphenyl, diphenyl disulfide, and 2,2′-dithiobis(benzothiazole) were obtained from commercial sources and were all recrystallized from absolute ethanol. Bis(4-bromophenyl) disulfide was prepared from benzenethiol and bromine.[34] Cyclic aryl disulfide oligomers **2** were synthesized according to a previously reported method.[5] Compound **11** was synthesized from bis(4-fluorobenzoyl)-3,4,5,6-tetraphenylbenzene as described previously.[13]

Polymerization of 4-Bromobenzenethiol. A typical example is given as follows. 4-Bromobenzenethiol (1.000 g, 5.29 mmol), bis(4-bromophenyl) disulfide (0.0199 g, 0.0529 mmol), and *m*-terphenyl (1.0 g) were charged in a Pyrex test tube (1.5 × 15 cm), and the test tube was placed in a salt bath preheated to 270 °C so that the contents were immersed to a depth of around 2 cm. The test tube was capped with a septum, and a slow flow of N_2 was passed through. Upon completion of the reaction (96 h), 3 mL of 1-chloronaphthalene was added to dilute the reaction mixture. The contents were poured into 200 mL of methanol to precipitate out the polymer. The methanol solution was heated to boiling and filtered. A white powder (0.54 g, yield 95%) was obtained after washing with 30 mL of hot $CHCl_3$, 30 mL of methanol, and drying at 100 °C in vacuo for 24 h.

Copolymerization of 4,4′-Thiobis(benzenethiol) with Dibromo Compounds. A typical example is given as follows. 4,4′-Thiobis(benzenethiol) (0.5 g, 2.0 mmol), 1,4-dibromobenzene (0.4710 g, 2.0 mmol), bis(4-bromophenyl) disulfide (0.0145 g, 0.04 mmol), and *m*-terphenyl (1.0 g) were charged in a Pyrex test tube (1.5 × 15 cm), and the test tube was placed in a salt bath preheated to 270 °C so that the contents were immersed to a depth of around 2 cm. The test tube was capped with a septum, and a slow flow of nitrogen was passed through. Upon completion of the reaction (96 h), 3 mL of 1-chloronaphthalene was added to dilute the reaction mixture. The contents were poured into 200 mL of methanol to precipitate out the polymer. The methanol solution was heated to boiling and filtered. A white powder (0.56 g, yield 90%) was obtained after washing with 30 mL of hot chloroform and 30 mL of methanol and drying at 100 °C in vacuo for 24 h.

Acknowledgment. This research was supported by the Natural Sciences and Engineering Research Council of Canada. We are indebted to Prof. E. Tsuchida and Dr. K. Miyatake of Waseda University, Japan, for the high-temperature GPC measurements.

References and Notes

(1) Hay, A. S.; Blanchard, H. S.; Endres, G. F.; Eustance, J. W. *J. Am. Chem. Soc.* **1959**, *81,* 6335.
(2) Hay, A. S. *J. Polym. Sci.* **1962**, *58,* 581.
(3) Hay, A. S. U.S. Patent 4,028,341, 1977.
(4) Hay, A. S. U.S. Patent 3294760, 1966.
(5) Ding, Y.; Hay, A. S. *Macromolecules* **1996**, *29,* 6386.
(6) Staffin, G. D.; Price, C. C. *J. Am. Chem. Soc.* **1960**, *82,* 3632.
(7) Fahey, D. R.; Ash, C. E. *Macromolecules* **1991**, *24,* 4242.
(8) Lopez, L. C.; Wilkes, G. L. *Rev. Makromol. Chem. Phys.* **1989**, *C29,* 83.
(9) Rule, M.; Fagerburg, D. R.; Watkins, J. J.; Lawrence, P. B. *Makromol. Chem., Rapid Commun.* **1991**, *12,* 221.
(10) Lowman, D. W.; Fagerburg, D. R. *Macromolecules* **1993**, *26,* 4606.
(11) Wang, Z. Y.; Hay, A. S. *Macromolecules* **1991**, *24,* 333.
(12) Ding, Y.; Hay, A. S. *Macromolecules* **1996**, *29,* 4811.
(13) Ding, Y.; Hay, A. S. *Macromolecules* **1997**, *30,* 2527.
(14) Archer, A. C.; Lovell, P. A. *Polymer* **1995**, *36,* 4315.
(15) Archer, A. C.; Lovell, P. A. *Polymer* **1995**, *36,* 4327.
(16) Miyatake, K.; Jikei, M.; Yamamoto, K.; Tsuchida, E. *Makromol. Chem.* **1996**, *197,* 595.
(17) Tsuchida, E.; Yamamoto, K.; Jikei, M.; Nishide, H. *Macromolecules* **1990**, *23,* 930.
(18) Tsuchida, E.; Shouji, E.; Yamamoto, K. *Macromolecules* **1993**, *26,* 7144.
(19) Yamamoto, K.; Jikei, M.; Miyatake, K.; Katoh, J.; Nishide, H.; Tsuchida, E. *Macromolecules* **1994**, *27,* 4312.
(20) Tsuchida, E.; Suzuki, F.; Shouji, E.; Yamamoto, K. *Macromolecules* **1994**, *27,* 1057.
(21) Novi, M.; Petrillo, G.; Sartirana, M. L. *Tetrahedron Lett.* **1986**, *27,* 6129.
(22) Ding, Y.; Hay, A. S. *Macromolecules* **1997**, *30,* 1849.
(23) Fagerburg, D. R.; Watkins, J. J.; Lawrence, P. B. *Macromolecules* **1993**, *26,* 114.
(24) Lenz, R. W.; Handlovits, C. E.; Smith, H. A. *J. Polym. Sci.* **1962**, *58,* 351.
(25) Port, A. B.; Still, R. H. *J. Appl. Polym. Sci.* **1979**, *24,* 1145.
(26) One of the referees has pointed out that a film of PPS with a M_w less than 20 000 prepared by this way is brittle if allowed to crystallize, based on his personal experience. A flexible PPS film can be obtained with a M_w higher than 20 000.
(27) Cyclic(arylene disulfide) oligomers form PPS poly(arylene disulfide)s by a ring-opening polymerization reaction, see: Ding, Y.; Hay, A. S. *Polymer* **1997**, *38,* 2239. An equilibrium exists between diphenyl disulfide and diphenyl sulfide at around 300 °C (see: Harpp, D. N.; Kader, H. A.; Smith, R. A. *Sulfur Lett.* **1982**, *1,* 59 and references therein). The use of a cyclic(arylene disulfide) as an initiator introduces a small excess of sulfur in the resulting polymer, which would probably be present as disulfide linkages or terminal SH groups.
(28) Tsuchida, E.; Yamamoto, K.; Shouji, E. *Macromolecules* **1993**, *26,* 7389.
(29) Park, L. S.; Lee, S. C.; Nam, J. I. *Polymer* **1996**, *37,* 1339.
(30) Park, L. S.; Lee, S. C.; Nam, J. I. *J. Polym. Sci., Polym. Chem. Ed.* **1996**, *34,* 2117.
(31) Benati, L.; Camaggi, C. M.; Zanardi, G. *J. Chem. Soc., Perkin. Trans. 1* **1972**, 2817.
(32) Tsuchida, E.; Yamamoto, K.; Jikei, M.; Miyatake, K. *Macromolecules* **1993**, *26,* 4113.
(33) Lovell, P. A.; Still, R. H. *Br. Polym. J.* **1990**, *22,* 27.
(34) Handlovits, C. E. *Macromol. Synth.* **1968**, *3,* 132.

MA970395F