Synthesis of Transparent and Thermally Stable Polycyanurates and Their Thermal Rearrangement

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ABSTRACT: Transparent and thermally stable polycyanurates, whose solubility can be changed by thermal rearrangement, have been synthesized as functional films used in the multilayer coating process. Before the synthesis of polycyanurates, the model compound, 2,6-bis(4-methoxyphenyl)–6-methoxy-1,3,5-triazine as a cyanurate is prepared and rearranged to an isocyanurate, 1,3-bis(4-methoxyphenyl)–5-methyl-1,3,5-triazinane-2,4, 6-trione in an excellent yield by thermal treatment. Based on this result, polycyanurates are prepared by the phase-transfer-catalyzed polycondensation of 2,4-dichloro-6-methoxy-1,3,5-triazine with bisphenol monomers in the presence of quaternary ammonium salts. The polycyanurate obtained from 9,9-

bis(hydroxyphenyl)fluorene exhibits a high glass transition temperature at 251 °C. The solubility of polycyanurate films containing 1 wt % of tetrabutylammonium bromide can be changed by thermal rearrangement. The partially rearranged films keep high transparency and low birefringence. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 3950–3955

KEYWORDS: change of solubility; high performance polymers; phase transfer polycondensation; polycyanurate; polyisocyanurate; tetrabutylammonium bromide; thermal properties; thermal rearrangement; transparency; transparent and thermally stable polymers

INTRODUCTION The development of flexible displays is a fast growing field due to the possibility of cost effective processing. Flexible displays consist of many functional transparent films, which are required for the multilayer coating process and environmental stabilities. Thus, a postcuring procedure is necessary for the film to prevent each layer from mixing by applying the crosslinking reactions. For example, poly(ary-lether-ketone)s with ethynyl as crosslinkable groups were cured at a very high temperature.^{1,2} Poly(arylether-ketone)s containing carboxylic acids were used to react with poly(vinyl alcohol) or bisphenols to prepare crosslinked polymers.^{3,4} Another postcuring procedure is an intramolecular cyclization. Poly(amic acid)s are soluble in aprotic solvents and converted to polyimides (PIs) by thermal treatment. The resulting PIs become insoluble in common organic solvents.⁵

Rearrangement, which is an intramolecular isomerization, is also a potential tool to alter the solubility of polymers. It induces the polarity change of the polymer, which means that the solubility of the resulting polymers will be different from that of the original polymers.

Recently, thermally stable and transparent films, whose solubility can be changed by thermal treatment or UV irradiation, were required as described above. Aromatic *s*-triazine-based polymers have attracted much interest academically and industrially, due to their unique properties, such as excellent thermal resistance, good chemical resistance, and high tensile strengths and moduli.^{6–8} These properties may be attributed to the rigid *s*-triazine units and the strong charge-transfer interactions between the *s*-triazine rings and the aromatic rings. Furthermore, triallyl cyanurate has been reported to rearrange to triallyl isocyanurate by thermal treatment.^{9,10}

Based on these findings, we report the synthesis of polycyanurates by the polycondensation of 2,4-dichloro-6-methoxy-1,3,5-triazine with bisphenols and their thermal rearrangement to the corresponding polyisocyanurates. It is found that this thermal rearrangement of polymers is one of the best methods to change the solubility of cast films.

EXPERIMENTAL

Materials

The materials were used without further purification unless otherwise noted. Bisphenol A and 9,9-bis(hydroxyphenyl)fluorene were purified by recrystallization from acetone/hexane. 2,4-Dichloro-6-methoxy-1,3,5-triazine (1) was donated by Sankyo Chemical, and was recrystallized from hexane.

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Synthesis of 2,6-Bis(4-methoxyphenyl)-6-methoxy-1,3,5-triazine (2)

A solution of 4-methoxyphenol (1.20 g, 9.60 mmol), tetrabutylammonium bromide (TBAB) (0.162 g, 0.504 mmol), and sodium hydroxide (0.480 g, 12.0 mmol) in water was added to a solution of **1** (0.720 g, 4.00 mmol) in chloroform (9.6 mL). The mixture was stirred vigorously for 3 h at room temperature. To this mixture, water (10 mL) and chloroform (10 mL) was added, and then the mixture was transferred to a separatory funnel, mixed thoroughly, and the organic layer was separated, dried over MgSO₄, and concentrated under reduced pressure with a rotary evaporator. The residue was recrystallized from cyclohexane to produce 1.14 g (80%) of **2** as a white crystal.

M.p. 106.5–107.0 °C. IR (KBr), ν (cm⁻¹): 1566 (C=C), 1504 (C=C), 1369 (C=N), 1203 (C-O-C). ¹H NMR (300 MHz, CDCl₃, δ , 25 °C): 7.08 (dd, J = 6.90 and 2.40 Hz, 4H; ArH), 6.89 (dd, J = 6.75 and 2.40 Hz, 4H; ArH), 3.93 (s, 3H; O-CH₃), 3.80 (s, 6H; O-CH₃). ¹³C NMR (75 MHz, CDCl₃, δ , 25 °C): 174.09, 173.96 (2 carbons), 157.49 (2 carbons), 145.36 (2 carbons), 122.38 (4 carbons), 114.63 (4 carbons), 55.72 (2 carbons), 55.68. Anal calcd. for C₁₈H₁₇N₃O₅: C, 60.84; H, 4.82; N, 11.82. Found: C, 61.07; H, 4.93; N, 11.79.

Synthesis of 1,3-Bis(4-methoxyphenyl)-5-methyl-1,3,5triazinane-2,4,6-trione (3)

A test tube charged with the compound **2** (0.164 g, 0.464 mmol) was heated at 260 °C for 10 min under nitrogen atmosphere. The product was purified by silica gel column chromatography (eluent: ethyl acetate/hexane (6/4, v/v)) to give the compound **3** (yield: 0.135 g, 82%). Recrystallization from toluene yielded a white crystal.

M.p. 161.4–162.6 °C. IR (KBr), ν (cm⁻¹): 1720 (C=O), 1547 (C=C), 1500 (C=C), 1211 (C-O-C). ¹H NMR (300 MHz, CDCl₃, δ , 25 °C): 7.14–6.82 (m, 8H, ArH), 3.82 (s, 3H, O-CH₃), 3.77 (s, 3H, O-CH₃), 3.59 (s, 3H, N-CH₃). ¹³C NMR (75 MHz, CDCl₃, δ , 25 °C): 169.75, 164.16 (2 carbons), 158.26–156.63 (2 carbons), 145.20–144.08 (2 carbons), 122.37–122.17 (4 carbons), 114.98–114.56 (4 carbons), 55.79–55.71 (2 carbons), 29.68. Anal calcd. for C₁₈H₁₇N₃O₅: C, 60.84; H, 4.82; N, 11.82. Found: C, 60.99; H, 5.04; N, 11.79.

Synthesis of Polycyanurate 4a

A solution of bisphenol A (1.14 g, 5.00 mmol), benzylcetyldimethylammonium chloride hydrate (BCDMAC) (0.250 g, 0.631 mmol), and sodium hydroxide (0.600 g, 15.0 mmol) in water was added to a solution of **1** (0.900 g, 5.00 mmol) in chloroform (13 mL). The mixture was stirred vigorously at 0 °C for 2 h. To this mixture was added 4-methoxyphenol (1.24 mg, 0.100 mmol), and then this mixture was stirred vigorously at 0 °C for 30 min. The organic layer was washed with water and poured into acetone. The fibrous polymer was obtained in good yield (1.31 g, 78%). Next, the obtained polymer was end-capped with acetic anhydride. A solution of the polycyanurate **4a** (1.31 g, 3.91 mmol), acetic anhydride (3.84 mL, 40.6 mmol), and pyridine (0.490 mL, 6.09 mmol) in 1,1,2,2-tetrachloroethane (21.2 mL) was stirred vigorously 45 °C for 2 h. The resulting solution was poured into the solution of acetone/methanol (2/1, v/v), giving the end-capped polymer **4a** (1.26 g, 76%). The number average molecular weight (M_n) and weight average molecular weight (M_w) values estimated from size exclusion chromatography (SEC) were 6.28×10^4 and 17.9×10^4 , respectively, with 2.85 of the polydispersity index (PDI = M_w/M_n).

IR (KBr), v (cm⁻¹): 1566 (C=C), 1504 (C=C), 1361 (C=N), 1211 (C-O-C). ¹H NMR (300 MHz, CDCl₃, δ , 25 °C): 7.25 (dd, J = 6.75 and 1.80 Hz, 4H, ArH), 7.08 (dd, J = 6.90 and 1.80 Hz, 4H, ArH), 3.94 (s, 3H, O-CH₃), 1.68 (s, 6H, C-CH₃). ¹³C NMR (75 MHz, CDCl₃, δ , 25 °C): 174.06 (2 carbons), 173.60, 149.71 (2 carbons), 148.07 (2 carbons), 128.08 (4 carbons), 120.98 (4 carbons), 55.75, 42.68 (2 carbons), 31.14. Anal calcd. for C₁₉H₁₈N₃O₃: C, 67.84; H, 5.39; N, 12.49. Found: C, 67.97; H, 5.20; N, 12.42.

Synthesis of Polycyanurate 4b

The polymer **4b** was prepared by the same procedure of **4a** using monomer **1** with 9,9-bis(hydroxyphenyl)fluorene as described above except for using TBAB as a phase transfer catalyst (1.27 g, 81%). The $M_{\rm n}$ and $M_{\rm w}$ values estimated from SEC were 3.82 \times 10⁴ and 8.21 \times 10⁴, respectively, with 2.15 of PDI.

IR (KBr), v (cm⁻¹): 1566 (C=C), 1500 (C=C), 1369 (C=N), 1211 (C=O-C). ¹H NMR (300 MHz, CDCl₃, δ , 25 °C): 7.76-7.01 (m, 16H, Ar*H*), 3.88 (s, 3H, O-C*H*₃). ¹³C NMR (75 MHz, CDCl₃, δ , 25 °C): 173.95 (2 carbons), 173.46, 150.8 (2 carbons), 150.52 (2 carbons), 143.49 (2 carbons), 140.17 (2 carbons), 129.41 (4 carbons), 128.01 (2 carbons), 127.09 (2 carbons), 126.32 (2 carbons), 121.31 (2 carbons), 120.42 (2 carbons), 64.74, 55.76. Anal calcd. for C₂₉H₂₀N₃O₃: C, 75.97; H, 4.40; N, 9.16. Found: C, 75.97; H, 4.53; N, 9.01.

Measurement

The ¹H and ¹³C NMR spectra were recorded on a BRUKER DPX-300S spectrometer at resonant frequencies of 300 MHz for ¹H and 75 MHz for ¹³C nuclei using CDCl₃ as the solvent and tetramethylsilane as the reference. The FTIR spectra were measured by a Horiba FT-120 Fourier transform spectrophotometer. M_n and M_w values were measured by SEC on a JASCO GULLIVER 1500 system equipped with two polystyrene gel columns (Plegel 5 μ m MIXED-C) eluted with chloroform at a flow rate of 1.0 mL min^{-1} calibrated by polystyrene standard samples. The UV-visible optical absorption spectra were recorded on a Hitachi U-3210 spectrophotometer at room temperature. The absorbance of polymer solutions was evaluated in the wavelength range of 200-800 nm. Elemental analyses were performed on a Yanaco MT-6 CHN recorder elemental analysis instrument. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analysis system at a heating rate of 10 $^{\circ}$ C min⁻¹ for thermogravimetry (TG) and on a differential scanning calorimetry (DSC) 6200 a heating rate of 10 $^{\circ}$ C min⁻¹ for DSC under nitrogen. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of polycyanurate films with more than 3





SCHEME 1 Synthesis of model compound 2 and its thermal rearrangement to the corresponding isocyanurate 3.

 μ m thickness were measured with using a prism coupler (Metricon, model PC-2000) equipped with a He-Ne laser light source (wavelength: 632.8 nm). The in-plane/out-of-plane birefringence (Δn) was calculated as the difference between $n_{\rm TE}$ and $n_{\rm TM}$. The average refractive index ($n_{\rm av}$) was calculated using eq 1:

$$n_{\rm AV} = \sqrt{(2n_{\rm TE}^2 + 2n_{\rm TM}^2)/3}$$
(1)

RESULTS AND DISCUSSION

Model Reaction

As described in the Introduction, triallyl cyanurate thermally rearranges to triallyl isocyanurate.9,10 However, no studies on the thermal rearrangement of polycyanurates have been published. Therefore, before the synthesis of polycyanurates, the compound. 2,6-bis(4-methoxyphenyl)-6-methoxymodel 1,3,5-triazine (2) was prepared by the interfacial reaction of 2,4-dichloro-6-methoxy-1,3,5-triazine (1) in chloroform with 4-methoxyphenol in an aqueous alkaline solution (Scheme 1), and its thermal rearrangement was studied. Thermal treatment of compound 2 was carried out in a test tube at 260 °C for 10 min, producing the isocyanurate, 1,3-bis (4-methoxyphenyl) – 5-methyl-1,3,5-triazinane-2,4,6-trione (3), in good yield (Scheme 1). The chemical structure of 3 was assigned on the basis of FTIR, ¹H and ¹³C NMR spectroscopy, and elemental analysis. The FTIR spectrum exhibited strong carbonyl absorption at 1712 $\rm cm^{-1}$ and no trace of a C=N stretching absorption was detected at 1369 cm⁻¹. The ¹H and





 13 C NMR spectra of **3** are presented in Figure 1 with assignments of all signals. The signal at 3.59 ppm in Figure 1(A) is assignable to the methyl group. Two singlet signals for methoxy protons attached to the aromatic ring are observed at 3.82 and 3.77 ppm, probably due to the boat and the chair conformations. In the 13 C NMR spectrum [Fig. 1(B)], each aromatic and methoxy carbon exhibits two signals, which is also explained by the existence of two conformers as described above.¹² Elemental analyses also supported the formation of compound **3**.

Synthesis of Polycyanurates

Nakamura et al. reported the synthesis of polycyanurates by the interfacial polycondensation of 2,4-dichloro-6-substituted-1,3,5-triazines with various aromatic diols in the presence of cationic emulsifiers.⁹ According to this report, the phase-transfer-catalyzed polycondensation of compound 1 with bisphenol monomers, bisphenol A, and 9,9-bis(hydroxyphenyl)fluorine was carried out in a chloroformaqueous alkaline solution at room temperature to afford polycyanurates 4. Quaternary ammonium salts such as BCDMAC and TBAB were employed as a phase-transfer catalyst. The polycondensations proceeded smoothly and gave polycyanurates 4 with high molecular weights (Scheme 2). The end-cap of polymers was carried out by adding 4methoxyphenol at the chloro-1,3,5-triazine end polymers, followed by acetylation of the hydroxy end polymers with acetic anhydride. The results are summarized in Table 1. The BCDMAC with a long alkyl group is very effective for the polymerization using bisphenol A, on the other hand, TBAB with short alkyl chains is suitable for the polymerization using 9,9-bis(hydroxyphenyl)fluorene. These results may be explained by the different characteristics of BCDMAC and TBAB, which act as an emulsifier and a phase transfer catalyst, respectively. The more organic structure of 9,9-bis(hydroxyphenyl)fluorene compared to bisphenol A favors a phase transfer catalyst to transfer the anion in the water phase to the organic phase.¹⁰ The $M_{\rm n}$ s and PDI of polycyanurates **4a** and **4b** are 62.8 \times 10³ and 2.85, and 38.2 imes 10^3 and 2.15, respectively, determined by SEC using a polystyrene standard.

The structures of polycyanurates **4** were characterized by ¹H and ¹³C NMR and FTIR spectroscopy. The characteristic peaks of polycyanutrates **4a** and **4b** were observed at 1361 and 1369 cm⁻¹, respectively, which are attributable to the C=N stretching. Figure 2(A) shows the ¹H NMR spectrum of polycyanutrate **4b**. The resonances at 7.76–7.01 and 3.88 ppm are assignable to the aromatic and methoxy protons. The assignments of all carbon signals in the ¹³C NMR spectrum for polycyanutrate **4b** are summarized in Figure 2(B).



SCHEME 2 Synthesis of polycyanurates 4 from compound 1 with bisphenol monomers.

TABLE 1 Synthesis of Polycyanurates 4

Polymer	Catalyst	Temperature (°C)	Time (h)	$M_{\rm n}$ (SEC) ^a (kg mol ⁻¹)	PDI (SEC) ^a	$M_{\rm n}$ (NMR) ^b (kg mol ⁻¹)	Yield (%)
4a	BCDMAC ^c	0	2.5	62.8	2.85	85.2	75.5
	TBAB ^d	0	3	1.08	1.68	-	11.4
4b	BCDMAC	r.t.	7	5.64	1.84	-	14.9
	TBAB	r.t.	9.5	38.2	2.15	34.2	81.2

^a Determined by SEC.

^b Determined by ¹H NMR.

^c BCDMAC: benzylcetyldimethylammonium chloride hydrate.

^d TBAB: tetrabutylammonium bromide.

The 4-methoxy phenyl and acetyl protons of both terminal ends were observed at 3.79 and 2.28 ppm, respectively, in the magnified ¹H NMR spectrum of polycyanutrate **4a**. Furthermore, the elemental analysis also supported the formation of polycyanutrates **4**.

Polycyanurates are white solids and soluble in dichloromethane, chloroform, and NMP. A white transparent film was obtained by casting from a chloroform solution of **4**.



FIGURE 2 The (A) ¹H and (B) ¹³C NMR spectra for polycyanurate 4b.

Thermal Rearrangement

The thermal stabilities of polymers, such as high degradation temperature and high glass transition temperature, are one of the most important requirements for manufacturing optical films. The thermal properties of polycyanurates **4** were evaluated by TG and DSC. As shown in Figure 3, polycyanurates **4a** and **4b** exhibit 5% weight loss temperatures at 380 °C and 394 °C, respectively under nitrogen. Their glass transition temperatures (T_{gs}) determined by DSC measurements are 165 and 251 °C, respectively. Polycyanurate **4b** exhibits high T_{g} due to a bulky cardo structure (Fig. 4). Moreover, large exothermic peaks for polycyanurates **4a** and **4b** are found at 279 and 302 °C, respectively, where no weight loss is observed, suggesting the rearrangement of **4** to



FIGURE 3 TGA curves of polycyanurates **4** under nitrogen at a heating rate of 10 $^{\circ}$ C min⁻¹.



FIGURE 4 DSC curves of polycyanurates **4** under nitrogen at a heating rate of $10 \degree C \min^{-1}$.

polyisocyanurate 5. Based on these findings, the thermal rearrangement of polycyanurate 4a was investigated at 260 °C for 10 min under nitrogen. After thermal treatment, the flexible film became brittle likely due to the decrease of the molecular weight, indicating that some side reactions occurred during the rearrangement. To avoid this problem, a thermal rearrangement of polycyanurate ${\bf 4}$ at a lower temperature in the presence of catalysts would be effective. Grosu et al. reported that isocyanurate derivatives were obtained by the rearrangement reaction from cyanurate derivatives in a process catalyzed by TBAB or tetrabutylphophonium bromide at 120 °C without any solvent.¹¹ Thus, the thermal rearrangement of polycyanurate 4a was carried out at various temperatures in the presence of TBAB, and it was found that the thermal rearrangement proceeded at 180 °C. As a result, the $T_{\rm g}$ value of **4a** increased to 237 °C (**5a**) (Supporting Information Fig. S1). The effect of TBAB loading on the thermal rearrangement was studied, and the changes of the FTIR spectra in the thermally treated polycyanutate 4a are shown in Figure 5. The intensity of the characteristic carbonyl absorption peak of polyisocyanurate increases with increasing the amount of TBAB. To change the solubility of polycyanurates, a complete rearrangement would not be

 TABLE 2 Solubility of Polycyanurates 4 and Partially Rearranged Polycuanurate 5

Polymer	CHCl₃	CH_2CI_2	NMP	DMAc	THF
4a	++	++	+	-	-
5a	_	_	+	_	_
4b	++	++	++	-	-
5b	-	+	++	-	_

++: Soluble, +: partially soluble, -: insoluble.

required. In fact, the 4a film containing 1 wt % of TBAB became insoluble in chloroform after thermal treatment at 180 °C for 30 min. The degree of rearrangement was estimated from the decrease of relative intensity of the absorption band at 1361 cm^{-1} corresponding to the C=N stretching as 15%. Similarly, the changes of IR spectra in the thermally treated polycyanurate 4b indicate that the degree of rearrangement from **4b** to polyisocyanurate also increases with increasing the amount of TBAB (Fig. 5). The 4b film containing 1 wt % of TBAB became insoluble in chloroform at 200 °C for 10 min, and its degree of rearrangement was 8.5% estimated by the method described above using the absorption band at 1369 cm⁻¹. These resulting polymers are referred to as partially rearranged polyisocyanurates 5a and 5b, respectively. The solubility of all polymers is listed in Table 2. The inherent viscosity of **4a** and **5a** (before and after thermal rearrangement) has been investigated. Unfortunately, the $\eta_{\rm inh}$ value decreased from 0.96 to 0.27 dL g⁻¹ which indicates that the degradation of main chains occurred to some extent. However, the solubility of polymers in CHCl₃ and CH₂Cl₂ reduced enough almost without scarifying their film property after the thermal rearrangement.

Optical Properties

Figure 6 shows the UV-vis absorption spectra of polycyanurate **4** and partially rearranged polycyanurate **5** after the thermal treatment. All polymers exhibit high transparency in the visible region (λ : 400-800 nm) with transmittance over 90% at 400 nm even after thermal rearrangement. The high



FIGURE 5 FTIR spectra on the thermally treated polycyanurate (A) 4a and (B) 4b in the presence of various amounts of TBAB.



FIGURE 6 The UV-vis absorption spectra of polycyanurates **4** and partially rearranged polycyanurates **5** after thermal treatment.

transparency may originate from the isolated aromatic rings. No coloration in the films after thermal rearrangement was observed (Fig. 6).

The refractive indices and their birefringence for polymers are summarized in Table 3. All polymers have relatively high refractive indices due to the aromatic units, and show low birefringence. In fact, the birefringence values of the polymers **4b** and **5b** are very low due to a bulky cardo structure, which prevents in-plane orientation of the molecular chains. These results indicate that polycyanurate **4b** is promising for high T_g and transparent materials whose solubility can be changed by thermal treatment.

CONCLUSIONS

High-molecular-weight polycyanurate 4 had been successfully prepared by the phase-transfer-catalyzed polycondensation of monomer 1 with bisphenol monomers in the presence of quaternary ammonium salts. Polymer 4b exhibited a 5% weight loss temperature and $T_{\rm g}$ at 394 and 251 °C, respectively. Polycyanurate 4 partially rearranged to polyisocyanurate by thermal treatment. The solubility of polymer 4 films containing 1 wt % of TBAB could be changed by thermal rearrangement. The partially rearranged films 5 kept high transparency and low birefringence. Therefore, polycyanurate 4 is one of the candidates for functional transparent films, which require a multilayer coating process and environmental stabilities. Furthermore, the rearrangement of polymers by thermal treatment is one of the best methods to prevent mixing of each layer for the multilayer coating process.

TABLE 3 Optical Properties of Polycyanurates 4 and Partially

 Rearranged Polycyanurates 5

Polymer	n _{TE} ^a	<i>n</i> _{TM} ^b	Δn^{c}	<i>n</i> _{AV} ^d	e ^e
4a	1.5964	1.5924	0.0041	1.5951	2.54
5a	1.5985	1.5937	0.0048	1.5969	2.55
4b	1.6368	1.6356	0.0012	1.6364	2.68
5b	1.6424	1.6416	0.0008	1.6421	2.70

^a The in-plane refractive indices at 633 nm.

^b The out-of-plane refractive indices at 633 nm.

^c Birefringence: $\Delta n = n_{\text{TE}} - n_{\text{TE}}$.

^d Average refractive index: $n_{AV} = [(2n_{TE}^2 + n_{TE}^2)/3]^{1/2}$.

^e Dielectric constant: $\varepsilon = 1.0 n_{AV}^2$.

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