Aromatic Nucleophilic Substitution Polymerization of Dichloro-1,3,5-Triazines with Alkanedithiols

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AROMATIC NUCLEOPHILIC SUBSTITUTION POLYMERIZATION OF DICHLORO-1,3,5-TRIAZINES WITH ALKANEDITHIOLS

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ABSTRACT

Reaction of 2,4-dichloro-6-phenyl-1,3,5-triazine with alkane-dithiols in the presence of a base in THF afforded the corresponding condensation polymers containing triazinylthio group in moderate yields. This polymerization reaction 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. When the reaction was carried out at a higher temperature or for a longer reaction time, the yield of the insoluble polymer was increased. The THF-soluble polymers were also soluble in toluene, and they had the ability to extract sodium and potassium ions from aqueous picrates. The polymers functioned as catalysts for substitution reactions of an alkyl bromide and the reduction of a ketone with sodium borohydride under liquid–liquid phase transfer conditions with a reactivity superior to that of the monomeric analog.

INTRODUCTION

Halobenzenes not activated by electron-withdrawing substituents are inert to the usual nucleophilic reagents. Therefore, in aromatic nu-

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cleophilic substitution polymerizations, aryl halides carrying groups such as cyano, nitro, carbonyl, and sulfonyl have been employed as monomers [1-7]. On the other hand, several transition metal catalyzed condensation polymerizations have recently been reported for nonactivated dihaloben-zenes [8-12]. Previously, we found that the condensation polymerization of 2,6-dichloropyridine with alkanedithiols proceeded smoothly in dipo-lar aprotic solvents [13], and the resulting polymers functioned as phase-transfer catalysts for liquid–liquid two-phase reactions due to the strong interaction of the pyridylthio group with alkali metal cations [14, 15].

It is well known that chlorine atoms attached directly to 1,3,5-triazine rings are reactive and can be displaced readily and successively if suitable conditions are used by nucleophilic reagents [16]. Therefore, we anticipat-ed that dichloro-1,3,5-triazines would function analogously in aromatic substitution polymerizations. In support of this idea, it has been reported that the reaction of dichlorotriazines with diamines or Bisphenol A gave the corresponding polymers [17–22].

This paper describes the condensation polymerization of 2,4-dichloro-1,3,5-triazines with alkanedithiols under mild conditions, and it also examines the catalytic activity of the polymers in phase-transfer reactions.

EXPERIMENTAL

Materials

2,4-Dichloro-6-phenyl-1,3,5-triazine (1a) was prepared according to Alber's method [23]; mp 120°C ([23], 121°C). 2,4-Dichloro-6-phenoxy-1,3,5-triazine (1b) was prepared by the reaction of cyanuric chloride with sodium phenoxide; mp 114°C ([24], 114°C). 2,4-Dichloro-6-phenyl-mercapto-1,3,5-triazine (1c) was prepared by the reaction of cyanuric chloride with sodium thiophenoxide; mp 69°C ([25], 72–73°C). n-Octyl bromide, acetophenone, and solvents were distilled before use. Other reagents were obtained commercially and used without further purifica-tion.

Reaction of 1a with Sodium Ethanethiolate in THF

To a slurry of sodium hydride (∿60% oil suspension, 1.3 g, 33 mmol) and THF (25 mL) was added ethanethiol (1.86 g, 30 mmol) at 0°C. To

this mixture a solution of 1a (2.26 g, 10 mmol) in THF (50 mL) was added slowly at 0°C and further allowed to react with stirring at room temperature for 10 h. The reaction mixture was poured into a large amount of water, extracted with chloroform, 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 2.69 g (97%). NMR (in CDCl$_3$): δ = 1.40 (t, 6H), 3.25 (q, 4H), 7.55 (m, 3H), and 8.55 ppm (m, 2H). IR: 790, 825, 855, 975, 1245, 1320, 1380, 1445, 1490, 1590, 1605, and 2925 cm^{-1}.

Analysis. Calculated for C$_{13}$H$_{15}$N$_3$S$_2$: C, 56.29; H, 5.45; N, 15.15%. Found: C, 56.78; H, 5.61; N, 15.55%.

Reaction of 1a with Sodium Methanethiolate under Phase Transfer Conditions

A mixture of 1a (2.26 g, 10 mmol) in chloroform (25 mL), 15% aqueous sodium methanethiolate (14.0 g, 30 mmol), and benzyltriethylammonium chloride (0.23 g, 1 mmol) was stirred at room temperature. After 10 h, the organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. The solvent was evaporated under vacuum to give a white solid. The solid was recrystallized from ethanol. The yield was 2.41 g (97%); mp 93°C ([26], 94–95°C).

Condensation Polymerization in THF

In a three-necked flask equipped with a stirrer and a reflux condenser were placed sodium hydride (0.12 g, 5 mmol) and THF (50 mL). To this mixture, decanedithiol (0.5 g, 2.4 mmol) was added and stirred for 30 min. Then a solution of 1a (0.54 g, 2.4 mmol) in THF (10 mL) was added slowly and stirred for 24 h at room temperature. After the reaction was finished, the mixture was poured into water (200 mL). The resulting solid was filtered and dried. The solid was dissolved in chloroform and filtered. The chloroform-soluble fraction was reprecipitated with ether to yield 0.15 g of a white solid (5ac). The reduced viscosity of this material, measured at a concentration of 0.2 g/dL at 30°C, was 0.24 dL/g in chloroform and 0.29 dL/g in trifluoroacetic acid. This procedure generated an insoluble material (6ac), 0.4 g yield, which showed a reduced viscosity of 0.31 dL/g in trifluoroacetic acid under the same conditions mentioned above.

Analysis. Calculated for C$_{19}$H$_{25}$N$_3$S$_2$: C, 63.47; H, 7.00; N, 11.67%.

Found for 5ac: C, 62.80; H, 7.02; N, 10.73%. Found for 6ac: C, 62.85; H, 7.07; N, 11.46%.

Other polymers were prepared by analogous procedures.

Condensation Polymerization under Phase Transfer Conditions

A typical experiment is as follows. In a 50-mL flask equipped with a reflux condenser and a magnetic stirrer were placed 40% aqueous sodium hydroxide (4.8 g, 48 mmol) and benzyltriethylammonium chloride (55 mg, 0.24 mmol). To this solution was added a solution of 1a (0.54 g, 2.4 mmol) and decanedithiol (0.50 g, 2.4 mmol) in o-dichlorobenzene (10 mL) which was stirred at room temperature for 10 h. After the reaction was finished, the mixture was poured into water (100 mL). The precipitated solid was filtered and washed with chloroform. The chloroform-insoluble material was obtained in 0.34 g yield. The filtrate was extracted with chloroform and poured into ether to precipitate the polymer. The yield was 0.13 g.

Extraction of Alkali Metal Picrates

The extraction experiment was performed by the same method described previously [27].

Phase Transfer Reaction Catalyzed by 5

Phase transfer reactions were carried out by the previously described procedures [14]. After the reaction was finished, the mixture was poured into methanol to precipitate the solid. The filtrate was analyzed by gas chromatography. The precipitated solid was washed with 5% hydrochloric acid and dried. The IR spectrum was in good agreement with that of the polymer catalyst.

Measurements

IR spectra were measured with a Hitachi-285 spectrometer. NMR spectra were recorded with a Hitachi R-600 spectrometer using tetramethylsilane as an internal standard. UV spectra were taken with a Hitachi ESP-3T spectrometer. Differential scanning calorimetry (DSC) curves were obtained by using a Rigaku 8131-BL. Differential thermal analysis (DTA) and thermogravimetry (TG) were 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 ($\overline{M}_n$) and weight-average molecular weight ($\overline{M}_w$) were determined by means of gel permination chromatography (GPC) by using polystyrene calibration standards on a Tosoh-HLD803 apparatus. Gas chromatography (Ohkura 802) was used for separation and yield determination.

RESULTS AND DISCUSSION

Model Reactions

Before the condensation polymerization, the reactions of 2,4-dichloro-6-phenyl-1,3,5-triazine (1a) with alkanethiolates (2) as model reactions were examined. The results are summarized in Table 1.

$$(1)$$

	R		R
2a	CH$_3$	3a	CH$_3$
2b	CH$_2$CH$_3$	3b	CH$_2$CH$_3$
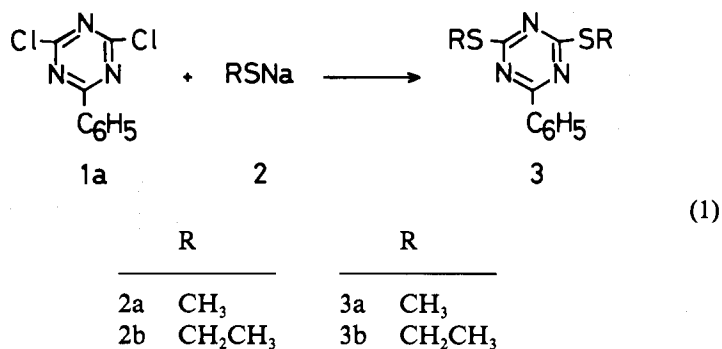
1a reacted smoothly with ethanethiol in THF in the presence of sodium hydride at room temperature for 10 h to afford the corresponding substitution product 3b in 97% yield. However, dipolar aprotic solvents such as dimethylsulfoxide and N,N-dimethylformamide could not be used in this reaction because these solvents react readily with 1a.

Further, 1a reacted with sodium methanethiolate even under chloroform–water two-phase conditions. When this reaction was carried out in the presence of phase transfer catalysts such as benzyltriethylammonium chloride and tetrabutylammonium hydrogen sulfate, the product was obtained quantitatively. In addition, benzene and o-dichlorobenzene were also suitable solvents in this reaction.

TABLE 1. Reaction of 1a with Thiolates[a]

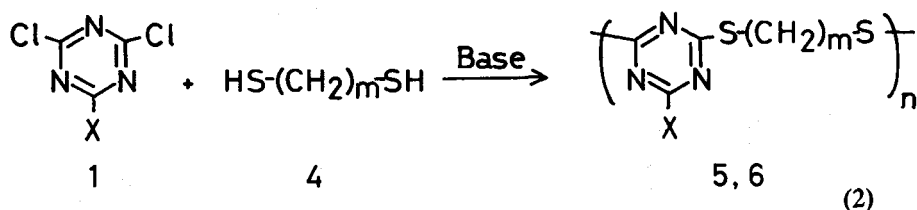| Run	Thiolate	Solvent[b]	Catalyst[c]	Temperature, °C	Time, h	Yield, %
1	2b	THF	—	RT	10	97
2	2b	THF	—	60	5	91
3	2a	$CHCl_3/H_2O$	—	RT	10	85
4	2a	$CHCl_3H_2O$	BTEAC	RT	10	97
5	2a	$CHCl_3/H_2O$	TBAHS	RT	10	95
6	2a	C_6H_6/H_2O	TBAHS	RT	10	95
7	2a	o-DCB/H_2O	TBAHS	RT	10	96
8	2a	o-DCB/H_2O	TBAHS	100	3	92

[a]Other reaction conditions are shown in the Experimental section.
[b]o-DCB: o-dichlorobenzene.
[c]BTEAC: benzyltriethylammonium chloride. TBAHS: tetrabutylammonium hydrogensulfate.

Polymer Synthesis

By using conditions which were similar to the model reactions, condensation polymerizations of dichloro-1,3,5-triazines such as 1a, 2,4-dichloro-6-phenoxy-1,3,5-triazine (1b), and 2,4-dichloro-6-phenylmercapto-1,3,5-triazine (1c) with alkanedithiols such as phenylmercapto-1,3,5-triazine (1c) with alkanedithiols such as 1,4-butanedithiol (4a), 1,6-hexanedithiol (4b), and 1,10-decanedithiol (4c) were carried out (Eq. 2). The results are summarized in Table 2.

$$\begin{array}{ccc}
\underset{\displaystyle 1}{\text{Cl}\!-\!\!\overset{N}{\underset{\underset{X}{N}}{\diagdown}}\!\!-\!\text{Cl}} & + \; \text{HS-(CH}_2)_m\text{SH} \; \xrightarrow{\text{Base}} & \underset{\displaystyle 5,6}{\left(\overset{N}{\underset{\underset{X}{N}}{\diagdown}}\!-\!\text{S-(CH}_2)_m\text{S}\right)_n}
\end{array} \qquad (2)$$

	X	m		X	m
1a	C_6H_5	4a	4	5aa, 6aa	C_6H_5	4
1b	C_6H_5O	4b	6	5ab, 6ab	C_6H_5	6
1c	C_6H_5S	4c	10	5ac, 6ac	C_6H_5	10
				5bb, 6bb	C_6H_5O	6
				5bc, 6bc	C_6H_5O	10
				5cb, 6cb	C_6H_5S	6
				5cc, 6cc	C_6H_5S	10

The reaction of 1a with 4c in THF in the presence of sodium hydride at room temperature for 10 h afforded polymer (5ac) having a reduced viscosity of 0.14 dL/g in 25% yield (Run 5). The structure was confirmed by comparing its IR and NMR spectra with those of the monomeric analogs 3. The IR spectrum exhibited a characteristic band at 830 cm^{-1} based on the 1,3,5-triazine ring. The NMR spectrum in deuterio-trifluoroacetic acid consisted of multiple peaks at $\delta = 1.57$ (12H) and 1.98 (4H) for methylene protons, a triplet peak at 3.48 (4H) for the methylene adjacent to the sulfur, and 7.71 (2H), 7.90 (1H), and 8.30 (2H) ppm for aromatic protons. Elemental analysis also supported the structures described in Eq. (2). This polymer (5ac) was soluble in THF, benzene, o-dichlorobenzene, and chloroform, but it was insoluble in n-hexane, ether, acetone, and methanol.

When this reaction was carried out for 24 h, an insoluble polymer

TABLE 2. Condensation Polymerization of Dichlorotriazines with Alkanedithiols in the Presence of Sodium Hydride[a]

Run	Dichlorotriazine	Dithiol	Solvent	Temperature	Time, h	Yield, %		η_{sp}/c,[b] dL/g
						5	6	
1	1a	4a	THF	RT	24	32	18	0.16
2	1a	4b	THF	RT	5	8	0	0.09
3	1a	4b	THF	RT	15	15	0	0.12
4	1a	4b	THF	RT	24	12	25	0.15
5	1a	4c	THF	RT	10	25	0	0.14[c]
6	1a	4c	THF	RT	24	18	46	0.24
7	1a	4c	THF	Reflux	5	4	49	0.15
8	1a	4c	o-DCB	RT	24	16	6	0.08
9	1a	4c	C_6H_6	RT	24	13	5	0.06
10	1b	4b	THF	RT	24	33	36	0.14
11	1b	4c	THF	RT	24	5	39	0.25
12	1b	4c	THF	Reflux	24	11	44	0.26
13	1c	4b	THF	RT	24	15	47	0.13
14	1c	4c	THF	RT	24	23	41	0.12

[a]Reaction conditions: Dichlorotriazine = 2.4 mmol, Dithiol = 2.4 mmol. NaH = 5 mmol, solvent = 60 mL.
[b]Measured at a concentration of 0.2 g/dL in $CHCl_3$ at 30°C
[c]$\bar{M}_n$ = 4000, $\bar{M}_w$ = 14,000 were estimated by GPC correlation to standard polystyrene.

(6ac) in THF was produced in 46% yield, together with the soluble polymer, 5ac (18%). 6ac was not soluble in common solvents or dipolar aprotic solvents although it was readily soluble in trifluoroacetic acid. The NMR spectrum of 6ac is shown in Fig. 1, which closely matches that of the THF soluble polymer (5ac). The IR spectrum of 6ac was very similar to that of 5ac (Fig. 2). The elemental analysis also satisfied the structure of the condensation polymer. Furthermore, the reduced viscosity in trifluoroacetic acid was somewhat higher than that of 5ac. The THF insoluble polymer (6ac) was also formed when the reaction was carried out at reflux temperature. This tendency was also observed with other dithiols and a different substituent in 2,4-dichloro-1,3,5-triazines (Table 2). The reduced viscosity of THF-soluble polymers was in the range of 0.06–0.26 dL/g in chloroform. The number-average molecular weight ($\bar{M}_n$) and the weight-average molecular weight ($\bar{M}_w$) of 5ac were estimated to be 4000 and 14,000, respectively (Run 5).

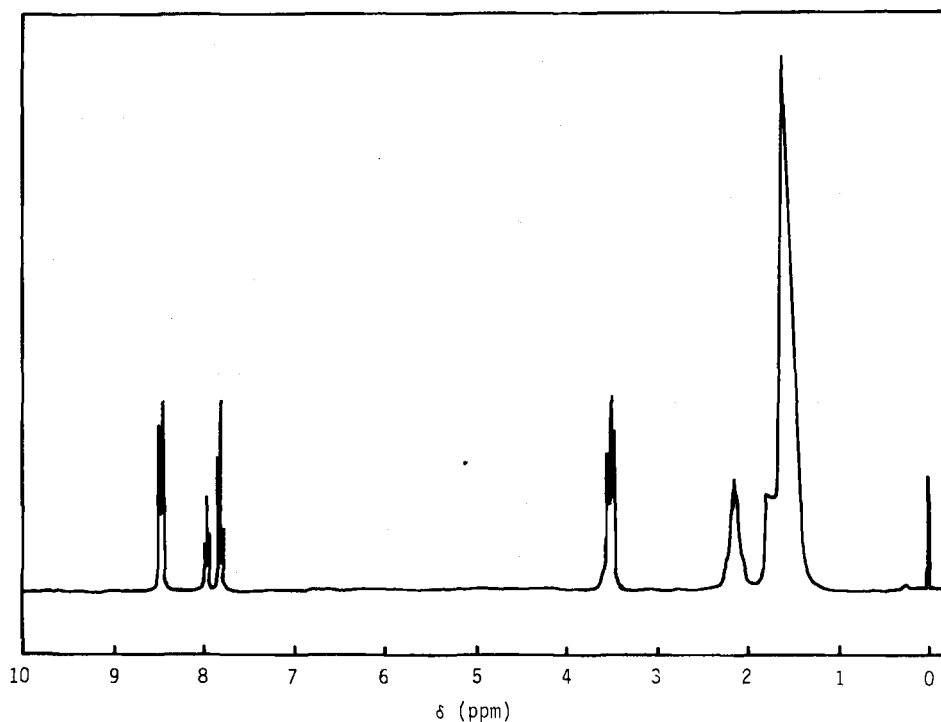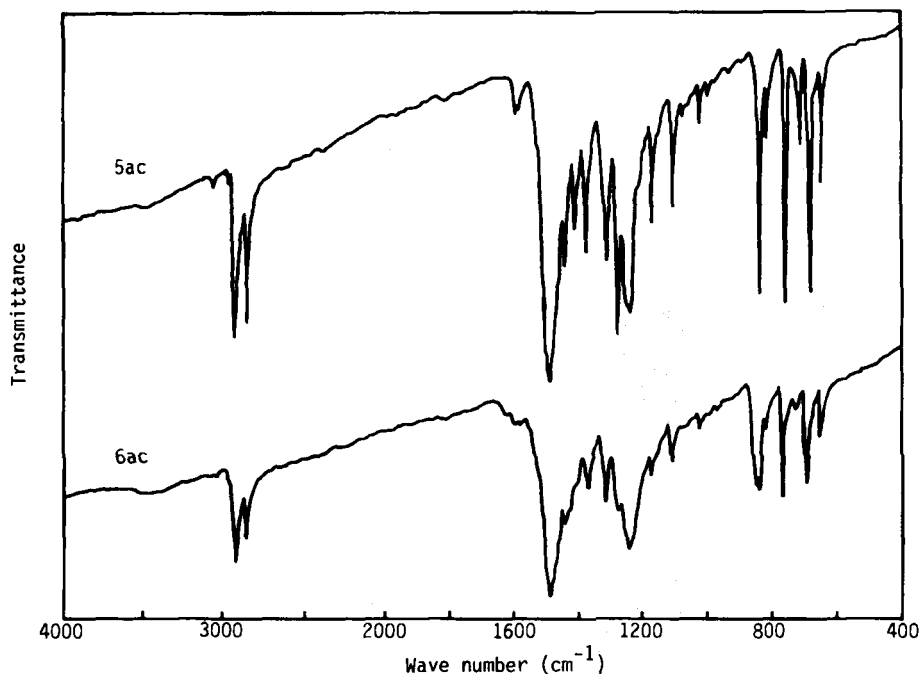FIG. 1. NMR spectrum of 6ac in CF₃COOD.

FIG. 2. IR spectra of 5ac and 6ac.

This condensation polymerization was also performed in liquid–liquid two-phase system. The results are shown in Table 3. When 1a and 4c were stirred in the presence of sodium hydroxide at room temperature for 10 h using o-dichlorobenzene–water two-phase conditions, the corresponding soluble polymer 5ac was obtained in 22% yield. As expected from the results of model reactions, the yield could be increased remarkably by adding phase transfer catalysts. A similar acceleration effect by phase transfer catalysts has been reported for the preparation of poly(alphatic sulfides) [27]. In addition, under these conditions the yield of the THF-insoluble polymer also increased as the conversion increased. However, the polymer yield in these reactions was not high, though the starting materials had already been consumed. This was due to the production of a large amount of oligomers.

Differential scanning calorimetry (DSC) was performed on these polymers. All the poly(alkyltriazinyl sulfides) exhibited well-defined melting transitions. This is correlated to the fact that x-ray diffraction patterns of

TABLE 3. Condensation Polymerization of 1a and 4c under
Two-Phase Conditions[a]

Run	Catalyst	Yield, %		η_{sp}/c^b of 5ac
		5ac	6ac	
1	—	22	0	0.11
2	BTEAC	15	39	0.13
3	TBAHS	0	80	—

[a]Reaction conditions: room temperature; time = 10 h; 1a = 2.4 mmol; 4c = 2.4 mmol; [NaOH] = 16.5 mol/L (in H_2O), 7 ml; o-DCB = 5 mL, catalyst = 0.24 mmol.
[b]Measured at a concentration of 0.2 g/dL in $CHCl_3$ at 30°C.

the polymers obtained with CuK_α radiation showed a high degree of crystallinity. Thermogravity (TG) and differential thermal analysis (DTA) for these polymers were carried out at a heating rate of 10°C/min. Typical thermograms for 5ac are shown in Fig. 3. The DTA curve exhibited an endotherm around 85°C, corresponding to the melting point, and a strong exotherm around 372°C, which correlated well with TG study, showing that the initial weight loss occurred at about this temperature. On the other hand, THF-insoluble polymer 6ac showed melting points at 173 and 215°C. Two melting points have also been observed in polypropylene [29, 30] and syndiotactic polystyrene [31]. Thermal behavior data of these condensation polymers are summarized in Table 4.

Catalytic Activity in Phase Transfer Reactions

Polymeric analogs of dipolar aprotic solvents and polymers containing pyridine ring have recently been found to display catalytic activity for nucleophilic substitution reactions of alkyl bromides with alkali metal thiocyanates under toluene–water two-phase conditions [14, 32, 33]. We think a plausible mechanism of these catalytic reactions is as follows. The active sites in the polymers coordinate to an alkali metal ion at the interface, resulting in transfer of the reagent from the aqueous phase to the organic phase; the resulting anion attacks the substrate in the organic phase.

Polymers 5 are soluble in benzene, toluene, and methylene chloride but are insoluble in water. For these polymers to work as phase transfer catalysts, they should extract alkali metal ions from the aqueous phase.
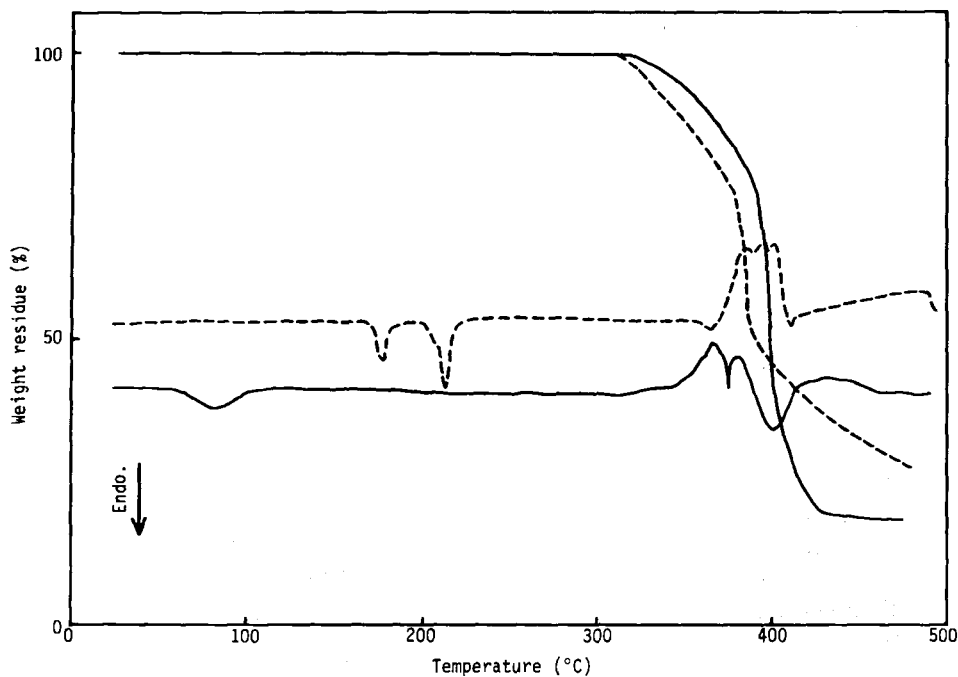
FIG. 3. TG and DTA curves of 5ac (——) and 6ac (- -).

TABLE 4. Thermal Behavior Data of
Poly(Aklyltriazinyl Sulfides)[a]

Polymer	mp, °C	T_d, °C
5ac	85	372
6aa	176	356
6ab	146, 158	357
6ac	173, 215	360

[a]Determined by TG and DTA at a heating rate
of 10°C/min in air.

Therefore, in order to obtain information on this point, extraction of sodium and potassium picrates was examined. The results are shown in Table 5.

As can be seen from the table, 3a and 5 can extract potassium and sodium ions, and the cation extraction ability of polymers 5 is higher than that of the monomeric analog *3a*. A similar phenomenon has been found in the case of polymeric analogs of dipolar aprotic solvents [32]. However, the extraction ability of 5 was lower than that of the corresponding poly(alkylpyridyl sulfides) [15]. In addition, the extraction ability decreased in the order of 5ac > 5ab > 5aa. This finding indicates that the chelation to alkali metal ions becomes effective due to the increase of flexibility of polymer backbone by the introduction of the methylene group.

The catalytic activity of these poly(alkyltriazinyl sulfides) was tested in the reaction of *n*-octyl bromide with potassium thiocyanate under phase transfer conditions. The results are shown in Table 6.
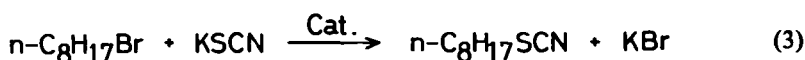
$$n\text{-}C_8H_{17}Br + KSCN \xrightarrow{\text{Cat.}} n\text{-}C_8H_{17}SCN + KBr \qquad (3)$$

TABLE 5. Extraction of Picrates by Alkyltriazinyl Sulfides[a]

	Picrate salt extracted, %	
Alkyltriazinyl sulfide	Na+	K+
3a	3	1
5aa	4	1
5ab	6	2
5ac	8	4

[a]Solvent system: Toluene/H_2O (10 mL/ 5 mL); [picric acid] = 5.5×10^{-5} mol/L (in H_2O); [NaOH or KOH] = 1.0×10^{-2} mol/L (in H_2O); alkyltriazinyl sulfide = 5.0×10^{-5} mol based on triazine unit.

TABLE 6. Phase Transfer Reactions Catalyzed by
Poly(Alkyltriazinyl Sulfides)[a]

Run	Substrate	Reagent	Catalyst	[Catalyst][b]/ [Substrate]	Yield, %
1	n-$C_8H_{17}Br$	KSCN	—	—	Trace
2			3a	0.18	11
3			5aa	0.18	30
4			5ab	0.18	56
5			5ac	0.18	66
6			5ac	0.3	92
7			6aa	0.18	19
8			BTEAC	0.18	47
9	$C_6H_5COCH_3$	$NaBH_4$	—	—	Trace
10			3a	0.1	19
11			5aa	0.1	23
12			5ab	0.1	27
13			5ac	0.1	40
14			5ac	0.3	94

[a]Reaction conditions. Runs 1-8: 100°C, 30 h, n-$C_8H_{17}Br$ = 1.65 mmol, [KSCN] = 8.0 mol/L (in H_2O), 5 mL. Runs 9-14: room temperature, 20h, $C_6H_5COCH_3$ = 1.5 mmol, $NaBH_4$ = 1.2 mmol, 1% aqueous NaOH = 0.1 mL, C_6H_6 = 4 mL.
[b]Calculated based on triazine unit.

Though this reaction did not proceed in the absence of catalyst, 3a accelerated the reaction slightly. Furthermore, the activity of all poly(alkyltriazinyl sulfides) used here was higher than that of the monomeric analog 3a, and it was comparable to that of benzyltriethylammonium chloride as a representative phase transfer catalyst. Thus, it was shown that the catalytic activity of these polymers was affected by their cation extracting ability and their solubility in the organic phase. These polymers also displayed catalytic activity in the reduction of acetophenone by sodium borohydride under phase transfer conditions.

CONCLUSION

Poly(alkyltriazinyl sulfide)s were readily prepared by the aromatic nucleophilic substitution polymerization of dichloro-1,3,5-triazines with al-

kanedithiols in the presence of a base in THF or in liquid–liquid two-phase systems. These polymers adsorbed sodium and potassium cations and displayed catalytic activity for the phase transfer reaction of an alkyl bromide with potassium thiocyanate.

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