Development of High-Performance Networked Polymers Consisting of Isocyanurate Structures Based on Selective Cyclotrimerization of Isocyanates

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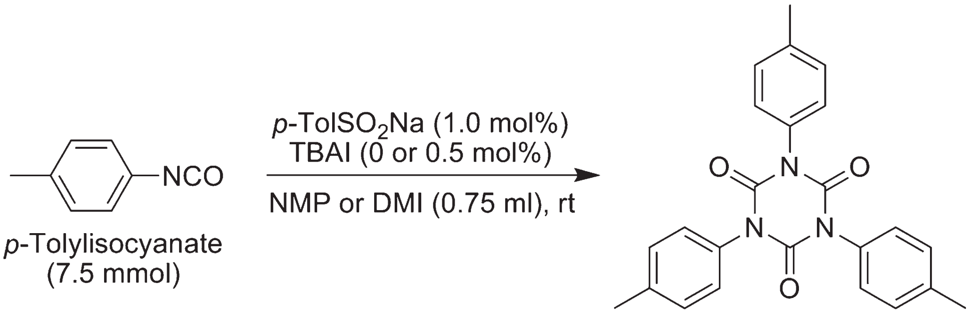
ABSTRACT: Selective and quantitative cyclotrimerization of *p*-tolylisocyanate proceeded by using sodium *p*-toluenesulfinate as a catalyst and 1,3-dimethylimidazolidinone as a solvent. Exploitation of this system to the cyclotrimerization of methylene diphenyl 4,4′-diisocyanate (MDI) permitted formation of the corresponding networked polymer, which was selectively consisted of isocyanurate moiety and thus exhibited excellent thermal stability. Utilization of phenyl isocyanate (PhNCO) as a comonomer with varying feed ratio $[\mathrm{MDI}]_0/[\mathrm{PhNCO}]_0$ allowed successful control of flexibility of the networked polymers, while retaining its high thermal stability. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 5186–5191, 2011

KEYWORDS: cyclopolymerization; high-performance polymers; isocyanurate; networks

INTRODUCTION The aromatic heterocyclic structure of 1,3,5-triazine-2,4,6-trione, known as isocyanurate, has been prepared by catalytic cyclotrimerization of the corresponding isocyanate.[1] Isocyanurate structure exhibits the highest thermal stability in various derivatives of isocyanates, such as oxazolidinone, carbodiimide, urea, urethane, biuret, and allophanate.[2–4] Because of the thermal stability, isocyanurate linkage has been frequently used in polyurethane chemistry to enhance thermal resistance, flame retardation, and chemical resistance of polyurethanes.[5] If suitable diisocyanates were used in the cyclotrimerization system, three-dimensional networked polymers consisting of thermally stable isocyanurate rings can be synthesized as promising candidates of high performance materials. However, there have been only a few reports on synthesis and properties of networked polymers based on the cyclotrimerization of diisocyanates. It has been reported that the treatment of an equimolar mixture of phenyl isocyanates (PhNCO) and methylene diphenyl 4,4′-diisocyanate (MDI) with a catalytic amount of *N*,*N*′,*N*″-tris[(dimethylamino)propyl]-*s*-hexahydrotriazine induced the cyclotrimerization of isocyanate moieties. The resulting product was separated into an ethanol-insoluble fraction and an ethanol-soluble one, and the former exhibited high thermal stability, leading to less than 5% weight loss at 400 °C.[6] This report indicated that networked polymers consisting of isocyanurate rings would be promising as high performance materials. A similar study on the cyclotrimerization of MDI has been reported, where stannous octoate was used as a catalyst.[7,8] In this case, formation of undesired structures involving urea, biuret, and uretidione was confirmed by a solid-state NMR spectroscopy. Although there have been similar studies on the cyclotrimerizations of 1,6-hexamthylenediisocyanate and 2,4-tolylenediisocyanate as diisocyanate-type monomers, the conversions of those monomers and selectivity of the reactions have not been satisfactory yet to achieve the potential of isocyanurate-based materials.[9–13]

In this work, we targeted networked polymers consisting of isocyanurate structures with minimized chemical defect based on highly efficient and selective cyclotrimerization of isocyanate. With using MDI and PhNCO as bifunctional and monofunctional monomers, respectively, a series of networked polymers selectively consisted of isocyanurate moieties with different crosslinking density were synthesized. Thermogravimetric analysis (TGA) of the resulting networked polymers clarified their excellent thermally stable nature. In addition, flexibility of the networked polymer films was successfully controlled by varying the feed ratio $[\mathrm{MDI}]_0$:$[\mathrm{PhNCO}]_0$, leading to the successful fabrication of highly thermally stable and flexible networked polymer films. To our best knowledge, this is the first example to achieve both these favorable properties usually in a trade-off relationship by the cyclotrimetization of isocyanates.



SCHEME 1 Cyclotrimerzation of *p*-tolylisocyanate.

EXPERIMENTAL

Materials and Instruments

MDI was purchased from Wako Pure Chemical Industry (Osaka, Japan) and distilled under reduced pressure. PhNCO was purchased from Tokyo Chemical Industry (Tokyo, Japan) and distilled under reduced pressure. Sodium *p*-toluenesulfinate (*p*-TolSO$_2$Na) and tetrabutylammonium iodide were purchased from Tokyo Chemical Industry (Tokyo, Japan) and dried under reduced pressure prior to use. 1,3-Dimethyl-2-imidazolidinone (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. IR spectra were recorded on a Thermo Scientific NICOLET iS10 FTIR spectrometer equipped with a SMART iTR ATR sampling accessory. Differential scanning calorimetry (DSC) was carried out with a Seiko Instrument Inc. DSC-6200 using aluminum pan under a 20 mL/min N$_2$ flow at the heating rate of 5 °C/min. Thermal gravimetric analysis (TGA) was performed with a Seiko Instrument Inc. TG-DTA 6200 using aluminum pan under a 50 mL/min N$_2$ flow at a heating rate of 10 °C/min.

Cyclotrimerization of *p*-Tolylisocyanate

All cyclotrimerization reactions were carried out under nitrogen. To a solution of *p*-TolSO$_2$Na (0.075 mmol, 0.013 g) in DMI (0.75 mL), *p*-tolylisocyanate (7.5 mmol, 0.95 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 (0.95 g, 7.2 mmol, 96%) as a white powder.

^{1}H NMR (CDCl$_3$): $\delta = 7.23$ (s, 12H), 2.32 ppm (s, 9H)^{13}C NMR (CDCl$_3$): $\delta = 148.8$, 139.2, 131.2, 130.0, 128.1, 21.17 ppm. FTIR (ATR): 1,694, 1,511, 1,401, 806, 748 cm^{-1}. Mp = 270 °C.

Synthesis of Networked Polymers

A typical procedure: In a dry test tube equipped with three-way stopcock, MDI (3.0 mmol, 0.75 g), PhNCO (1.2 mmol, 0.13 mL) and DMI (0.28 mL) were mixed. To the resulting solution, a solution of *p*-TolSO$_2$Na [6.4 mg, 0.036 mmol (0.5 mol % to NCO groups)] in DMI (0.72 mL) was added at 25 °C. After 15 min, 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 over night to yield the networked polymer **1c** (0.83 g, 94%).

FTIR (ATR): 1,694, 1,506, 1,393, 1,020, 755 cm^{-1}.

Preparation of Networked Polymer Films

Networked polymer films were prepared in a glove box at 25 °C under nitrogen. A typical procedure: A mold (6 cm × 4 cm × 100 μm) was fabricated with two pieces of PTFE-tape-coated slide glass and PTFE spacer (100-μm thickness). In a dry test tube equipped with a three-way stopcock, MDI (3.0 mmol, 0.75 g), PhNCO (1.2 mmol, 0.13 mL) and DMI (0.28 mL), and a solution of *p*-TolSO$_2$Na [6.4 mg, 0.036 mmol (0.5 mol % to NCO groups)] in DMI (0.72 mL) were mixed, and the resulting mixture was put into the mold within 1 min. After 2 h, the resulting film was taken out from the mold, immersed in water at 25 °C for 12 h, and dried under vacuum at 150 °C over night.

RESULTS AND DISCUSSION

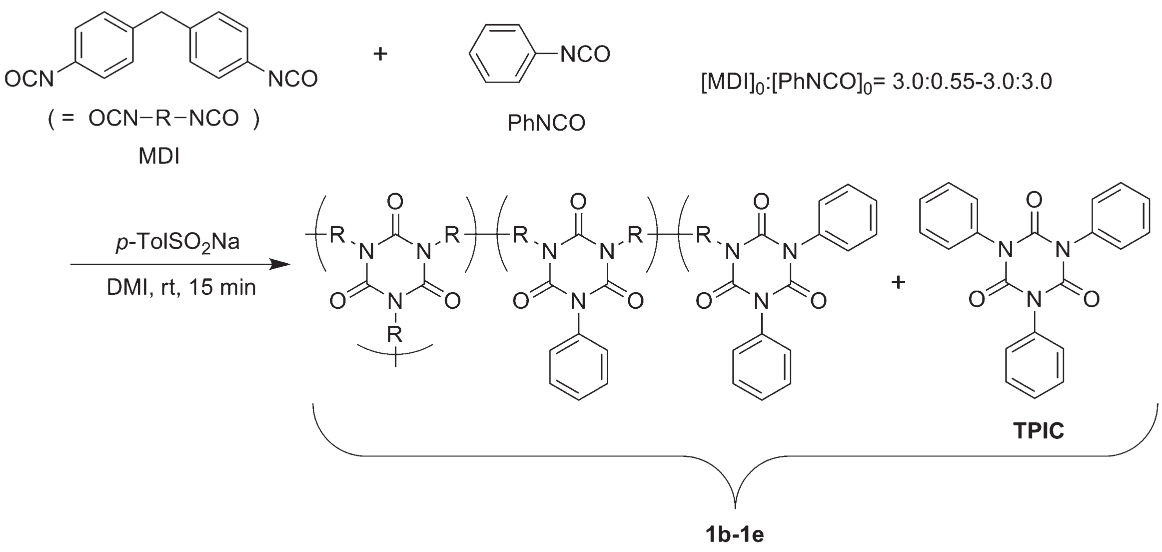
Cyclotrimerization of *p*-Tolylisocyanate as a model reaction

Prior to studying cyclotrimerization of diisocyanate, we investigated the cyclotrimerization of *p*-tolylisocyanate as a model reaction (Scheme 1). So far, a number of catalysts for the cyclotrimerization of monofunctional isocyanates have been reported. For example, phosphines,[14,15] tertiary amines,[1,16] alkoxyallenes,[17] *N*-heterocyclic carbenes,[18] various metal fluorides,[19] cyanates[20] and carboxylates,[21] and organometallics[22,23] have been used for this purpose. However, these conventional catalysts have suffered several disadvantages such as low activity, poor selectivity leading to

TABLE 1 Reaction Conditions for Cyclotrimerization of *p*-Tolylisocyanate

Entry	*p*-TolSO$_2$Na (mol %)	TBAI (mol %)	Solvents	Time	Yield[a] (%)
1	1.0	0.5	NMP	15 min	94
2	1.0	0.5	DMI	15 min	98
3	1.0	0	DMI	2 h	96

[a] Isolated yield by column chromatography.



SCHEME 2 Cyclotrimerzation of MDI in the presence of PhNCO.

formation of byproducts such as dimers and carbodiimides, and instability under air and moisture.

Recently, Moghaddam et al. reported that a combination of sodium *p*-toluenesulfinate (*p*-TolSO$_2$Na) and tetrabutylammonium iodide (TBAI) catalyzes cyclotrimerization of isocyanates efficiently.[24] As this catalyst system permitted quantitative conversion of isocyanates into the corresponding isocyanurates without giving any byproducts, we used it in our initial investigation of the cyclotrimerization of *p*-tolylisocyanate.

In addition to the utilization of this highly efficient catalysis system, we examined the utilization of a small amount of aprotic polar solvents that can dissolve *p*-TolSO$_2$Na. Another expectation for such solvents was their affinity with the reaction intermediates such as 1:1 and 1:2 adducts of sulfinate with isocyanate to assist progress of the cyclotrimerization reaction. *N*-methylpyrrolidone (NMP) and 1,3-dimethyl-2-imidazolidinone (DMI) were used herein.

When *p*-tolylisocyanate (7.5 mmol) was stirred with 1.0 mol % of *p*-TolSO$_2$Na and 0.5 mol % of TBAI in 0.75 mL of NMP, the cylotrimerization proceeded rapidly with considerable heat evolution (Table 1, entry 1). The corresponding isocyanurate, which was precipitated out from the solution within 15 min, was isolated in 94% yield. The structure of the isocyanurate was confirmed by IR and NMR spectra. On the other hand, when DMI was used as a solvent, the reaction proceeded more efficiently, leading to isolation of the corresponding isocyanurate in 98% yield (entry 2). It is noteworthy that the utilization of DMI allowed simplification of the reaction system, that is, *p*-TolSO$_2$Na exhibited high catalytic activity even without addition of TBAI (entry 3). The cyclotrimerization proceeded smoothly at 25 °C, and *p*-tolylisocyanate was quantitatively consumed within 2 h to give the corresponding isocyanurate in 96%. Although the high reaction rate was sacrificed in this case, the resulting moderate reaction rate was turned out to be favorable in fabrication of networked polymer films (*vide infra*).

TABLE 2 Reaction Conditions and Thermal Properties of the Products 1a–e Obtained by Cyclotrimerization of MDI in the Absence or Presence of PhNCO

Entry	Product	*p*-TolSO$_2$Na (mol % to NCO)	[MDI]$_0$/[PhNCO]$_0$ (mol ratio)	Conversion[a] (%)	T_g[b] (°C)	Td$_5$[c] (°C)	Td$_{10}$[c] (°C)	Char yield[d] (%)
1	**1a$_1$**	1.0	3.0/0	>99	–[e]	374	397	74
2	**1a$_2$**	0.5	3.0/0	97	–[e]	448	465	75
3	**1a$_3$**	0.1	3.0/0	93	–[e]	445	465	76
4	**1b**	0.5	3.0/0.55	>99	–[e]	422	442	70
5	**1c**	0.5	3.0/1.2	>99	–[e]	422	434	67
6	**1d**	0.5	3.0/2.0	>99	–[e]	422	437	66
7	**1e**	0.5	3.0/3.0	>99	–[e]	414	428	58

[a] Determined by FTIR spectrum.
[b] Determined by DSC under N$_2$.
[c] Determined by TGA under N$_2$.
[d] Chair yield at 500 °C under N$_2$.
[e] Glass transition temperature was not detected (<300 °C).

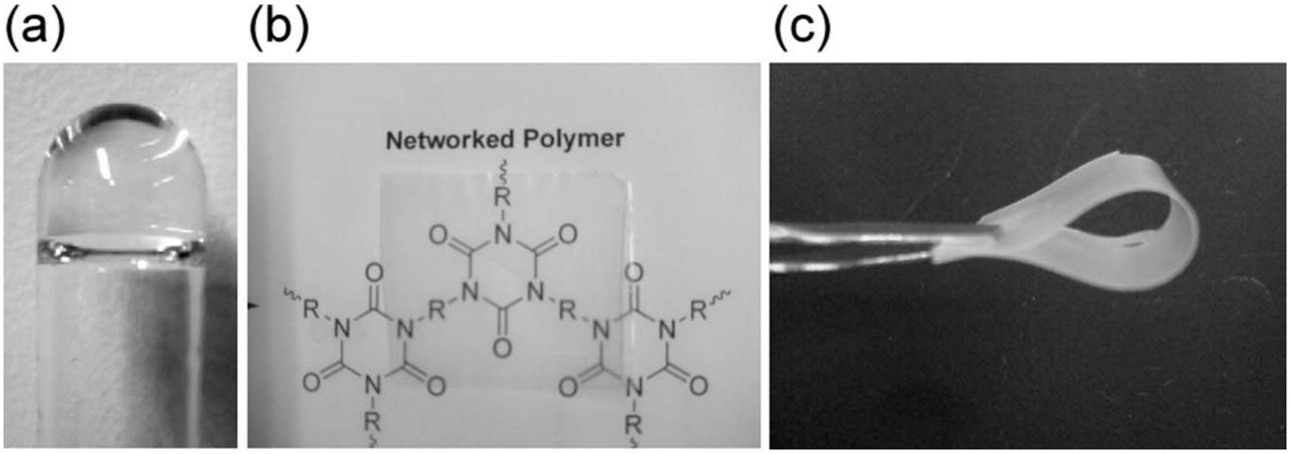


FIGURE 1 Photographs of (a) the networked polymer $\mathbf{1a_1}$ (containing DMI and *p*-TolSO$_2$Na), (b) a film of $\mathbf{1a_2}$ and (c) a film of **1d** under a flexible load.

Synthesis of Networked Polymers Based on Cyclotrimerization of Isocyanates

After confirming that the quantitative cyclotrimerization of *p*-tolylisocyanate was achieved by using *p*-TolSO$_2$Na and DMI as a catalyst and a solvent, respectively, we applied this system to synthesis of networked polymers with using MDI as a diisocyanate (Scheme 2). When MDI (3.0 mmol) and *p*-TolSO$_2$Na (1.0 mol % to isocyanate groups) were mixed in DMI (1.0 mL) at 25 °C in a test tube, a drastic exotherm took place to suggest MDI underwent the cyclotrimerization (Table 2, entry 1). Within 2 min, the mixture lost its fluidity and then vitrified to give a transparent and almost colorless solid in the vessel as shown in Figure 1(a). FTIR analysis revealed that the isocyanate moiety was completely consumed within 15 min. Figures 2(a) and (b) show the FTIR spectra of MDI and the resulting mixture, respectively. As shown in Figure 2(a), a strong absorption attributable to isocyanate was observed at 2250 cm^{-1} before the reaction. After the reaction, this peak disappeared [Fig. 2(b)], to imply the isocyanate groups were consumed almost completely. In addition, the cyclotrimerization of MDI proceeded efficiently, even by using reduced amounts of *p*-TolSO$_2$Na (0.5 and 1.0 mol %; entries 2 and 3). As a result, more than 90% of isocyanate was converted to give the corresponding networked polymers $\mathbf{1a_2}$ and $\mathbf{1a_3}$.

The advantage of the use of *p*-TolSO$_2$Na as a catalyst over those of conventional catalysts was confirmed by the following comparative experiment: The cyclotrimerization of MDI was carried out under the same conditions except replacing *p*-TolSO$_2$Na with *N*,*N*′,*N*″-tris[(dimethylamino)propyl]-*s*-hexahydrotriazine, whose utilization as a catalyst for cyclotrimerization of MDI has been reported.[6] As a result, unreacted isocyanate of ~14% remained in the obtained networked polymer. The influence of these residual isocyanate moieties on the thermal properties of the networked polymers will be discussed below.

The networked polymers $\mathbf{1a_1}$, $\mathbf{1a_2}$, and $\mathbf{1a_3}$ were washed by Soxhlet's extractor with chloroform and dried in a vacuum oven at 150 °C. All the products were obtained quantitatively. DSC and TGA measurement were performed in order to investigate the thermal stability of the networked polymers. Figures 3(a) and (b) show the DSC thermograms and TGA curves, respectively, of these networked polymers. For all the samples, glass transition temperatures (T_g) were not observed in a range from 50 to 300 °C [Fig. 3(a)], implying that the polymer chains were not free to move due to the high crosslinking density of these networked polymers. From the TGA curves, the values of Td$_5$ and Td$_{10}$ (5 and 10% weight loss temperature, respectively) and char yield at 500 °C of these networked polymers were determined and listed in Table 2. As shown in Table 2, the networked polymers $\mathbf{1a_1}$, $\mathbf{1a_2}$, and $\mathbf{1a_3}$ exhibited high thermal stability. Td$_5$ and Td$_{10}$ of $\mathbf{1a_1}$, the networked polymer with the highest conversion of isocyanate, were unexpectedly lower than those of the other ones $\mathbf{1a_2}$ and $\mathbf{1a_3}$. This observation implied that

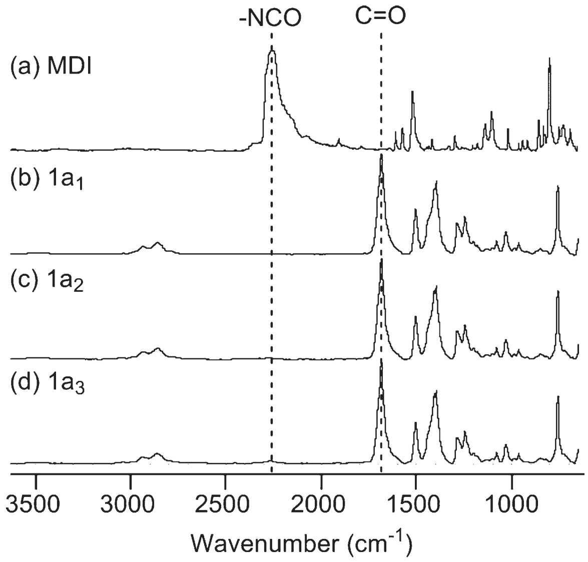


FIGURE 2 FTIR spectra of (a) MDI and the crude products (b) $\mathbf{1a_1}$, (c) $\mathbf{1a_2}$ and (d) $\mathbf{1a_3}$ obtained by cyclotrimerization of MDI.

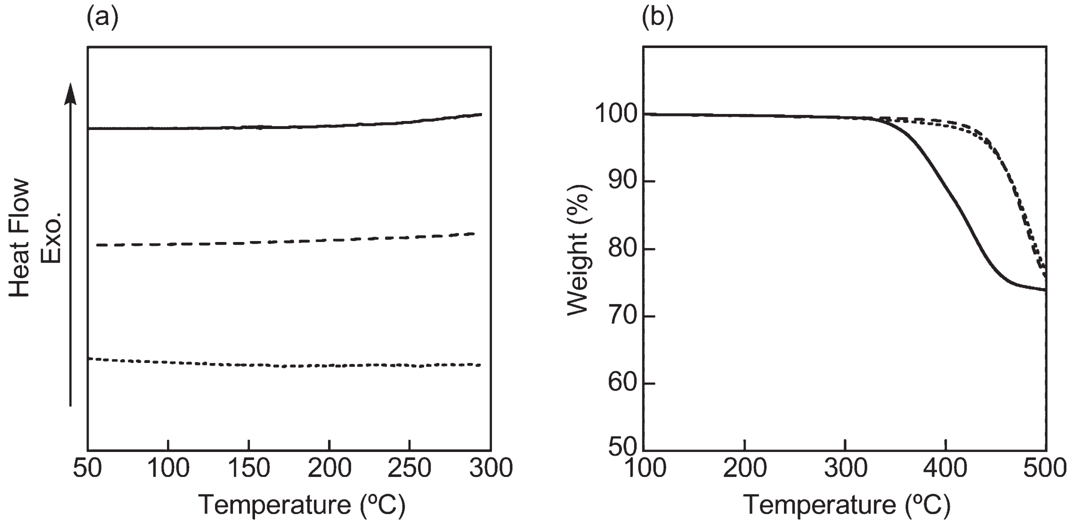


FIGURE 3 (a) DSC thermograms and (b) TGA curves of the networked polymers obtained by cyclotrimerization of MDI; **$1a_1$** (solid line), **$1a_2$** (dashed line), and **$1a_3$** (dotted line).

the use of a higher amount of *p*-$TolSO_2Na$ would lead to a more difficulty in removing the catalyst completely from the networked polymer by Soxhlet extraction and then would promote the thermal decomposition of the networked polymer by the residual catalyst.

Networked polymers with different crosslinking density were obtained by addition of PhNCO as a comonomer (Scheme 2; Table 2, entries 4–7). The polymerizations were performed under the optimum conditions for the cyclotrimerization of MDI involving utilization of 0.5 mol % of *p*-$TolSO_2Na$ that afforded the networked polymer **$1a_2$** (entry 2). Feed ratio $[MDI]_0/[PhNCO]_0$, conversion of isocyanate determined by FTIR spectra, and the thermal properties of the resultant products **1b**, **1c**, **1d**, and **1e** are listed in Table 2. Using PhNCO as a comonomer, the conversion of isocyanate groups increased. This increase in reactivity can be attributed to the reduction of viscosity of the reaction mixtures by a role of PhNCO as a diluent. Herein, it is expected that this copolymerization would proceed statistically, because there would be only a negligible difference in reactivity between the two aromatic isocyanates under the conditions. Such a statistic copolymerization would afford a mixture of networked polymers and *N*,*N*′,*N*″-triphenylisocyanurate (TPIC), the cyclotrimerization product of PhNCO. However, contrary to our expectations, TPIC was not eluted at all from the copolymerization products **1b**, **1c**, **1d,** and **1e** by Soxhlet extraction, implying that TPIC would be included in the networked structure via certain attractive interactions between isocyanurate rings, which may allow stacking of these planer structures to reinforce the networked polymers.

The glass transition temperatures of the products were not observed between 50 and 300 °C. Figure 4 shows the TGA curves of these products **1b**, **1c**, **1d**, and **1e**. The values of Td_5 and Td_{10} and the char yield at 500 °C of these products were listed in Table 2. The thermal stability of them became lower as the initial content of PhNCO increased. However, the thermal stability of **1e**, which was obtained by copolymerization of MDI and PhNCO in the highest initial content of PhNCO, was still high so that Td_5 exceeded 400 °C.

Films of **$1a_2$** and **1b**–**1e** were easily prepared by performing the cyclotrimerization in a mold under the same conditions for the experiments in test tubes. As mentioned above, the rate of the cyclotrimerization of isocyanate with using *p*-$TolSO_2Na$ as a catalyst without adding TBAI was moderate, to permit preparation of homogeneous mixtures of isocyanates and the catalyst without being interfered by serious increase in viscosity. The moderate reaction rate was also favorable for pouring the formulations into a mold, which sometimes takes time. The resulting films were isolated by washing them with water to remove DMI and *p*-$TolSO_2Na$ and dried under vacuum. As shown in Figure 1(b), the films thus obtained were colorless and transparent. These networked polymer films exhibited high thermal stability, as shown in Table 3. In parallel, we prepared a film of a cyclotrimetization product of MDI in a similar procedure, with using

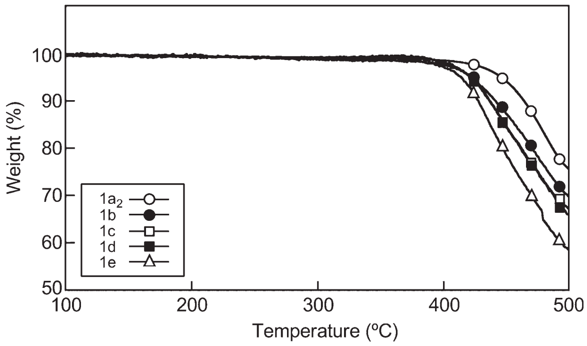


FIGURE 4 TGA curves of the products obtained by cyclotrimerization of MDI in the presence of PhNCO; **$1a_2$** (open circle), **1b** (filled circle), **1c** (open square), **1d** (filled square), and **1e** (open triangle).

TABLE 3 Thermal Properties of the Films $1a_2$ and 1b–1e Obtained by Cyclotrimerization of MDI in the Absence or Presence of PhNCO

Film	$[MDI]_0/[PhNCO]_0$ (mol ratio)	Td_5[a] (°C)	Td_{10}[a] (°C)	Char yield[b] (%)
$1a_2$	3.0/0	447	467	75
1b	3.0/0.55	451	471	75
1c	3.0/1.2	441	466	70
1d	3.0/2.0	428	461	65
1e	3.0/3.0	395	450	61

[a] Determined by TGA under N_2.
[b] Chair yield at 500 °C under N_2.

N,*N*′,*N*″-tris[(dimethylamino)propyl]-*s*-hexahydrotriazine as a catalyst. The thermal stability of the resulting film was much lower (Td_5: 429 °C and Td_{10}: 464 °C) than the networked polymer film of **$1a_2$** obtained by the *p*-$TolSO_2Na$-catalyzed cyclotrimetization reaction. Theses results clarified that the high conversion of isocyanate achieved by the utilization of the highly active catalyst *p*-$TolSO_2Na$ was essential for the high thermal stability of the film. The film of the networked polymer **$1a_2$** was rather brittle due to its relatively high crosslinking density; however, the films of **1b**–**1d** obtained by the copolymerization of MDI and PhNCO were flexible as shown in Figure 1(c).

SUMMARY

The present work has proven the high potential of the cyclotrimerization of isocyanates to develop high-performance materials with transparency and flexibility in a film state. By minimizing chemical defect based on highly efficient and selective cyclotrimerization that was achieved by employing *p*-$TolSO_2Na$ as a catalyst, the resulting networked polymers consisting of isocyanurate rings exhibited high heat resistance due to the intrinsic thermal stability of isocyanurate. The structural diversity of isocyanates is another important advantage of the present approach, which will expand its application fields.

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