Cyclotrimerization of Diisocyanates Toward High-Performance Networked Polymers with Rigid Isocyanurate Structure: Combination of Aromatic and Aliphatic Diisocyanates for Tunable Flexibility

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ABSTRACT: A series of networked polymers bearing isocyanurate moiety was synthesized by cyclotrimerization of diisocyanates, with employing methylenediphenyl 4,4′-diisocyanate and 1,6-hexamethylenediisocyanate (HMDI) in several feed ratios. In spite of the large difference in intrinsic reactivity between these two diisocyanates, their coannulation proceeded efficiently by using sodium *p*-toluenesulfinate (pTol-SO_2Na) and 1,3-dimethyl-2-imidazolidinone as a catalyst and a solvent, respectively. The resulting networked polymers were transparent and exhibited excellent thermal stability. In addition, HMDI-rich feed ratios allowed for the formation of networked polymers with increased flexibility. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 2631–2637

KEYWORDS: cyclotrimerization; films; high performance polymers; isocyanurate; networks; thermal properties

INTRODUCTION The development of transparent and heat resistant polymer materials is attracting much attention from aerospace and electronics fields. Flexibility is also an important property for polymer materials for next generation displays, solar cells, and e-paper. From these backgrounds, recently, we have focused on the development of high-performance networked polymers bearing isocyanurate moieties.[1,2] This cyclic structure has some advantageous features involving its excellent thermal stability[3–5] and its facile synthesis by the cyclotrimetization of a wide range of isocyanates.[6] So far, isocyanurate linkage has been frequently used in polyurethane chemistry to enhance heat resistance, flame retardation, and chemical resistance of polyurethanes.[7] In addition, there have been a few reports on cyclotrimetization of diisocyanates that afforded the corresponding networked polymers bearing isocyanurate groups.[8–15] We reinvestigated the cyclotrimerization conditions, leading to the achievement of rapid and quantitative formation of isocyanurate by employing sodium *p*-toluenesulfinate (*p*TolSO_2Na) and 1,3-dimethyl-2-imidazolidinone (DMI) as the optimized catalyst and the solvent, respectively. Under the conditions, methylenediphenyl 4,4′-diisocyanate (MDI) underwent cyclotrimerization to afford the corresponding networked polymer that was consisted of isocyanurate moieties with minimized chemical defect, and thus was colorless, transparent, and stable up to >400 °C. Furthermore, flexibility of the film-shaped networked polymers was successfully attained by addition of various monoisocyanate to the reaction system.[1,2] However, the addition of a large amount of monoisocyanate leads to decrease in thermal stability and tensile strength.

Herein, we report a dual-diisocyanate system for synthesizing networked polymers that exhibit excellent thermal stability, transparency, and flexibility. The feature of this system is the combination of an aromatic diisocyanate and an aliphatic diisocyanate, and to the best of our knowledge, such a combination is the first example in this area. The diisocyanates employed herein were MDI and 1,6-hexamethylenediisocyanate (HMDI) which bear a rigid aromatic structure and a flexible linear alkyl spacer, respectively.

EXPERIMENTAL

Materials and Instruments

p-Tolylisocyanate (TI) and propyl isocyante (PI) were purchased from Tokyo Chemical Industry (Tokyo, Japan) and distilled under reduced pressure. MDI and 1,6-hexamethylenediisocyante (HMDI) were purchased from Wako Pure Chemical Industry (Osaka, Japan) and distilled under reduced pressure. Sodium *p*-toluenesulfinate (*p*TolSO_2Na) was purchased from Tokyo Chemical Industry (Tokyo, Japan) and dried under reduced pressure prior to use. DMI was purchased from Wako Pure Chemical Industry (Osaka, Japan) and distilled under reduced pressure over calcium hydride.

Proton NMR spectra were recorded on Varian UNITY INOVA 400 in $CDCl_3$ with TMS as an internal standard. Gas chromatography–mass spectrometry (GC–MS) analysis was carried out on a Shimadzu GC–MS QP5050 machine with helium as the carrier gas. The GC column was a RTX-5SilMS (30 m × 0.25 mm ID with a coated film thickness of 0.25 μm). The GC furnace temperature initially was held at 60 °C for 1 min and next was programmed to 300 °C and held for 15 min; then, it was programmed to 300 °C at 20 °C/min. The GC/MS interface was set at 280 °C. All samples were dissolved in dichloromethane before injection. IR spectra were recorded on a Thermo Scientific NICOLET iS10 FTIR spectrometer equipped with a SMART iTR ATR sampling accessory. The features of the cross-section of the films were investigated by a scanning electron microscope (SEM, JEOL JSM-6010LA). Differential scanning calorimetry (DSC) was carried out with a DSC-6200 (Seiko Instrument) using aluminum pan under an N_2 flow of 20 mL/min at the heating rate of 5 °C/min. Thermal gravimetric analysis (TGA) was performed with a TG-DTA 6200 (Seiko Instrument) using alumina pan under an N_2 flow of 50 mL/min at a heating rate of 10 °C/min.

Cyclotrimerization of TI

To a solution of pTolSO$_2$Na (0.03 mmol, 0.053 g) in DMI (1.0 mL), TI (6.0 mmol, 0.76 ml) was added under dry condition. After stirring the solution at 25 °C for 2 h, purification of the resulting precipitate by column chromatography (silica gel, eluted with dichloromethane) gave *N,N′,N″*-tris-(*p*-tolyl)isocyanurate (0.77 g, 5.8 mmol, 97%) as a white powder: $M_p = 270$ °C.

^{1}H NMR ($CDCl_3$): $\delta = 7.23$ (s, 12H), 2.32 ppm (s, 9H); FTIR (ATR): 1694, 1511, 1401, 806, 748 cm^{-1}.

Cyclotrimerization of PI

To a solution of pTolSO$_2$Na (0.015 mmol, 1.8 mg) in DMI (0.3 mL), PI (3.0 mmol, 0.28 mL) was added under dry condition. After stirring the solution at 80 °C for 24 h, the mixture was cooled to room temperature. Purification of the mixture by column chromatography (silica gel, eluted with dichloromethane) gave *N,N′,N″*-tris-(propyl)isocyanurate (0.20 g, 2.3 mmol, 78%) as colorless liquid.

^{1}H NMR ($CDCl_3$): $\delta = 3.85$ ppm (t, 6H), 1.66 ppm (m, 6H), 0.94 ppm (t, 9H); FTIR (ATR): 2963, 1678, 1452, 1381, 761 cm^{-1}.

Cyclotrimerization of TI and PI

To a solution of pTolSO$_2$Na (0.060 mmol, 11 mg) in DMI (0.50 mL), TI (3.0 mmol, 0.38 mL) and PI (3.0 mmol, 0.28 mL) were added under dry condition. The mixture was stirred at 80 °C for 5 h. After stirring the solution at 80 °C for 5 h, the mixture was cooled to room temperature. Purification of the mixture by column chromatography (silica gel, eluted with dichloromethane) gave the mixture of four isocyanurate compounds of quantitative yield.

Synthesis of Networked Polymers Based on Cyclotrimerization of MDI and HMDI

A Typical Procedure

In a dry test tube equipped with a three-way stopcock, MDI (3.0 mmol, 0.75 g), HMDI (3.0 mmol, 0.48 mL), DMI (0.25 mL), and a solution of pTolSO$_2$Na (11 mg, 0.060 mmol [0.5 mol % to NCO groups]) in DMI (0.75 mL) were mixed. Within 1 min, the resulting solution was put into a mold (60 mm × 40 mm × 0.10 mm), which was fabricated with two pieces of PTFE-tape-coated slide glass and PTFE spacer (thickness, 100 μm), placed in a glove box at 25 °C under nitrogen for 2 h. After 2 h, the mixture in a mold was continuously heated at 100 °C for 1 h and at 150 °C for 1 h. The cured film was taken out from the mold, immersed in water at 25 °C for 12 h, and dried under vacuum at 150 °C for overnight: FTIR (ATR): 1696, 1506, 1391, 1018, 754 cm^{-1}.

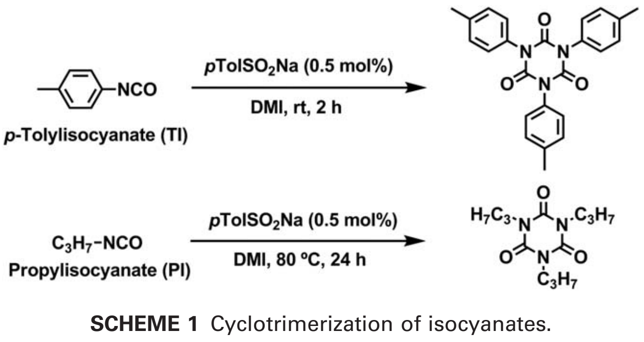
Synthesis of Networked Polymers Based on Cyclotrimerization of HMDI

In a 25-mL flask equipped with a condenser, HMDI (3.0 mmol, 0.48 mL), pTolSO$_2$Na (5.3 mg, 0.030 mmol [0.5 mol % to NCO groups]), and DMI (1.0 mL) were added under dry conditions, and the mixture was heated and stirred at 150 °C for 2 h. After reaction, the mixture was cooled to room temperature, and the conversion of the isocyanate groups was determined by FTIR analysis. The resulting solid was grinded and washed with chloroform in a Soxhlet's extractor, and dried in a vacuum oven at 150 °C for overnight to yield the networked polymer 5 (0.48 g, 94%): FTIR (ATR): 2933, 2860, 1674, 1454, 1373, 1327, 761 cm^{-1}.

RESULTS AND DISCUSSION

Cyclotrimerization of TI and *n*-PI as a Model Reaction

Prior to performing cyclotrimerization of diisocyanate, we investigated cyclotrimerization of TI and PI as a model reaction (Scheme 1). Recently, we have reported a highly efficient cyclotrimerization of TI with employing sodium *p*-toluenesulfinate (pTolSO$_2$Na) and DMI as the optimized catalyst and the solvent, respectively.[1] With 0.5 mol % of pTolSO$_2$Na, the cyclotrimerization completed at room temperature within 2 h to give the corresponding isocyanurate was isolated in 97% yield. In contrast to this successful cyclotrimerization of an aromatic isocyanate, it was much less efficient in aliphatic. The cyclotrimerization of PI under the optimum conditions for that of TI did not proceed at room temperature,



SCHEME 1 Cyclotrimerization of isocyanates.

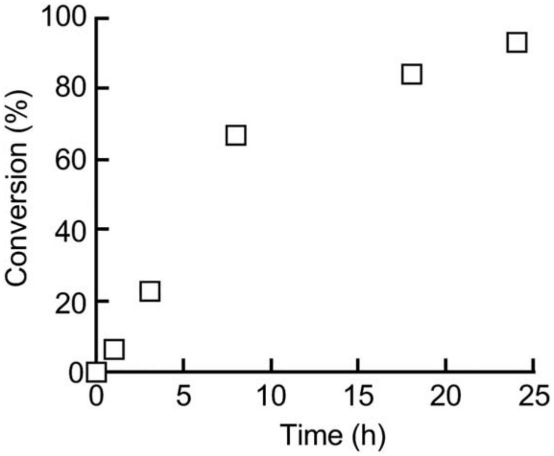


FIGURE 1 Time dependence of conversion for the cyclotrimerization of PI at 80 °C. The conversions were determined by ^{1}H-NMR.

and for the efficient progress of the reaction, a higher temperature (80 °C) and a prolonged reaction time (24 h) were required (Figure 1). This significant difference in reactivity between aromatic and aliphatic isocyanates is attributable to the difference in their intrinsic electrophilicity, that is, the more electrophilic aromatic isocyanate can accept the nucleophilic attack of the sulfinate catalyst more easily than the aliphatic isocyanate.

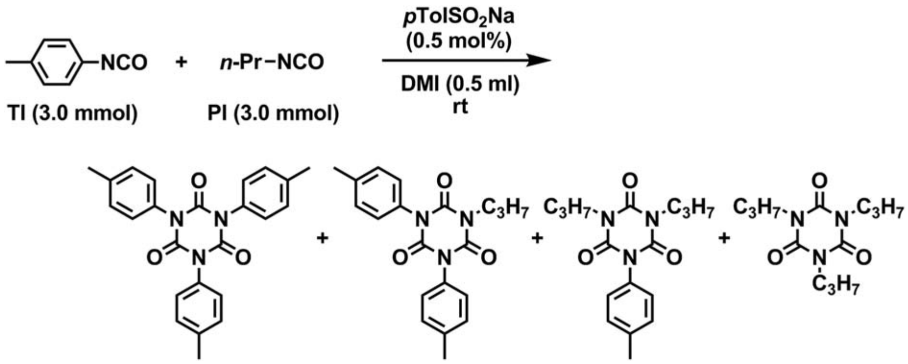
Upon confirming the large difference between the efficiency in cyclotrimerization between TI and PI, a cyclotrimetization system where these two isocyanates coexist in a molar ratio of 1:1 became our interest (Scheme 2). The system was investigated at room temperature and 80 °C, and the corresponding time dependencies of conversions of the two isocyanates are shown in Figure 2(a,b). The reaction behaviors thus clarified involve several characteristic features as follows. (1) At room temperature, TI was smoothly consumed; however, the consumption became much slower than that in the absence of PI, presumably owing to the dilution with PI. (2) Even at room temperature, a noticeable amount of PI was consumed, to imply that the presence of TI caused a certain promoting effect Figure 2(a). (3) At 80 °C, this promoting effect became much more remarkable, leading to the quantitative consumption of PI within 5 h. It is worth emphasizing again that it took 24 h for 90% conversion of PI in the absence of TI. As shown in Figure 2, it is apparent that TI acts as a role of accelerator for the cyclotrimerization of PI. In the dual system of TI and PI, the sulfinate anions as a catalyst preferentially attack to the more electrophilic TI in the initial state, leading to the formation of intermediates such as 1:1 or 1:2 adducts of sulfinate with TI. It is seen that these intermediates having the higher nucleophilicity can assist progress of the cyclotrimerization of PI.

For getting more insight into the system, the reaction products were analyzed by GC/MS. Figure 3 shows the obtained total ion count chart. The peaks *a* and *d*, whose corresponding *m*/*z* values were 255 and 399, were attributable to the cyclotrimerization product of PI and that of TI, respectively. The other two peaks, whose corresponding *m*/*z* values were 303 and 351, were assigned to the isocyanurates formed by the coannulation of PI and TI at ratios of 1:2 and 2:1, respectively.

In summary, the model system investigated herein clarified that aromatic and aliphatic isocyanates undergo the cyclotrimerization not in an orthogonal manner in spite of the significant difference in reactivity between them. Their ability to undergo coannulation in a statistic manner allowed us to expect that the dual system composed of aromatic and aliphatic diisocyanates described below can potentially give networked polymers bearing isocyanurate cores formed by coannulation of them, but not an interpenetrated network formed by parallel progress of two independent cyclotrimerizations of them.

Synthesis of Networked Polymers by a Dual System Composed of Aromatic and Aliphatic Diisocyanates

With employing the combination of pTolSO$_2$Na and DMI as a catalyst and a solvent, respectively, we next investigated synthesis of networked polymers with using MDI and HMDI as an aromatic and an aliphatic diisocyanates, respectively (Scheme 3). To obtain the networked polymers as films, the reactions were performed in a thin mold. Mixtures of the isocyanates in several feed ratios, catalyst, and solvent were prepared and each of them was poured into the mold, left to



SCHEME 2 Coannulation of TI and PI.

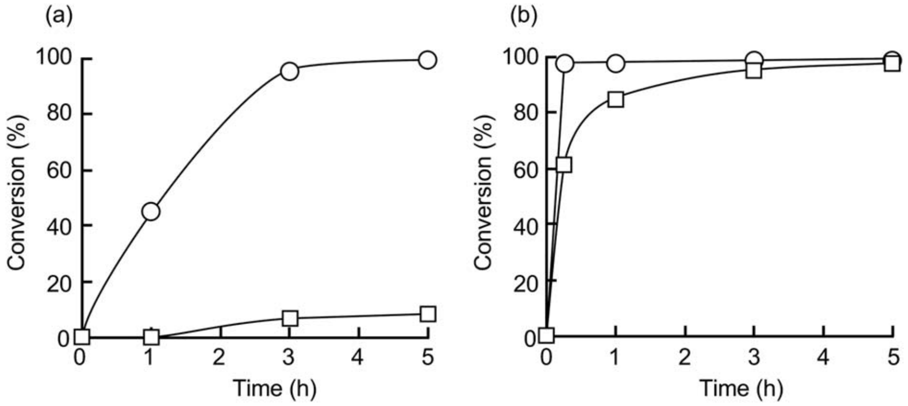


FIGURE 2 Time dependencies of conversion for the coannulation of TI (circle) and PI (square) at (a) room temperature and (b) 80 °C. The conversions were determined by ^{1}H-NMR.

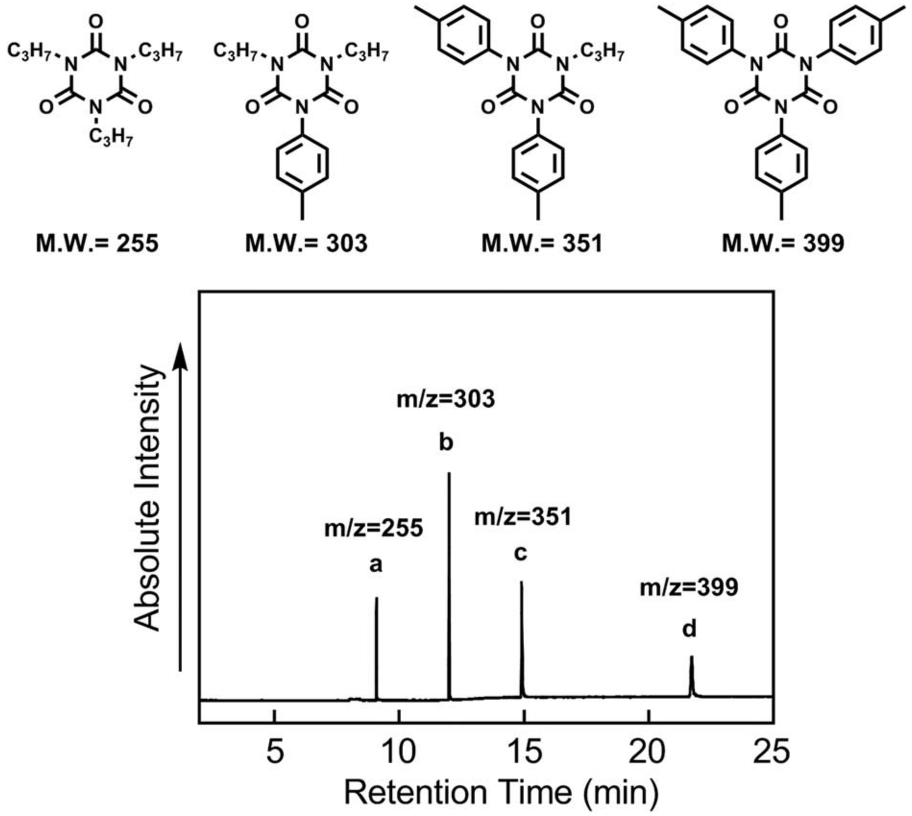
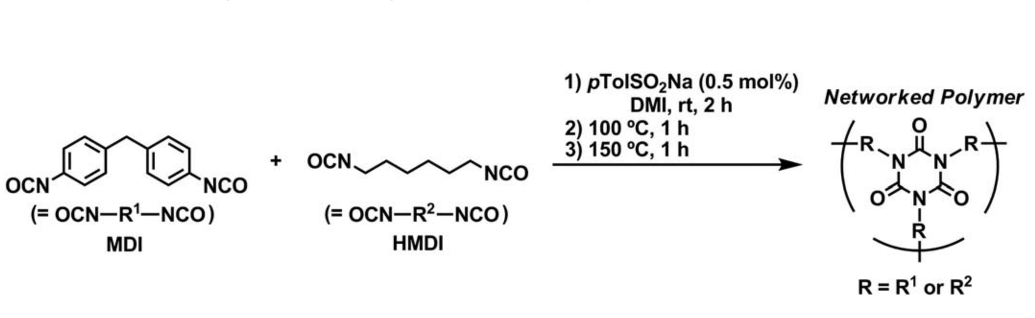


FIGURE 3 GC profile of crude product obtained by coannulation of TI and PI at 80 °C.



SCHEME 3 Synthesis of the networked polymer by coannulation of MDI and HMDI.

TABLE 1 Thermal Properties of the Networked Polymers 1–5 Obtained by Coannulation of MDI and HMDI

Product	$[MDI]_0$/ $[HMDI]_0$ (mol ratio)	Td_5[a] (°C)	Td_{10}[a] (°C)	Char yield[b] (%)	T_g[c] (°C)
1	3.0/0	455	475	79	N.D.[d] (50–300)
1[e]	3.0/0	447	467	75	N.D.[d] (50–300)
2	3.0/1.0	452	466	62	N.D.[d] (50–300)
3	3.0/2.0	446	460	48	N.D.[d] (50–300)
4	3.0/3.0	440	455	40	N.D.[d] (50–300)
5	0/3.0	404	441	<5	115

[a] Determined by TGA under N_2.

[b] Chair yield at 500 °C under N_2.

[c] Determined by DSC under N_2.

[d] Not detected.

[e] The cyclotrimerization was carried out at room temperature (see ref. 1).

stand at room temperature for 2 h, heated at 100 °C for 1 h, and finally heated at 150 °C for 2 h to obtain the corresponding networked polymers as films (Table 1). The experiments involve the cyclotrimerization of MDI and that of HMDI, which gave the corresponding networked polymers as comparatives. In the case of HMDI, the homogeneous networked polymer film could not be prepared because of the formation of foam owing to a drastic exotherm occurred during reaction. Instead, the cyclotrimerization of HMDI was performed in a test tube. Figure 4 shows IR spectra of MDI, HMDI, and the films fabricated by coannulation of MDI and HMDI in three different feed ratios and just taken from the mold. As shown in Figure 4(a,b), the strong absorption attributable to isocyanate was observed at 2250 cm^{-1}. After the reaction, this absorption became negligible [Fig. 4(c–g)] to imply that the isocyanates were consumed completely. Surprisingly, the cyclotrimerization of HMDI proceeded more rapidly and quantitatively compared with the model reaction. This is based on that fact that the local concentration of isocyanate groups increased during the formation of the network structure.

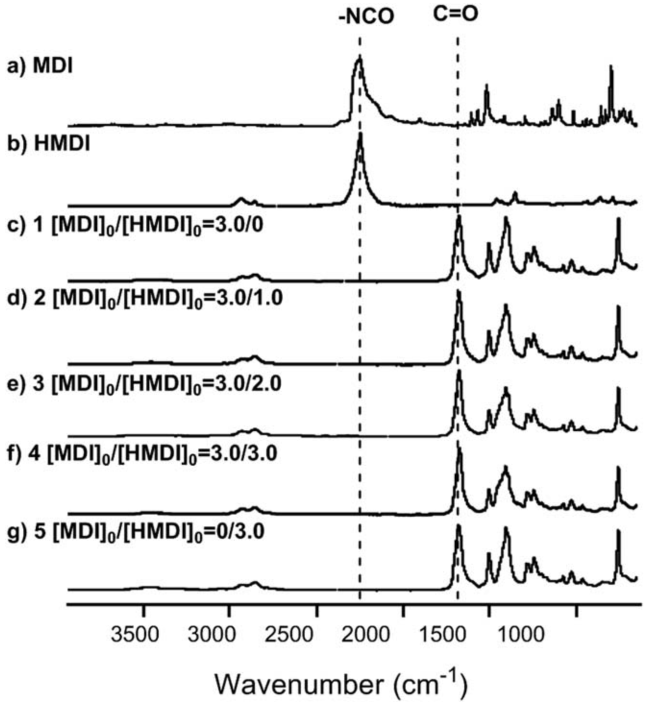
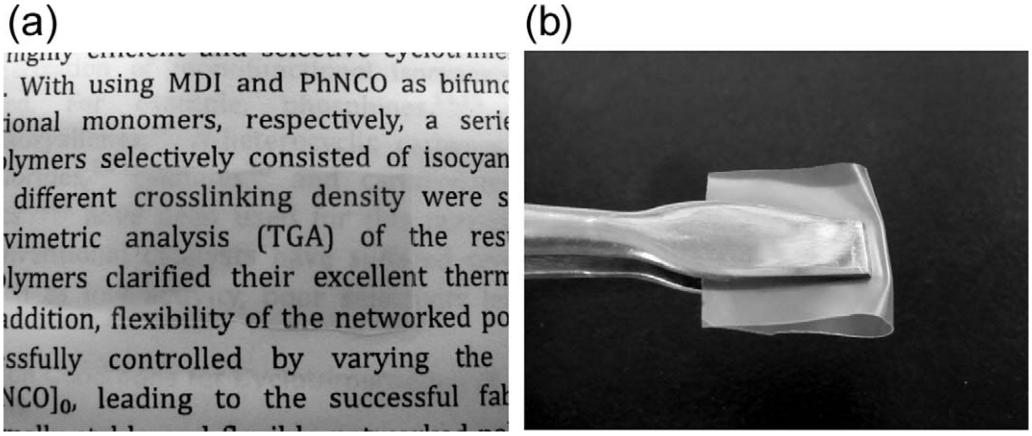


FIGURE 4 FTIR spectra of (a) MDI, (b) HMDI, the networked polymers (c) 1, (d) 2, (e) 3, (f) 4, and (g) 5 by coannulation of MDI and HMDI.

After the IR analysis, the products were immersed in water to remove water-soluble *p*$TolSO_2Na$ and DMI and dried at 150 °C in a vacuum oven. Figure 5(a) shows the photographs of the film of networked polymer **2** and thus obtained as a representative example. All the films obtained in this study were colorless and transparent. The film of the networked polymer **1** obtained by the cyclotrimetization of MDI was rather brittle presumably owing to its relatively rigid structure. On the other hand, the networked polymer films **2–4** obtained by the combination of MDI and HMDI were flexible owing to the presence of alkyl chains. In addition, the fracture of the films was not observed even under bending load



. With using MDI and PhNCO as bifunc
ional monomers, respectively, a serie
lymers selectively consisted of isocyan
different crosslinking density were s
vimetric analysis (TGA) of the res
lymers clarified their excellent therm
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FIGURE 5 Photographs of (a) the networked polymer film 2 and (b) film 2 under a bending load.

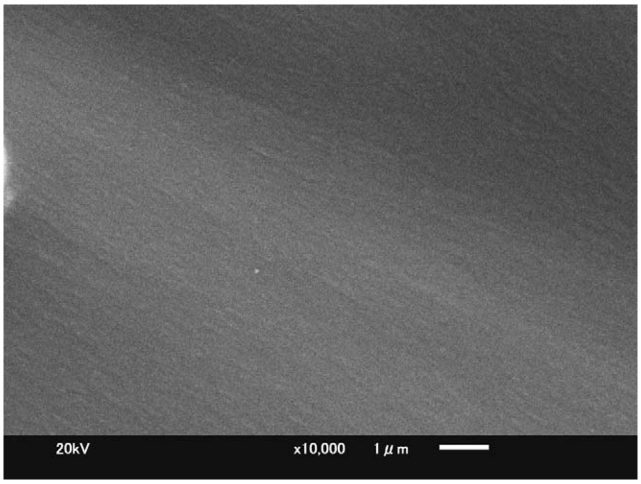

FIGURE 6 SEM image of cross-section of networked polymer film 2.

as shown in Figure 5(b). Figure 6 shows the SEM image of the cross-section of the networked polymer 2, which did not indicate any recognizable phase separation.

The networked polymers were analyzed by TGA and DSC to investigate their thermal stability. Figures 7 and 8 show the resulting thermograms. The corresponding Td_5 and Td_{10} (5 and 10% weight loss temperature, respectively), char yield at 500 °C, and glass transition temperature (T_g) are listed in Table 1. Previously, we have reported the Td_5 and Td_{10} values of a networked polymer obtained by cyclotrimerization of MDI at room temperature, which were 447 and 467 °C, respectively.[1] In this case, the conversion of isocyanate determined by IR analysis was 97%. In comparison with this, the thermal stability of the networked polymer 1 obtained in this study was slightly improved, presumably because of the quantitative conversion of isocyanate attained by the higher reaction temperature. The Td_5 values of the networked polymers 2–4 obtained by the MDI–HMDI dual system were $\geq$440 °C although those became lower accordingly to the increase in the initial content of HMDI.

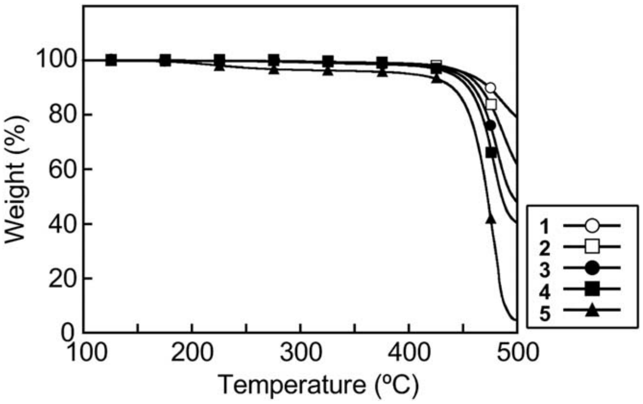

FIGURE 7 TGA curves of the networked polymers 1–5.

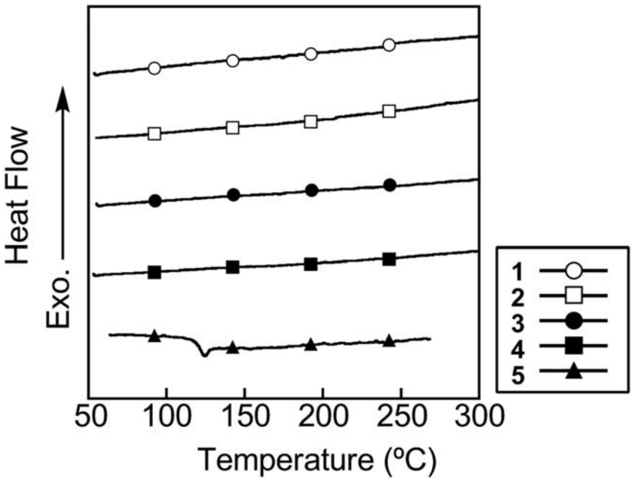

FIGURE 8 DSC curves of the networked polymers 1–5.

The T_g of the networked polymer 1 was not observed in a range from 50 to 300 °C, implying that the motion of the polymer chains was strictly restricted owing to the rigid structure of these networked polymers. On the other hand, the networked polymer 5 bearing flexible alkyl chains exhibited grass transition at 115 °C. For the networked polymers **2–4**, T_gs were not observed by DSC in a temperature range from 50 to 300 °C, suggesting that the present MDI–HMDI dual system involved statistic coannulation of MDI and HMDI as observed in the model system with the use of corresponding monofunctional isocyanates, TI and PI.

CONCLUSIONS

Coannulation of TI and PI proceeded efficiently by using sodium pTolSO$_2$Na and DMI as a catalyst and a solvent, respectively. Based on this finding, networked polymers were synthesized by a MDI–HMDI dual-diisocyanate system. The resulting products were selectively consisted of isocyanurate moiety and thus exhibited transparency and excellent thermal stability. Utilization of HMDI with varying feed ratio allowed successful control of flexibility of the networked polymer films, without serious deterioration of thermal stability. These networked polymers consisting of isocyanurate moieties are expected to be used as a high-performance material in a wide range of applications.

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