Synthesis of Polyisocyanurates by Thermal Rearrangement of Polycyanurates

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ABSTRACT: Polyisocyanurates have been successfully prepared by the thermal rearrangement of polycyanurates, which were obtained from 2,4-dichloro-6-methoxy-1,3,5-triazine and bisphenol monomers. The thermal rearrangement was carried out in the presence of a small amount of tetrabutylammonium bromide (TBAB) as a catalyst at 200 °C for 30 or 60 min in an argon atmosphere, and the degree of arrangement was greater than 95%. Transparent and amorphous polyisocyanurate films were obtained and showed a good thermal stability with a 5% weight loss temperature above 340 °C in nitrogen and the glass transition temperature above 210 °C. Films with a 10-μm thickness exhibited an excellent transparency above 90% at 400 nm. Furthermore, the thermal rearrangement of 2,6-bis(4-methoxyphenyl)-6-methoxy-1,3,5-triazine to 1,3-bis(4-methoxyphenyl)-5-methyl-1,3,5-triazinane-2,4,6-trione was investigated in detail. It was found that the complete thermal rearrangement was successfully accomplished in the presence of 2 wt % TBAB at 150 °C for 20 min in an argon atmosphere. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *53*, 692–698

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INTRODUCTION Flexible displays have shown a growing interest from numerous consumer electronics manufacturers to apply this display technology in e-readers, mobile phones, and other consumer electronics, that consist of many functional transparent films, which are required for a multilayer coating process and environmental stability. One of the problems with the multilayer coating process is mixing each layer. To prevent this mixing, a post-curing procedure based on crosslinking reactions is generally applied to decrease the solubility of the polymers. As examples, poly(aryletherketone)s with ethynyl groups as crosslinkable groups were cured at a very high temperature.[1,2] The poly(aryletherketone)s containing carboxylic acids were reacted with poly(vinyl alcohol) or bisphenols to prepare the crosslinked polymers.[3,4] Another post-curing procedure is the intramolecular cyclization. Poly(amic acid)s were soluble in aprotic solvents and converted to polyimides (PIs) by thermal treatment. The resulting PIs became insoluble in the common organic solvents.[5]

The other method is the change in polarity of the polymers. A typical example is found in photoresists for microlithography such as chemical amplification resists, in which the acid-catalyzed deprotection reaction converts a hydrophobic polymer to a hydrophilic polymer, providing a significant change in the polarity and hence solubility of the polymer. This polarity change was exploited in dual-tone imaging simply by changing the polarity of the developer solvent.[6] These materials, however, release low-molecular weight materials or gases during the deprotection reaction; this would present a serious problem in practical applications in the optoelectronic industry.

Rearrangement, which is an intramolecular isomerization, is also a potential tool to alter the solubility of polymers.[7] It induces a polarity change in the polymers, which means that the solubility of the resulting polymers is different from that of the original polymers. In a previous paper,[8] we reported that an intramolecular isomerization was also a potential tool to alter the solubility of polymers, in which polycyanurates were partially rearranged to polyisocyanurates by a thermal treatment. However, the flexible films of the polycyanurates after a thermal treatment became brittle likely due to a decrease in the molecular weight, indicating that some side reactions occurred during the rearrangement. Transparent functional films are required to have good mechanical properties and high glass transition temperatures. Therefore, we focused on the complete thermal rearrangement of polycyanurates to polyisocyanurates while maintaining good film properties.

Polyisocyanurates are light-stable and thermally stable plastics and have been used as insulating and paper coatings.[9–11] They are prepared by the trimerization of diisocynates or dicyanates,[12] followed by heating with a catalyst. Therefore, the products are crosslinked polymers, and to the best of our knowledge, there has been no report on the synthesis of linear polyisocyanurates.

In this study, we report the thermal rearrangement of 2,4-bis(4-methoxyphenyl)-6-methoxy-1,3,5-triazine (**1**) under various conditions and the successful thermal rearrangement of polycyanurates to polyisocyanurates. Furthermore, the thermal properties, solubility, and optical transparency of the polyisocyanurates are also described in detail.

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 toluene and acetone/hexane, respectively. 2,4-Dichloro-6-methoxy-1,3,5-triazine (**1**) was donated by Sankyo Chemical, and was recrystallized from hexane. 2,6-Bis(4-methoxyphenyl)-6-methoxy-1,3,5-triazine (**2**) and 1,3-bis(4-methoxyphenyl)-5-methyl-1,3,5-triazinane-2,4,6-trione (**3**) were synthesized according to a previous article.[8]

Model Reaction

A sealed vial charged with the compound **2** (0.164 g, 0.464 mmol) was preliminary dried under vacuum at 50 °C for 1 h, and then heated at 270 °C for 30 min under argon atmosphere. In the case that 2 wt % of tetrabutylammonium bromide (TBAB) was added, the sample was heated at 150 °C for 30 min under argon atmosphere. All the resulting mixtures were dissolved in $CDCl_3$, and directly characterized by ^1H NMR measurement. In order to obtain a pure isocyanurate compound **3**, the crude sample was recrystallized from toluene to give a white crystal. The yield was 0.14 g (86%). IR (KBr), ν (cm^{-1}): 1720 (C=O), 1547 (C=C), 1500 (C=C), 1211 (C—O—C). ^1H NMR (600 MHz, $CDCl_3$, δ, ppm, 25 °C): 7.14–6.82 (m, 8H, ArH), 3.82 (s, 3H, O—CH_3), 3.77 (s, 3H, O—CH_3), 3.59 (s, 3H, N—CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, ppm, 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.

Polymer Synthesis

Polycyanurate 6a.

A solution of bisphenol A (2.51 g, 11 mmol), benzylcetyldimethylammonium chloride hydrate (BCDMAC) (0.550 g, 0.138 mmol), and sodium hydroxide (1.32 g, 33 mmol) in water (35 mL) was added to a solution of **1** (2.00 g, 11 mmol) in chloroform (35 mL). The mixture was stirred vigorously at 0 °C for 2 h. To this mixture added 4-methoxyphenol (4.5 mg), and this mixture was stirred 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 (2.76 g, 75%). The number average molecular weight (M_n) and weight average molecular weight (M_w) values estimated from size exclusion chromatography (SEC) were 67,000 and 180,000, respectively, with 2.69 of the polydispersity index (PDI = M_w/M_n). IR (KBr), ν (cm^{-1}): 1566 (C=C), 1504 (C=C), 1361 (C=N), 1211 (C—O—C). ^1H NMR (600 MHz, $CDCl_3$, δ, ppm, 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—CH_3), 1.68 (s, 6H, C—CH_3). ^{13}C NMR (150 MHz, $CDCl_3$, ppm, 25 °C): 174.06 (2 carbons), 173.60, 149.71 (2 carbons), 148.07 (2 carbons), 128.08 (4carbons), 120.98 (4 carbons), 55.75, 42.68 (2 carbons), 31.14.

Polycyanurate 6b.

The polymer **6b** was prepared by the same procedure of **6a** using monomer **1** with 9,9-bis(hydroxyphenyl)fluorine and TBAB as a phase transfer catalyst. The M_n and M_w values estimated from SEC were 38,200 and 82,100, respectively, with 2.15 of PDI.

Thermal Rearrangement of Polymer 6a.

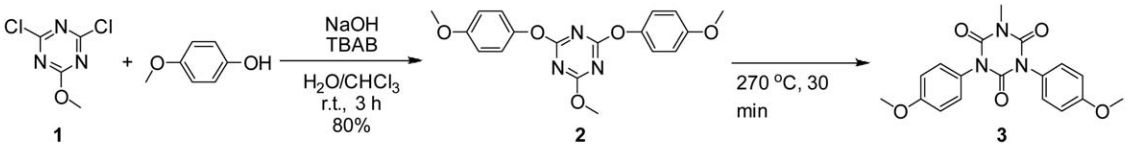
The polymer film was prepared by casting the solution of **6a** and TBAB (2 wt % to monomer unit) in chloroform (10 wt %) on a glass slide. The film was dried at 60 °C *in vacuo* for 24 h, and heated at 200 °C for 60 min in the sealed vial under an argon atmosphere. The resulting film was subjected to IR, ^1H and ^{13}C NMR, SEC, and UV–vis measurements.

Solubility Test for 6 and 7.

A vial equipped with a stirring bar was charged with 10 mg of the polymer **6** or **7** and 1 mL of a common solvent (acetone, tetrahydrofuran, chloroform, dichloromethane, or *N,N*-dimethylacetamide), and the mixture was stirred for 1 h at r.t. The resulting solubility of **6** and **7** is listed in Table 4.

Measurement.

The ^1H and ^{13}C NMR spectra were recorded on a JEOL ECA600 instrument at resonant frequencies of 600 MHz for ^1H and 150 MHz for ^{13}C nuclei using $CDCl_3$ as a solvent and tetramethylsilane as a reference. The Fourier transform infrared (FTIR) spectra were measured by a JASCO FT/IR-4100 spectrophotometer. Number- (M_n) and weight average molecular weight (M_w) values were measured by SEC on a JASCO GULLIVER 1500 system equipped with a RI detector and two polystyrene gel columns (Plegel 5 μm MIXED-C) eluted with chloroform at a flow rate of 1.0 mL min^{-1} at 40 °C calibrated by polystyrene standard samples. The UV–visible optical absorption spectra were recorded on a JACSO V-670 spectrophotometer at room temperature. The absorbance of polymer films was evaluated in the wavelength range of 200–800 nm. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6200 thermal analyzer at a heating rate of 10 °C min^{-1} for thermogravimetric analysis (TGA)



SCHEME 1 Synthesis and thermal rearrangement of model compound **2**.

and on a HITACHI X-DSC 7000 (DSC) 6200 at a heating and cooling rate of 10 °C min^{-1} for differential scanning calorimetry (DSC) under nitrogen.

RESULTS AND DISCUSSION

Model Reaction

To clarify the cause of the decrease in the molecular weight of the polycyanurate, the thermal rearrangement of 2,6-bis(4-methoxyphenyl)-6-methoxy-1,3,5-triazine (**2**) to 1,3-bis(4-methoxyphenyl)-5-methyl-1,3,5-triazinane-2,4,6-trione (**3**) was investigated in detail (Scheme 1).

Based on a previous article,[8] compound **2** was heated at 270 °C for 30 min in the air. The ^{1}H NMR spectrum of the obtained products is shown in Figure 1(b). Besides the signals derived from **3**, the characteristic signals assigned to the methoxy and phenyl protons for 4-methoxyphenol (**4**) are clearly observed at 3.75 and 6.75 ppm, respectively. The other signals of the by-product, which are assignable to an isocyanurate derivative generated by the cleavage of **3**, appear at 3.35 and 3.55 ppm. Furthermore, the formation of methanol is not observed in the ^{1}H NMR spectrum of the products. The molar ratio of **3** to **4** is around 84/16, which was calculated based on the integral ratio of the methoxy protons of **3** and **4**. On the other hand, when the thermal treatment of **2** was carried out at 270 °C for 30 min in an argon atmosphere, no formation of **4** is observed as shown in Figure 1(c). These results suggest that humidity induces some side reactions when forming **4**. The thermal rearrangement of cyanurate to isocyanurate is a type of Chapman rearrangement, in which *N,N*-diaryl amides are formed when aryl imidates are heated.[13] Aryl imidates are easily hydrolyzed by water to produce the corresponding amides.[14] Therefore, a thermal treatment was performed at 270 °C for 20 min in the presence of equimolar amounts of water to **2** as shown in Figure 1(d). The molar ratio of **3** to **4** decreased to 39/61, indicating that the side reaction is attributed to the existence of water, which probably hydrolyzes **2** to produce **4** (Scheme 2).

As compound **2** has an alkyl imidate and two aryl imidates, the hydrolysis of **2** by water would also produce methanol. However, the reactivity of aryl imidate for hydrolysis is higher than that of alkyl imidates, because **4** is a better leaving group compared to methanol due to its higher acidity. Thus, the model reactions described above only formed **4**.

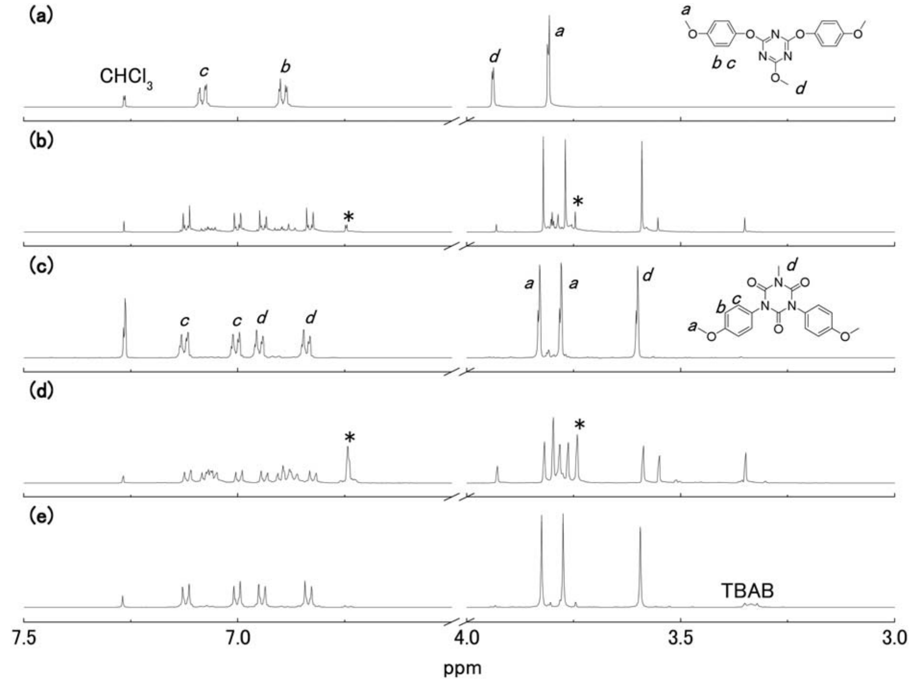
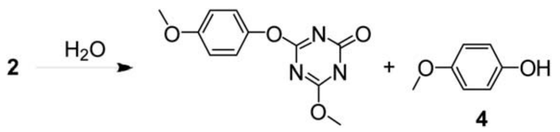


FIGURE 1 ^{1}H NMR spectra of (a) starting material **2**, and the product after thermal treatment in the condition of (b) 270 °C for 30 min in air, (c) 270 °C for 30 min under argon, (d) 270 °C for 30 min in air in the presence of water (1 equiv.), and (e) 150 °C for 20 min under argon in the presence of TBAB (2 wt %). Asterisk denotes the signals derived from 4-methoxyphenol.



SCHEME 2 A plausible side reaction.

In the ^{1}H NMR spectrum of **3**, two singlet signals for the methoxy protons are observed at 3.82 and 3.77 ppm, probably due to the *cis* and *trans* isomers of the chair conformation. Based on the same reason, two different phenylene rings exist in two conformational isomers showing two sets of the two doublet peaks.

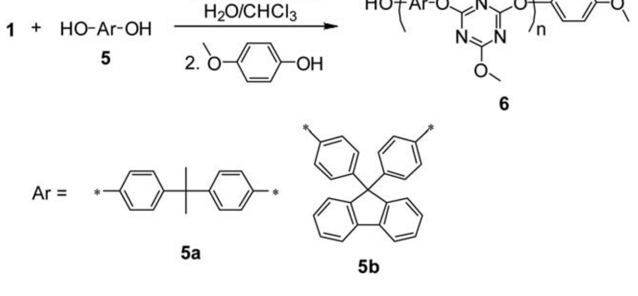
To decrease the temperature of the thermal treatment, the thermal rearrangement of **2** was carried out at 150 °C for 20 min in the presence of 2 wt % TBAB according to a previous article,[8,15] and it was found that the complete thermal rearrangement of **2** to **3** was attained in an argon atmosphere [Fig. 1(e)].

Thermal Rearrangement of Polycyanurates to Polyisocyanurates

Polycyanurates (**6**) were prepared by the phase-transfer catalyzed polycondensation of 2,4-dichloro-6-methoxy-1,3,5-triazine (**4**) with bisphenol monomers, bisphenol A (**5a**), and 9,9-bis(hydroxyphenyl)fluorene (**5b**) in the presence of quaternary ammonium salts following procedures in previous articles (Scheme 3).[8,16,17]

First, the polymer **6a** film containing 2 wt % TBAB was thermally treated at 180 °C for several minutes in air (humidity: around 60%). The molecular weights of **6a** listed in Table 1 rapidly decrease, and after 10 min, the molecular weight of **6a** could not be evaluated by SEC because the molecular weight decreased below the molecular weight exclusion limit. This degradation behavior clearly supports the results of the model reactions described above.

Based on the results of the model reactions, the thermal rearrangement of the polycyanurate **6a** film was then carried out at 270 °C for 30 min in an argon atmosphere in which the number average molecular weight (M_n) and polydispersity (PDI) of **6a** were 35,000 and 2.80, respectively (Scheme 4). After the thermal treatment, the M_n decreased to 1900.



SCHEME 3 Synthesis of polycyanurate **6**.

TABLE 1 Molecular Weights of **6a** After Thermal Treatment at 180 °C in Air

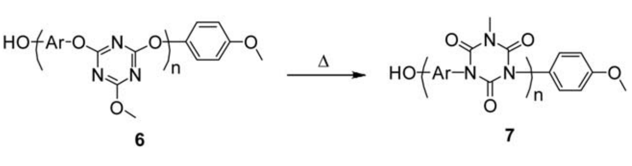
Run	Time (min)	M_n[a]	M_w[a]
1	0	104,000	185,000
2	1	50,000	102,000
3	3	36,000	77,000
4	5	23,000	45,000
5	10	N/D[b]	N/D[b]

[a] Determined by SEC eluted with chloroform using polystyrene standards.

[b] Not detected.

A few percent of the side reaction described above dramatically decreases the molecular weight of the resulting polyisocyanurates **7**. To avoid this problem, a low temperature thermal treatment was applied in which the number average molecular weight (M_n) and polydispersity (PDI) of **6a** were 67,000 and 2.69, respectively. The thermal rearrangement of the **6a** film containing 2 wt % TBAB was carried out at 180 °C for 30 min in an argon atmosphere. The film was colorless and transparent, and furthermore, maintained its shape. The ^{1}H NMR spectrum of the resulting polymer is shown in Figure 2 with assignments of all the signals. The signals at 3.59 and 3.94 ppm are assignable to the *N*-methyl protons for **7a** and methoxy protons for **6a**, respectively. The degree of rearrangement (DR) estimated from the integral ratio of these peaks is 64%. The M_n of the resulting polymer decreased to 45,000. The thermal treatment time was then extended to 60 min at 180 °C to improve the DR, which increased to 80%. For further improvement, the thermal treatment temperature was increased to 200 °C. The DR was then improved to 93% with a 30-min thermal treatment. Finally, the DR reached 97% at 200 °C with a 60-min thermal treatment, in which the M_n and PDI of the resulting polyisocyanurate **7a** were 14,000 and 2.72, respectively. These results are summarized in Table 2.

The structure of the polymer **7a** (DR = 97%) was characterized by FTIR, and ^{1}H and ^{13}C NMR spectroscopies. The FTIR spectrum exhibits a strong carbonyl absorption at 1718 cm^{-1} and no trace of a C=N stretching absorption is detected at 1361 cm^{-1} as shown in Figure 3. The ^{1}H and ^{13}C NMR spectra are presented in Figure 2 with assignments of all the signals. The signals assigned to the *N*-methyl and methyl protons are observed at 3.59 and 1.66 ppm, respectively, and the peaks for the aromatic protons appear at 7.32, 7.18, 7.14, and 7.01 ppm just like the ^{1}H NMR spectra for the model compound **3** in Figure 2(b). In the ^{13}C NMR



SCHEME 4 Thermal rearrangement of **6**.

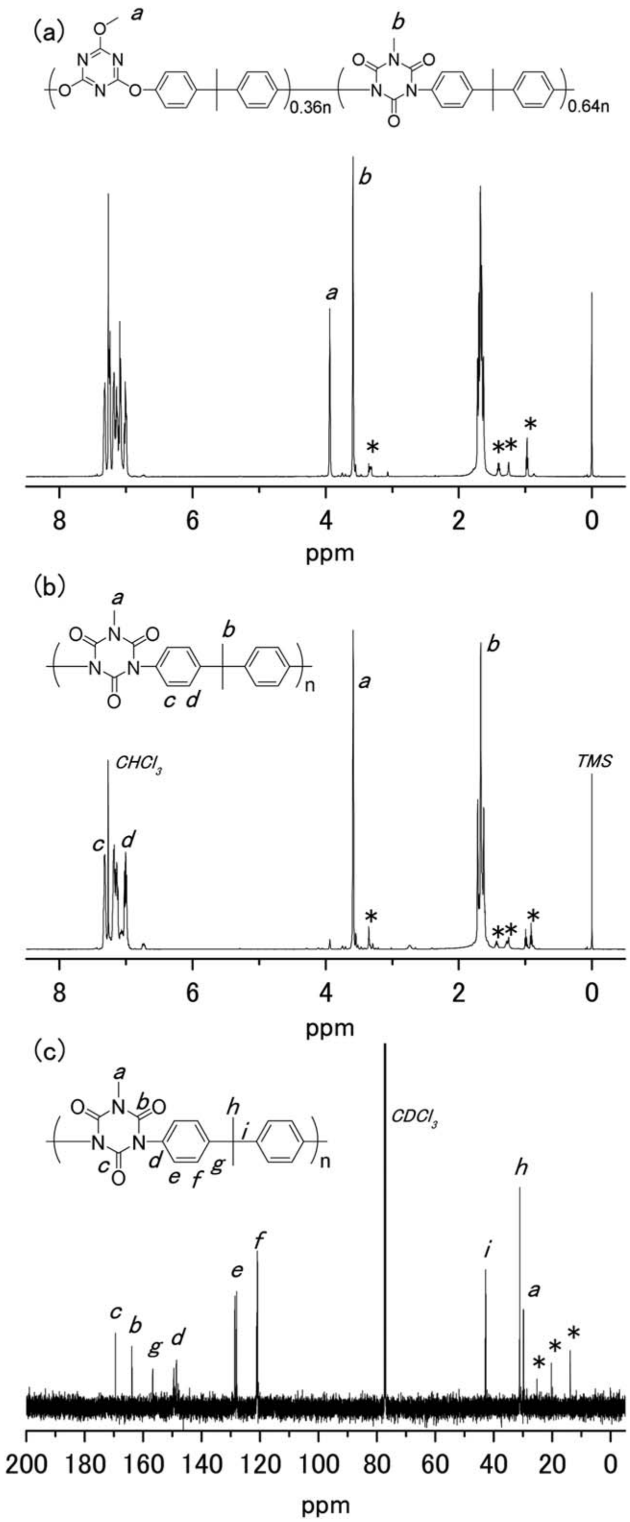


FIGURE 2 (a) ^{1}H NMR spectrum of **6a** film treated at 180 °C for 30 min and (b) ^{1}H and (c) ^{13}C NMR spectra of the polycyanurate **7a** after thermal rearrangement at 200 °C for 60 min. Asterisk denotes the signals of TBAB.

TABLE 2 Thermal Rearrangement of **6a** With TBAB (2 wt %) Under Various Conditions

Temp. (°C)	Time (min)	DR[a] (%)	M_n[b]	M_w/M_n[b]
180	30	64	45,000	2.66
180	60	80	22,300	2.96
200	30	93	26,000	2.17
200	60	97	14,000	2.72

[a] Degree of rearrangement determined by ^{1}H NMR.

[b] Determined by SEC eluted with DMF using polystyrene standards.

spectrum [Fig. 2(c)], the characteristic two carbonyl and *N*-methyl carbons appear at 169.44, 163.84, and 29.76 ppm, respectively, and the two peaks at 173.60 and 174.07 ppm due to the C═N carbons for polymer **6a** disappear. These spectra clearly support the formation of polymer **7a** with the M_n of 14,000.

Next, the thermal rearrangement of polycyanurate **6b,** which has a high rearrangement temperature (302 °C) in the absence of TBAB, was carried out at various temperatures and times in the presence of TBAB in an argon atmosphere. The M_n and PDI of **6b** were 38,000 and 2.15, respectively. The results are presented in Table 3. The **6b** film containing 2 wt % of TBAB was heated at 250 °C for 60 min. The DR and M_n of the resulting film were 50% and 21,800, respectively. Thus, the longer thermal treatment time of 120 min was applied to increase the DR. The DR, however, was not improved probably due to the decomposition of TBAB. To promote the thermal rearrangement, the **6b** film containing 5 wt % of TBAB was prepared and heated at 250 °C for 30 min. This thermal treatment produced **7b** with the DR of 95%, in which the M_n and PDI of the resulting **7b** were 15,600 and 3.54, respectively. The structure of the resulting polymer **7b** (DR = 95%) was characterized by FTIR and ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum is shown in Figure 4 with assignments of all the signals. The signals due to the *N*-methyl protons for **7b** and methoxy protons for **6b** are clearly observed at 3.53 and 3.88 ppm, respectively.

Solubility of 7

The solubility of **7** is listed in Table 4. The polymers **6** are soluble in halogenated alkanes. On the other hand, **7** being

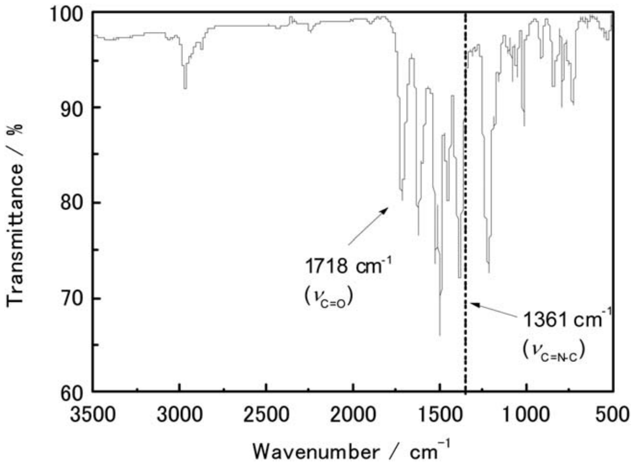


FIGURE 3 FTIR spectrum of **7a**.

TABLE 3 Thermal Rearrangement of **6b** at 250 °C Under Various Conditions

TBAB (wt %)	Time (min)	DR[a] (%)	M_n[b]	M_w/M_n[b]
2	60	50	21,800	2.41
2	120	49	12,400	2.55
5	30	95	15,600	3.54

[a] Degree of rearrangement determined by ^{1}H NMR.

[b] Determined by SEC eluted with DMF using polystyrene standards.

TABLE 4 Solubility of **6** and **7**[a]

Polymer	Acetone	THF[b]	$CHCl_3$	CH_2Cl_2	DMAc[c]
6a	−	−	++	++	−
7a	−	++	++	++	++
6b	−	−	++	++	−
7b	−	−	++	++	++

[a] ++: Soluble, −: insoluble.

[b] Tetrahydrofuran.

[c] *N,N*-Dimethylacetamide.

more polar than **6** is very soluble in halogenated alkanes, and the dipolar aprotic solvent, *N,N*-dimethylacetamide (DMAc). This result strongly shows that rearrangement is a potential tool to alter the solubility of polymers.

Thermal Properties of 7

The thermal properties of **7** were evaluated by TGA and DSC measurements under a nitrogen atmosphere. The results are summarized in Table 5. As shown in Figure 5, both polymers show good thermal stabilities with a 5% weight-loss temperature (T_{d5}) at 344 °C. The glass transition temperature (T_g) of the polymers, which is one of the most important parameters for optical device fabrication, was determined by DSC, as shown in Figure 5. Polyisocyanurates **7a** and **7b** show T_g values of 219 and 291 °C, respectively. The significantly higher T_g of **7b** is mainly attributed to the bulky cardo structure of the fluorene unit.

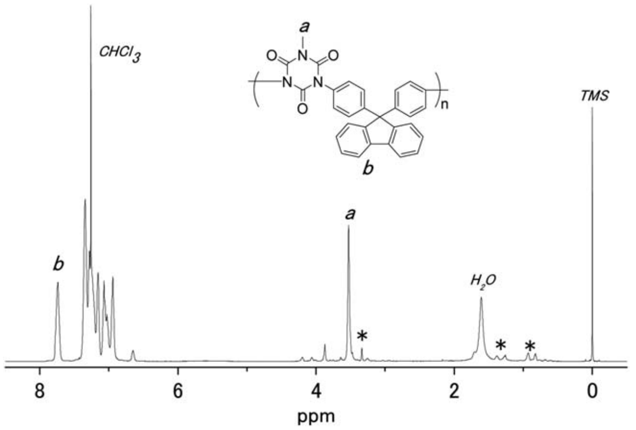


FIGURE 4 ^{1}H NMR spectrum of **7b**. Asterisk denotes the signals of TBAB.

TABLE 5 Thermal Properties of **7**

Polymer	T_{d5}[a] (°C)	T_{d10}[a] (°C)	T_g[b] (°C)
7a	344	356	219
7b	361	375	291

[a] Determined by TGA.

[b] Determined by DSC in the second heating scan.

Optical Properties of 7

Figure 6 shows the UV–vis absorption spectra of **7a** and **7b** with a thickness of about 10 μm. Both polymers show a high transparency over 90% at 400 nm in the visible region ($\lambda = 400 - 800$ nm) even after almost complete thermal rearrangement. The high transparency originates from the non-conjugated backbone of polyisocyanurate with a non-planar structure. These results indicate that the polyisocyanurates **7** are promising for high T_g and transparent materials.

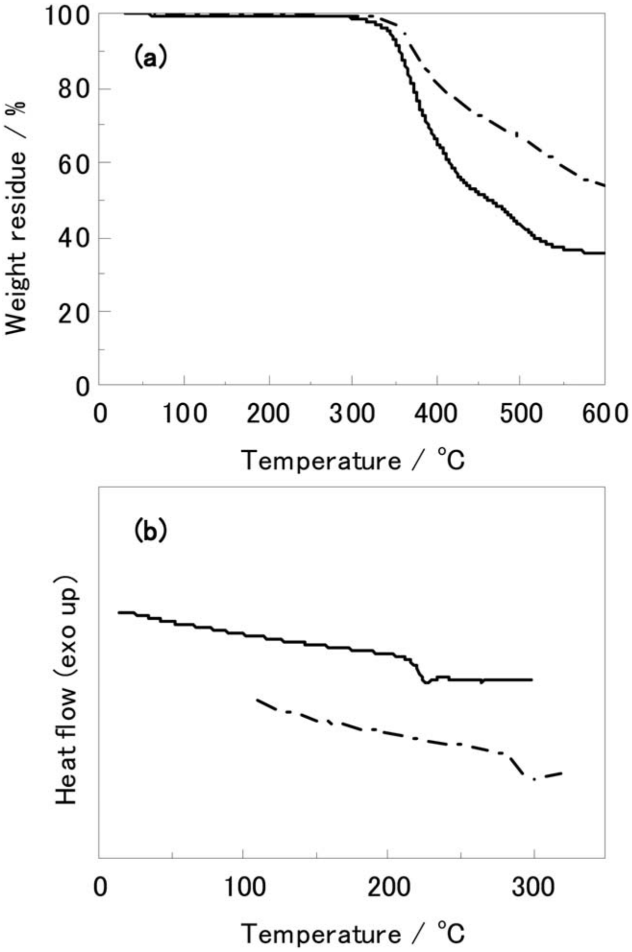


FIGURE 5 (a) TGA and (b) DSC profiles of **7a** (solid line) and **7b** (broken line).

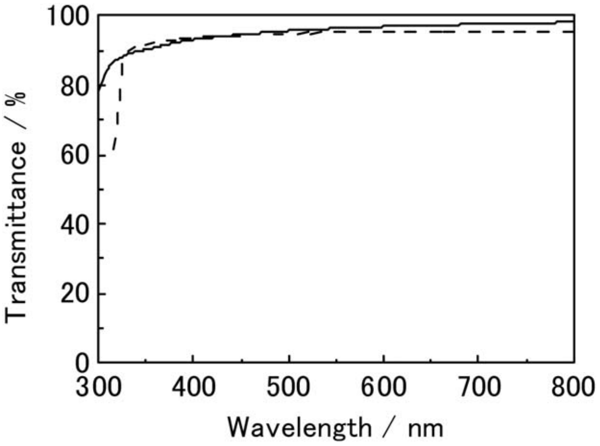


FIGURE 6 UV–vis absorption spectra of **7a** (solid line) and **7b** (broken line).

CONCLUSIONS

We have succeeded in the synthesis of linear polyisocyanurates by thermal rearrangement of polycyanurates. First, the thermal rearrangement of **1** to **2** was studied in detail. The complete thermal rearrangement of **1** to **2** was successfully accomplished at 270 °C for 20 min in an argon atmosphere. On the other hand, thermal treatment in air induced side reactions, in which the humidity promoted some side reactions by forming **3**. Based on these findings, the thermal rearrangement of polycyanurates **6a** and **6b** films containing a small amount of TBAB was carried out at 200 °C for 60 and 30 min, respectively, in an argon atmosphere, producing polyisocyanurates **7a** and **7b** with the DR values of 97 and 95%, respectively, while maintaining molecular weights higher than 14,000. The **7a** and **7b** products showed a good solubility in organic solvents, good thermal stability with a 5% weight-loss temperature over 340 °C, and the high glass transition temperatures of 219 and 291 °C, respectively. At the same time, the optical transparencies of **7a** and **7b** were very high, being over 90% at 400 nm. These polymers can be good candidates as components for advanced optical device applications.

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