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Synthesis of Aromatic Polythioethers Containing 1,3,5-Triazine Ring by Aromatic Nucleophilic Substitution Polymerization

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SYNTHESIS OF AROMATIC POLYTHIOETHERS CONTAINING 1,3,5-TRIAZINE RING BY AROMATIC NUCLEOPHILIC SUBSTITUTION POLYMERIZATION

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ABSTRACT

Reaction of 2,4-dichloro-6-phenyl-1,3,5-triazines with bis(4-mercaptophenyl) sulfide in the presence of a base in THF afforded the corresponding condensation polymer as a whole aromatic polythioether in moderate yield. The polymerization of several 2,4-dichloro-1,3,5-triazine derivatives with this dithiols also proceeded in the *o*-dichlorobenzene–water two-phase system by using phase transfer catalysts. The resulting polymers consisted of THF-soluble and -insoluble fractions. The x-ray diffraction pattern indicated that these THF-insoluble polymers have a highly crystalline nature. Further, the polymers obtained here showed high thermal stability.

INTRODUCTION

Recently considerable attention has been focused on poly(aromatic sulfides) due to their excellent thermal, chemical, and mechanical properties. Most of these have been synthesized by aromatic nucleophilic substitution polymerization at elevated temperature and high pressure in dipolar aprotic solvents [1–5]. This kind of condensation was found to proceed smoothly at room temperature by using aromatic dichlorides activated with electron-withdrawing groups and aromatic dithiols

by Imai et al. [6]. More recently, Tsuchida et al. successfully prepared polyphenylene sulfides by cationic oxidative polymerization of diphenyl disulfide [7–12] and by self-condensation of methyl(*p*-thiophenoxy)phenyl sulfoxide [13].

It is well known that π -electron-deficient aromatic halides easily undergo aromatic substitution reaction. Based on this fact, we performed the condensation polymerization of alkanedithiols with dichloropyridine [14] and with dichloro-1,3,5-triazines [15]. In this paper we describe the synthesis of new, wholly aromatic sulfides from the reaction of 2,4-dichloro-1,3,5-triazines with bis(4-mercaptophenyl) sulfide (BMPS) under mild conditions.

EXPERIMENTAL

Materials

2,4-Dichloro-6-phenyl-1,3,5-triazine (T1) was prepared according to Alber's method [16]; mp 120°C. 2,4-Dichloro-6-phenylamino-1,3,5-triazine (T2) was prepared by the reaction of cyanuric chloride with aniline [17]; mp 136°C. 2,4-Dichloro-6-(*N*-methyl-*N*-phenyl)amino-1,3,5-triazine (T3) and 2,4-dichloro-6-(*N,N*-diphenyl)amino-1,3,5-triazine (T4) were prepared by the reaction of cyanuric chloride with *N*-methylaniline and diphenylamine, respectively [17]; mp 133°C for T3, 176°C for T4. 2,4-Dichloro-6-phenoxy-1,3,5-triazine (T5) was prepared by the reaction of cyanuric chloride with sodium phenoxide [18]; mp 114°C. 2,4-Dichloro-6-phenylmercapto-1,3,5-triazine (T6) was prepared by the reaction of cyanuric chloride with sodium thiophenoxide [19]; mp 69°C. Bis(4-mercaptophenyl) sulfide (BMPS) was prepared according to Dutta's method [20]; mp 115°C.

Reaction of T1 with Thiophenol in the Presence of a Base in THF

To a slurry of sodium hydride (~60% oil suspension, 0.40 g, 10 mmol) and THF (30 mL) was added thiophenol (1.10 g, 10 mmol) at 0°C. To this mixture a solution of T1 (1.13 g, 5 mmol) in THF (20 mL) was added slowly at 0°C and allowed to react with stirring at room temperature for 5 hours. The reaction mixture was poured into a large amount of water, extracted with methylene chloride, and dried. After removal of the solvent, the resulting residue was purified by column chromatography (Wakogel C-200, methylene chloride as eluent). The yield was 1.53 g (99%). The physical and spectral data of the product agreed with those of an authentic sample of 2,4-bis(phenylthio)-6-phenyl-1,3,5-triazine [21].

Reaction of T1 with Sodium Thiophenoxide under Phase Transfer Conditions

A mixture of T1 (1.211 g, 3 mmol) in *o*-dichlorobenzene (15 mL), thiophenol (6.61 g, 6 mmol), 5% NaOH (aq) (5 mL), and tetra-*n*-butylammonium hydrogen sulfate (0.204 g, 0.6 mmol) was stirred at room temperature. After 20 hours the organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure to give a white solid in 1.03 g yield (92%). The IR spectrum of this solid was in complete agreement with

that of the compound obtained from the reaction of sodium thiophenoxide with T1 in THF.

Condensation Polymerization in THF

A typical experiment was as follows. In a three-necked flask equipped with a stirrer and a reflux condenser were placed sodium hydride (0.24 g, 10 mmol) and THF (100 mL). DMPS (1.252 g, 5 mmol) was added slowly to this mixture and stirred for 30 minutes. Then T1 (2.018 g, 5 mmol) was added and refluxed for 20 hours with stirring. After the reaction was finished, the reaction mixture was poured into a 5% HCl solution (300 mL). The resulting solid was filtered and dried. The solid was dissolved in THF and filtered to give a white solid (P1b) in 0.20 g yield (9.8%). The solvent was removed from the THF solution under reduced pressure, and the residue was reprecipitated with ether to give P1a in 1.91 g yield (94%).

Condensation Polymerization under Phase Transfer Conditions

A typical experiment was as follows. In a 50-mL flask equipped with a reflux condenser and a magnetic stirrer were placed T1 (1.211 g, 3 mmol), DMPS (0.751 g, 3 mmol), tetra-*n*-butylammonium hydrogen sulfate (0.206 g, 0.6 mmol), and *o*-dichlorobenzene (15 mL). A 5% sodium hydroxide solution was added to this solution and stirred for 20 hours at 100°C. After the reaction was finished, the mixture was poured into a 5% HCl solution (200 mL). The organic layer was separated and poured into acetone (200 mL). The precipitated solid was filtered and washed thoroughly with water. The solid was dissolved in THF and filtered to give a white solid (P1b) in 0.654 g yield (54%). The solvent was removed from the THF solution under reduced pressure, and the resulting residue was reprecipitated with ether to give P1a in 0.351 g yield (29%).

Measurements

IR spectra were measured with a Hitachi-285 spectrometer. Differential scanning calorimeter (DSC) curves were obtained by using a Rigaku 8131-BL. Thermogravimetry (TG) was performed with a Rigaku-Denki TG-DTA 8112 thermogravimeter. X-ray diffraction diagrams were taken with powdered samples by using CuK α radiation with a Rigaku 4032-A2 diffractometer. The number-average molecular weight (\bar{M}_n) and weight-average molecular weight (\bar{M}_w) were determined by means of gel permeation chromatography by using polystyrene calibration standards on a Tosoh-HLD803 apparatus.

RESULTS AND DISCUSSION

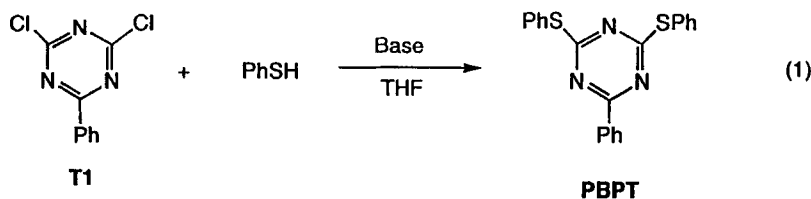
As a model reaction of the condensation polymerization, the reaction of 2,4-dichloro-6-phenyl-1,3,5-triazine (T1) with thiophenol was first examined at room temperature. The results are summarized in Table 1. When the reaction was carried out in THF for 5 hours in the presence of a base such as sodium hydride, sodium hydroxide, or collidine, 2-phenyl-4,6-bis(phenylthiol)-1,3,5-triazine (PBPT) was

TABLE 1. Reaction of T1 with Thiophenol at Room Temperature^a

Run	Base	Solvent	Time, hours	Catalyst	Yield of PBPT, %
1	None	THF	5	None	17
2	NaH	THF	5	None	99
3	NaOH	THF	5	None	89
4	Collidine	THF	5	None	96
5	NaOH	<i>o</i> -DCB/H ₂ O	5	None	25
6	NaOH	<i>o</i> -DCB/H ₂ O	5	<i>n</i> -Bu ₄ N ⁺ HSO ₄ ⁻	80
7	NaOH	<i>o</i> -DCB/H ₂ O	20	<i>n</i> -Bu ₄ N ⁺ HSO ₄ ⁻	92
8	NaOH	<i>o</i> -DCB/H ₂ O	20	<i>n</i> -Bu ₄ P ⁺ Br ⁻	90
9	NaOH	<i>o</i> -DCB/H ₂ O	20	Ph ₄ P ⁺ Br ⁻	89

^aReaction conditions. For Runs 1–4: THF = 50 mL, T1 = 5 mmol, thiophenol = 10 mmol, base = 10 mmol. For Runs 5–9: *o*-DCB (*o*-dichlorobenzene) = 15 mL, H₂O = 5 mL, NaOH = 6.3 mmol, thiophenol = 6 mmol, catalyst = 0.6 mmol.

obtained in high yield without detectable side reactions (Table 1). This reaction also proceeded cleanly even under *o*-dichlorobenzene–water two-phase conditions in the presence of tetra-*n*-butylammonium hydrogen sulfate as a phase transfer catalyst to afford the substitution product PBPT. The yield was very low in the absence of catalyst. Tetra-*n*-butylphosphonium bromide and tetraphenylphosphonium bromide were also good catalysts for this reaction.



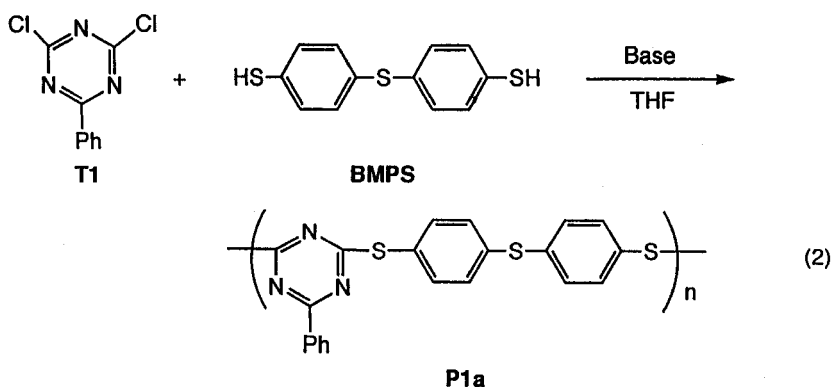
Under conditions similar to the model reaction, polycondensation of T1 with bis(4-mercaptophenyl) sulfide (BMPS) in the presence of sodium hydride in THF at room temperature for 20 hours afforded the corresponding polymers (P1a) with a reduced viscosity of 0.09 dL/g in quantitative yield. The structure was confirmed by comparing its IR spectrum with that of PBPST. The IR spectrum exhibited characteristic bands at 840 cm⁻¹ based on the 1,3,5-triazine ring and 810 cm⁻¹ based on the phenylene group. Elemental analysis also supported the structure described in Eq. (2). This polymer was soluble in THF and chloroform, but insoluble in *n*-hexane, ether, acetone, and methanol. When the reaction was carried out at reflux temperature, the yield and the viscosity were slightly increased. However, the use of sodium hydroxide and collidine instead of sodium hydride did not increase the viscosity of the polymer (Table 2).

TABLE 2. Condensation Polymerization of T1 with DMPS in THF^a

Base	Temperature	Yield of P1a, %	η_{sp}/C , ^b dL/g
NaH	RT	55	0.09
NaH	Reflux	85	0.11
NaOH	Reflux	72	0.08
Collidine	Reflux	84	0.07

^aReaction conditions: THF = 50 mL, T1, DMPS = 5 mmol, base = 10 mmol, time = 20 hours.

^b0.2 g/dL in H₂SO₄ at 30°C.



This condensation polymerization was also performed in a liquid-liquid two-phase system in the presence of tetra-*n*-butylammonium hydrogen sulfate as a phase transfer catalyst. When this reaction was carried out in the *o*-dichlorobenzene-water system at room temperature for 20 hours, an insoluble polymer in THF (P1b) was produced in 31% yield together with the soluble polymer (P1a) (12%). P1b was not soluble in common solvents or dipolar aprotic solvents, although it was readily soluble in sulfuric acid and trifluoroacetic acid. The IR spectrum of P1b was very similar to that of P1a. Elemental analysis also satisfied the structure of the condensation polymer. Further, the reduced viscosity of P1b in sulfuric acid was somewhat higher than that of P1a. When the reaction was carried out at reflux temperature, the polymer yields of P1a and P1b were increased, and the viscosities were also increased slightly. The relationship between the polymer yield and amount of catalyst was also examined. As can be seen from Table 3, the use of 20 mol% of catalyst is most suitable in this condensation. In addition, under these conditions the polymer yield was not high although the starting materials had already been consumed. This was due to the production of a large amount of oligomers.

Next, dichlorotriazines carrying several substituents such as anilino, *N*-methylanilino, diphenylamino, phenoxy, and thiophenoxy groups (T2-T6) were used as monomers. Polymerization of these monomers with BMPS under two-phase

TABLE 3. Condensation Polymerization of T1 with DMPS Catalyzed by Phase Transfer Catalysts^a

Catalyst	[Catalyst]/[T1]	Temperature, °C	Yield, %		η_{sp}/C^b	
			P1a	P1b	P1a	P1b
<i>n</i> -Bu ₄ N ⁺ HSO ₄ ⁻	0.2	RT	12	31	0.18	0.19
	0.2	100	29	54	0.19	0.23
	0.4	100	37	46	0.18	0.21
	0.1	100	21	40	0.13	0.16
	0.02	100	29	5	0.14	0.16
<i>n</i> -Bu ₄ P ⁺ Br ⁻	0.2	100	25	53	0.15	0.17
Ph ₄ P ⁺ Br ⁻	0.2	100	25	58	0.15	0.18

^a*o*-Dichlorobenzene = 15 mL, 5% NaOH (aq) = 5 mL, T1, DMPS = 3 mmol, time = 20 hours.

^b0.2 g/dL in H₂SO₄ at 30°C.

conditions in the presence of a phase transfer catalyst proceeded smoothly to give the corresponding polymers. The results are summarized in Tables 4 and 5. In the polymerizations of T2 with BMPS, a THF-soluble polymer with the highest molecular weight ($\bar{M}_w = 25,900$, $\bar{M}_n = 8300$) was obtained. This may be due to the high solubility of the resulting polymer compared with other polymers. In these polymerizations the yield of THF-insoluble polymers was higher than that of the corresponding THF-soluble polymers.

TABLE 4. Condensation Polymerization of 2,4-Dichloro-6-substituted-1,3,5-triazines with DMPS Catalyzed by Tetra-*n*-butylammonium Hydrogen Sulfate under Two-Phase Conditions^a

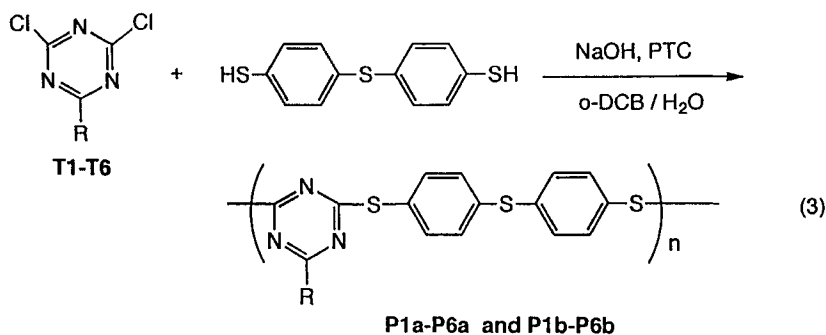
Monomer	Yield, %		η_{sp}/C^b	
	PXa	PXb	PXa	PXb
T1	29	54	0.19	0.23
T2	38	37	0.31	0.54
T3	5	89	0.11	0.18
T4	19	63	0.09	0.11
T5	65	0	0.52	—
T6	17	67	0.08	0.42

^a*o*-Dichlorobenzene = 15 mL, 5% NaOH (aq) = 5 mL, TX, DMPS = 3 mmol, [*n*-Bu₄N⁺HSO₄⁻]/[TX] = 0.2, temperature = 100°C, time = 20 hours.

^b0.2 g/dL in H₂SO₄ at 30°C.

TABLE 5. Elemental Analysis of Polytriazinylsulfides^a

Polymer		%C	%H	%N	%S
P1	Calcd	62.50	3.25	10.41	23.84
P1a	Found	60.48	3.53	9.17	23.12
P1b	Found	61.87	3.19	9.95	23.29
P2	Calcd	60.26	3.37	13.38	22.98
P2a	Found	60.20	3.45	12.52	22.43
P2a	Found	59.98	3.39	12.62	22.61
P3	Calcd	61.08	3.73	12.95	22.24
P3a	Found	60.38	3.67	12.36	20.99
P3b	Found	60.55	3.72	12.46	21.52
P4	Calcd	65.56	3.67	11.33	19.45
P4a	Found	64.11	3.98	10.16	17.14
P4b	Found	64.49	3.67	10.71	18.26
P5	Calcd	60.10	3.13	10.02	22.94
P5a	Found	59.27	2.76	9.77	23.48
P6	Calcd	57.88	3.01	9.65	29.45
P6a	Found	55.94	2.74	9.36	27.50
P6b	Found	57.02	2.88	9.21	29.30

^aPrepared under two-phase conditions.

	R
T1, P1a, P1b	C ₆ H ₅
T2, P2a, P2b	C ₆ H ₅ NH
T3, P3a, P3b	C ₆ H ₅ (CH ₃)N
T4, P4a, P4b	(C ₆ H ₅) ₂ N
T5, P5a	C ₆ H ₅ O
T6, P6a, P6b	C ₆ H ₅ S

In all cases the viscosities of THF-insoluble polymers were somewhat higher than those of the corresponding THF-soluble polymers. So the differences in the solubilities may be due to the molecular weight of the polymers, but the differences

TABLE 6. Thermal Behavior
Data of Polytriazinylsulfides^a

Polymer	mp, °C	T_d , °C
1a		389
1b	204, 225	412
2a		346
2b	231	352
3a		368
3b	162, 229	377
4a		326
4b		381
5a		397
6a		393
6b		394

^aDetermined by TG and DSC at a heating rate of 10°C/min in air.

in molecular weights are too small. Another reason may be differences in the crystalline natures of these polymers.

In order to confirm this point, P1a and P1b were subjected to wide-angle x-ray diffraction measurement by the powder method using nickel-filtered $\text{CuK}\alpha$ radiation. Polymer P1b exhibited one strong major peak reflection at 20° (2θ) and minor several peaks, indicating a high crystalline nature. The pattern of P1a showed a weaker crystalline nature.

Thermogravimetry (TG) of these polymers was carried out at a heating rate of 10°C/min. The initial losses of P1a and P1b occurred at 389 and 412°C, respectively. The DSC data curve of P1b exhibited two sharp endotherms at 204 and 225°C, although a clear melting point was not observed for P1a. The thermal behaviors of these condensation polymers are summarized in Table 6. The melting point was not observed for P4b and P5b, and the initial decomposition temperature was slightly reduced by introducing the phenylamino, phenoxy, and phenylmercapto groups instead of the phenyl group.

CONCLUSION

Aromatic polythioethers containing the 1,3,5-triazine ring were readily prepared by aromatic nucleophilic substitution polymerization of dichlorotriazines with an aromatic dithiol in the presence of a base in THF or liquid-liquid two-phase systems. The resulting polymers have a crystalline nature and high thermal stability.

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