Synthesis of Methacrylate Polymer Bearing Cyanate Groups and Its Chemoselective Reaction with Amines

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Received 21 May 2013; accepted 3 December 2013; published online 16 December 2013
DOI: 10.1002/pola.27053

ABSTRACT: A novel reactive polymer containing cyanate groups in the side chain was prepared by free radical polymerization of a cyanate-containing monomer, 2-(4-cyanatophenyl)ethyl methacrylate (**1**). The monomer **1** and its polymer, poly[2-(4-cyanatophenyl)ethyl methacrylate] (PCPMA), were stable under the air for a long period. The copolymerization of **1** and methyl methacrylate provided the corresponding copolymers with various cyanate contents. The availability of the cyanate-containing polymers as a reactive polymer was investigated. Model reaction using 4-cyanatotoluene revealed that a cyanate group reacted with aliphatic amines, whereas no reaction occurred in the presence of water, alcohols, and aromatic amines under mild conditions. Post-functionalization of PCPMA was demonstrated using aliphatic amines or diamines. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 699–706

KEYWORDS: crosslinking; functionalization of polymers; radical polymerization

INTRODUCTION Polymers containing reactive functional groups have widely been developed for various applications such as adhesives, coatings, and emulsion paints.[1,2] Post-functionalization at the reactive moieties in such polymers allows sophisticated control in the physical properties required for the applications. For example, isocyanate is one of the reactive functional groups and has been introduced in polymer backbones as a moiety, which reacts with various functional groups such as alcohols and amines in a benign condition. Among them, 2-isocyanatoethyl (meth)acrylate is a commercially available monomer, and its polymer has widely used in academic researches and industrial materials. Key functionalizations or crosslinking reactions at the isocyanate groups have been demonstrated for a wide range of diverse applications.[3–6] However, the high reactivity of isocyanates, which causes the deactivation and/or undesired crosslinking by the reaction with aerobic water in an atmospheric condition, reduces the storage stability of these reactive polymers. Recently, it has been reported that copolymerization with hydrophobic monomers suppresses the reactivity of isocyanate at room temperature, which renders easy handling and latent reactivity to the isocyanate-containing copolymers.[7,8]

Cyanate group is a structural isomer of isocyanate containing a carbon–nitrogen triple bond. The compounds containing two or more cyanate groups have been applied to engineering thermoset materials known as cyanate ester resins.[9] The cyanate ester resins consist of densely networked polycyanurates formed by cyclotrimerization of cyanate groups. Their excellent thermal, mechanical, and dielectric properties offer the industrial uses in aerospace, insulation, microelectronics, and adhesive. Blending the cyanate resins with the other type of thermosets such as epoxy and polybenzoxazine resins was also demonstrated to control their properties.[10–14] In the case of the epoxy/cyanate mixture resin, the toughness of the cured materials was improved by decreasing the glass transition temperature (T_g) compared to cyanate ester resins.[12]

Very few were reported on polymers containing cyanate groups at their side chain, and the availability as a prepolymer of polycyanurate thermosets was only discussed.[15,16] Because cyanate group is known to show a unique reactivity, the cyanate-containing polymers can be an alternative of reactive polymers for post-functionalization.[17] Here, we designed a novel reactive polymer containing cyanate groups in the side chain. A methacrylate monomer having a cyanate group was synthesized and polymerized via free radical polymerization method. The reactivity of cyanate groups on the polymer backbone with various reactants was investigated by a model reaction using 4-cyanatotoluene and various nucleophiles. The feasibility of post-functionalization and crosslinking reaction with aliphatic amines was discussed.

Additional Supporting Information may be found in the online version of this article.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF) and diethyl ether were distilled over sodium and benzophenone. Toluene, acetonitrile, and *N*-methyl-2-pyrrolidinone (NMP) were distilled over CaH_2. Triethylamine was distilled over KOH. Methyl ethyl ketone (MEK) was dried over 4 Å molecular sieves. Methacryloyl chloride and methyl methacrylate (MMA) were used as freshly distilled under vacuum. 2-(4-Hydroxyphenyl)ethyl methacrylate was prepared from 4-(2-hydroxyethyl)phenol and methacryloyl chloride according to the literature.[18] 4-Cyanatotoluene was prepared from *p*-cresol and cyanogen bromide by the modified procedure of the literature method.[19] The other reagents were used as received.

Synthesis of 2-(4-Cyanatophenyl)ethyl Methacrylate (1)

To a flask equipped with a stirring bar and an addition funnel were added 2-(4-hydroxyphenyl)ethyl methacrylate (6.00 g, 29.1 mmol), triethylamine (8.1 mL, 58.2 mmol), and dried diethyl ether (40 mL). A solution of cyanogen bromide (3.0 M in diethyl ether, 10.7 mL, 32.0 mmol) was added dropwise at −10 °C with vigorous stirring, and the mixture was stirred for 1.5 h. After the resulting mixture was washed with water and brine, the organic layer was dried over $MgSO_4$ and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography eluted with hexane and ethyl acetate (5/1 in volume ratio) to give a colorless liquid. The yield was 2.77 g (41%).

IR (neat): 2958, 2262, 2235, 1715, 1635, 1501, 1320, 1295, 1155, 1014, 940, 812 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.32 (d, 2H, $J = 9.2$ Hz), 7.24 (d, 2H, $J = 9.2$ Hz), 6.06 (s, 1H), 5.56 (s, 1H), 4.35 (t, 2H, $J = 6.8$ Hz), 3.01 (t, 2H, $J = 6.8$ Hz), 1.91 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 167.40, 151.73, 137.20, 136.24, 130.99, 125.86, 115.45, 108.94, 64.76, 34.45, 18.39.

Synthesis of Poly[2-(4-cyanatophenyl)ethyl methacrylate] (PCPMA)

To a tube equipped with a stirring bar and a stopcock were added **1** (1.00 g, 4.32 mmol), 2,2′-azobis(2,4-dimethylvaleronitrile) (ADVN) (0.022 g, 0.086 mmol), and MEK (2.2 mL) under nitrogen. The solution was degassed by freeze-pump-thaw cycles and stirred for 24 h at 60 °C under nitrogen. The mixture was cooled down to room temperature and poured into 20-fold amount of diethyl ether. The sticky precipitation was collected by decantation, dissolved in THF, and reprecipitated with hexane. The white polymer was filtered and dried. The yield was 0.95 g (95%).

IR (neat): 2956, 2264, 2237, 1728, 1604, 1504, 1448, 1167, 1086, 1016, 825, 750 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.38–7.17 (m, 4H), 4.11 (br, 2H), 2.94 (br, 2H), 1.94–1.48 (m, 2H), 1.03–0.45 (m, 3H).

Copolymerization of 1 with MMA

To a tube equipped with a stirring bar and a stopcock were added **1** (0.347 g, 1.50 mmol), MMA (0.150 g, 1.50 mmol), ADVN (14.9 mg, 0.060 mmol), and MEK (1.5 mL) under nitrogen. The solution was degassed by freeze-pump-thaw cycles and stirred for 24 h at 60 °C under nitrogen. The mixture was cooled down to room temperature and poured into 20-fold amount of hexane/diethyl ether. The precipitation was collected by filtration, dissolved in THF, and reprecipitated with hexane. The white polymer was filtered and dried. The yield was 0.269 g (54%).

IR (neat): 2991, 2949, 2264, 2235, 1722, 1603, 1502, 1444, 1389, 1238, 1186, 1144, 987, 808, 750 cm^{-1}. ^1H NMR ($CDCl_3$): 7.39–7.20 (m, 4H), 4.13 (br, 2H), 3.58 (br, 3H), 2.96 (br, 2H), 2.08–1.54 (m, 4H), 1.50–0.46 (m, 6H).

Synthesis of 4-Cyanatotoluene (2) as a Model Compound

To a flask equipped with a stirring bar and an addition funnel were added *p*-cresol (5.95 g, 55.0 mmol), triethylamine (8.40 mL, 60.5 mmol), and dried diethyl ether (80 mL). A solution of cyanogen bromide (3.0 M in diethyl ether, 20.0 mL, 60.0 mmol) was added dropwise at −10 °C with vigorous stirring, and the mixture was stirred for 1.5 h. After the precipitated salt was filtered off and washed with diethyl ether, the filtrate was washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography eluted with hexane to give a colorless liquid. The yield was 4.92 g (67%).

IR (neat): 2928, 2260, 2235, 1604, 1498, 1184, 1163, 1084, 1016, 808, 731 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.23 (d, 2H, $J = 8.8$ Hz), 7.17 (d, 2H, $J = 8.8$ Hz), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 151.06, 136.90, 130.93, 115.13, 109.19, 20.83.

Model Reaction of a Cyanate Group Using 2 with Various Nucleophiles

The reactions of cyanate ester **2** and various nucleophiles were carried out by the same procedure as follows. To a flask equipped with a stirring bar and a stopcock were added **2** (0.133 g, 1.00 mmol) and THF (2 mL) under nitrogen. A nucleophile (1.00 mmol) was added to this solution by a syringe, and the mixture was stirred for 24 h. An aliquot (20 μL) was taken out at different intervals, and each sample was subjected to ^1H NMR measurement in $CDCl_3$. The conversion was monitored by the consumption of **2** for each sample.

Synthesis of *N,N*-Diisopropyl-*O*-(*p*-tolyl)isourea (4)

To a flask equipped with a stirring bar and a stopcock were added **2** (0.133 g, 1.00 mmol) and THF (2 mL) under nitrogen. Diisopropylamine (0.14 mL, 1.0 mmol) was added to this solution, and the mixture was stirred at room temperature for 24 h. After the solution was concentrated by a rotary evaporator, the crude product was purified by silica gel column chromatography eluted with hexane and ethyl acetate (1/1 in volume ratio) containing 0.5 vol/vol % of triethylamine to give a colorless liquid. The yield was 0.14 g (60%).

IR (neat): 3342, 2968, 2928, 2872, 1630, 1508, 1429, 1365, 1313, 1209, 1161, 1134, 1082, 1034, 993, 889, 847, 816,

721 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.18 (d, 2H, $J = 8.0$ Hz), 6.97 (d, 2H, $J = 8.0$ Hz), 4.80–4.00 (br, 1H), 4.05 (sep, 2H, $J = 6.8$ Hz), 2.35 (s, 3H), 1.30 (d, 12H, $J = 6.8$ Hz). ^{13}C NMR ($CDCl_3$): δ 160.47, 149.14, 135.07, 130.46, 122.06, 46.57, 21.51, 20.96.

Synthesis of Phosphonium Salt (5)

To a flask equipped with a stirring bar and a stopcock were added **2** (0.133 g, 1.00 mmol) and THF (2 mL) under nitrogen. Triphenylphosphine (0.262 g, 1.0 mmol) was added to this solution, and the mixture was stirred at room temperature for 24 h. The mixture was poured into excess amount of hexane, and the precipitate was filtered. The crude product was washed with hexane and dried. The yield was 0.095 g (24%).

IR (neat): 1684, 1546, 1505, 1483, 1436, 1308, 1241, 1196, 1111, 1057, 997, 878, 849, 748, 720, 692 cm^{-1}. ^1H NMR ($CDCl_3$): δ 9.55 (s, 1H), 7.80–7.73 (m, 6H), 7.67–7.60 (m, 3H), 7.58–7.51 (m, 6H), 7.20 (d, 2H, $J = 8.4$ Hz), 7.16 (d, 2H, $J = 8.4$ Hz), 2.35 (s, 3H).

Synthesis of Poly{2-[4-(*N,N*-diisopropylcarbamimidoyloxy)phenyl]ethyl methacrylate} (6)

To a flask equipped with a stirring bar and a stopcock were added PCPMA (0.050 g, 0.22 mmol of unit) and THF (0.5 mL) under nitrogen. Diisopropylamine (46.3 μL, 0.33 mmol) was added to this solution, and the mixture was stirred at room temperature for 24 h. The solution was poured into hexane, and the viscous precipitate was collected by decantation. The polymer was washed with hexane and dried. The yield was 0.064 g (88%).

IR (neat): 3340, 2966, 2873, 1726, 1628, 1510, 1431, 1367, 1315, 1213, 1136, 1034, 993, 891, 852 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.22 (d, 2H, $J = 8.0$ Hz), 7.00 (d, 2H, $J = 8.0$ Hz), 4.80–3.90 (br, 1H), 4.14 (br, 2H), 4.02 (br, 2H), 2.91 (br, 2H), 2.10–1.70 (br, 2H), 1.27 (d, 12H, $J = 6.4$ Hz), 1.15–0.65 (m, 3H).

Synthesis of Poly{2-[4-(*N,N*-diethylcarbamimidoyloxy)phenyl]ethyl methacrylate} (7)

To a flask equipped with a stirring bar and a stopcock were added PCPMA (0.050 g, 0.22 mmol of unit) and THF (0.5 mL) under nitrogen. Diisopropylamine (34.1 μL, 0.33 mmol) was added to this solution, and the mixture was stirred at room temperature for 24 h. The solution was poured into hexane, and the viscous precipitate was collected by decantation. The polymer was washed with hexane and dried. The yield was 0.063 g (90%).

IR (neat): 3340, 2966, 2873, 1726, 1628, 1510, 1431, 1367, 1315, 1213, 1136, 1034, 993, 891, 852 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.21 (d, 2H, $J = 8.0$ Hz), 6.99 (d, 2H, $J = 8.0$ Hz), 4.40 (s, 1H), 4.13 (br, 2H), 3.39 (d, 4H, $J = 7.2$ Hz), 2.90 (br, 2H), 2.09–1.56 (br, 2H), 1.18 (t, 6H, $J = 7.2$ Hz), 1.08–0.62 (m, 3H).

Functionalization of Cyanate Group in PCPMA with *n*-Propylamine (8)

To a flask equipped with a stirring bar and a stopcock were added PCPMA (0.050 g, 0.22 mmol of unit) and THF (0.5 mL) under nitrogen. Propylamine (27.1 μL, 0.33 mmol) was added to this solution, and the mixture was stirred at room temperature for 24 h. The solution was poured into hexane, and the precipitate was collected by decantation. The polymer was washed with hexane and dried. The yield was 0.06 g (94%).

IR (neat): 3352, 2956, 2875, 2178, 1722, 1651, 1615, 1592, 1515, 1455, 1223, 1149, 968, 823, 749 cm^{-1}.

Functionalization of Cyanate Group in PCPMA with Triphenylphosphine (9)

To a flask equipped with a stirring bar and a stopcock were added PCPMA (0.050 g, 0.22 mmol of unit) and THF (0.5 mL) under nitrogen. Triphenylphosphine (0.065 g, 0.248 mmol) was added to this solution, and the mixture was stirred at room temperature for 24 h. The resulting mixture was poured into hexane, and the precipitate was collected by filtration. The polymer was washed with hexane and dried. The yield was 0.067 g (58%).

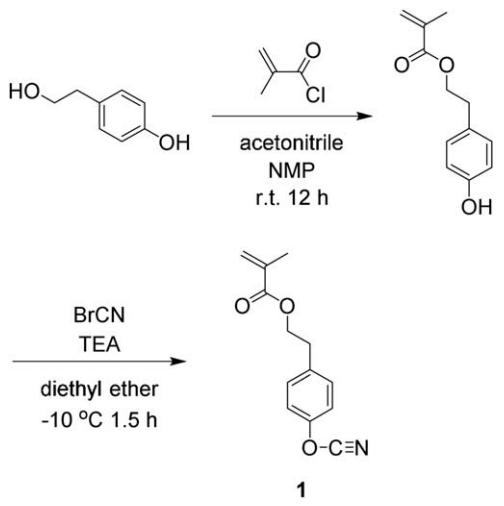
IR (neat): 2953, 1722, 1614, 1592, 1514, 1436, 1236, 1155, 1115, 997, 825, 721, 691 cm^{-1}.

General Procedure for Synthesis of Networked Polymers

To a flask equipped with a stirring bar and a stopcock were added PCPMA (0.050 g, 0.22 mmol of unit) and THF (0.45 mL) under nitrogen. A solution of diamine (0.044 mmol) in THF (0.05 mL) was added by a syringe, and the mixture was stirred at room temperature for 24 h. The resulting gel was poured into hexane, filtered, washed by hexane, and dried at 100 °C *in vacuo*.

Measurements

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECS 400 spectrometer at 400 and 100 MHz, respectively. Deuterated chloroform or dimethylsulfoxide was used as a solvent with tetramethylsilane as an internal standard. IR spectra were



1

SCHEME 1 Synthesis of monomer **1** containing cyanate group.

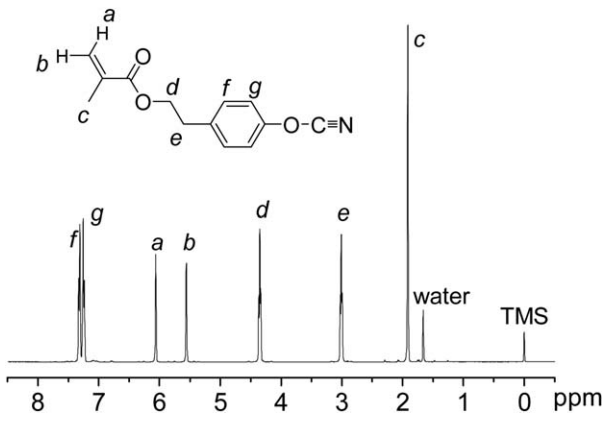


FIGURE 1 ^{1}H NMR spectrum of **1** in $CDCl_3$.

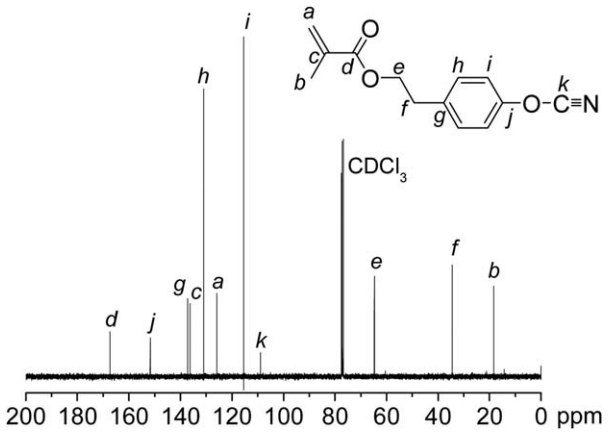
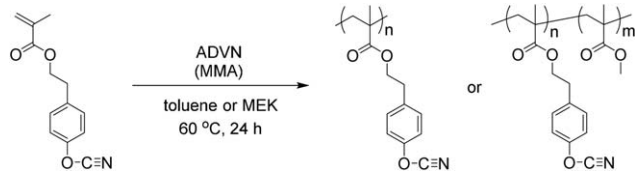


FIGURE 2 ^{13}C NMR spectrum of **1** in $CDCl_3$.

obtained on a Nicolet iS10 spectrometer (Thermo Fisher Scientific) equipped with a Smart iTR Sampling Accessory unit. Number- and weight-average molecular weights (M_n and M_w) were determined by gel permeation chromatography (GPC) analyses using a HLC-8320GPC (Tosoh Corporation) equipped with a TSKgel SuperHM-H column eluted with THF at a flow rate of 0.5 mL min^{-1} and calibrated by standard polystyrene samples. Differential scanning calorimetry (DSC) analyses were performed on a DSC 6200 instrument (Seiko Instruments) using an aluminum pan under 20 mL min^{-1} of nitrogen flow at a heating and cooling rate of 10 °C min^{-1}. Thermal gravimetric analysis (TGA) was performed on a TG/DTA 6200 instrument (Seiko Instruments) using an aluminum pan under 50 mL min^{-1} of nitrogen flow at a heating rate of 10 °C min^{-1}.



SCHEME 2 Free radical (co)polymerization of **1**.

RESULTS AND DISCUSSION

As a novel monomer containing a cyanate group, 2-(4-cyanatophenyl)ethyl methacrylate (**1**) was designed and synthesized in two-step reactions (Scheme 1). Esterification of 4-(2-hydroxyethyl)phenol using methacryloyl chloride afforded a methacrylate containing a phenol moiety. Then, the phenolic hydroxyl group was converted to a cyanate ester by the reaction with cyanogen bromide to give the monomer **1**. The chemical structure of **1** was confirmed by ^{1}H NMR, ^{13}C NMR, and IR spectra. All the signals in the ^{1}H NMR spectrum were reasonably assigned as shown in Figure 1. A characteristic signal at 108.94 ppm derived from the carbon of the cyanate group was observed in the ^{13}C NMR spectrum of **1** (Fig. 2). The introduction of the cyanate group was also confirmed by sharp peaks at 2235 and 2262 cm^{-1} derived from stretching vibration mode of C≡N bond in the IR spectrum. After purification by silica gel column chromatography, the monomer **1** was stable under the air for several months.

Free radical polymerization of **1** was conducted with ADVN as an initiator in toluene or MEK at 60 °C as shown in Scheme 2. After the precipitation with diethyl ether and hexane, poly[2-(4-cyanatophenyl)ethyl methacrylate] (PCPMA) with number-average molecular weights (M_n) of 28,000 and 16,400 using toluene and MEK as a solvent, respectively, and slightly broad molecular weight distributions (M_w/M_n) were obtained (Table 1, Runs 1 and 2). The polymer structure was confirmed by ^{1}H NMR (Fig. 3) and IR spectra. The strong peaks assignable to C≡N bond were observed at 2237 and

TABLE 1 Free Radical Polymerization of **1** and Copolymerization with MMA[a]

Run	Feed Ratio (**1**/MMA)	Solvent	Yield (%)	M_n[b]	M_w[b]	M_w/M_n[b]	Unit Ratio[c] (**1**/MMA)	T_g[d] (°C)
1	100/0	Toluene	67	28,000	106,000	3.79	–	66
2	100/0	MEK	95	16,400	66,400	4.04	–	65
3	50/50	Toluene	54	15,000	85,000	5.71	51/49	77
4	25/75	MEK	86	6,900	15,000	2.12	26/74	65
5	50/50	MEK	54	8,600	20,000	2.28	51/49	73
6	75/25	MEK	70	14,000	35,000	2.46	73/27	85

[a] Polymerization was carried out using 2 mol % of ADVN at 60 °C for 24 h.
[b] Determined by GPC eluted with THF using polystyrene standards.
[c] Determined by ^{1}H NMR.
[d] Determined by DSC in the second heating scan.

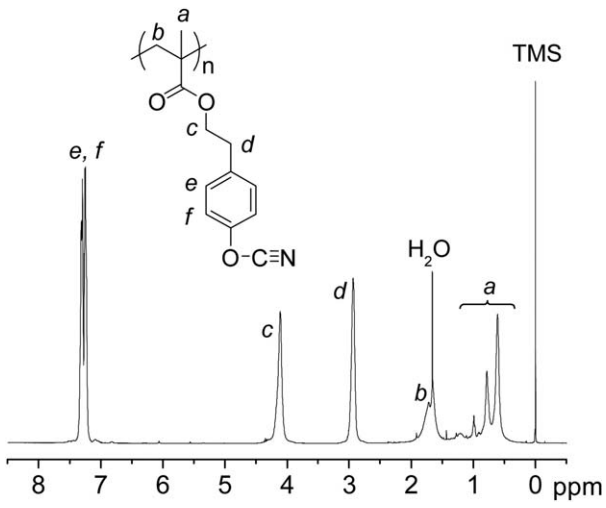


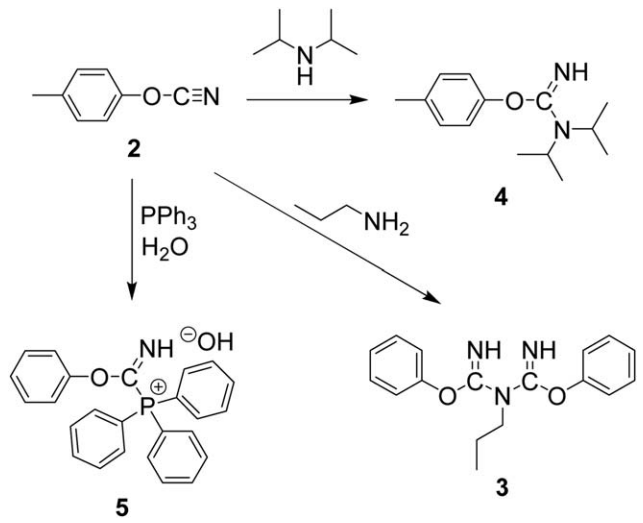
FIGURE 3 ^{1}H NMR spectrum of PCPMA in $CDCl_3$.

2264 cm^{-1} in the IR spectrum of PCPMA, which indicates that cyanate group of **1** remained unreactive during the radical polymerization. The polymer showed good solubility in common organic solvents such as acetone, ethyl acetate, toluene, THF, chloroform, DMSO, and *N*,*N*-dimethylformamide (DMF). The glass transition temperature (T_g) of PCPMA was determined as 66 °C by DSC measurement. Copolymerization of **1** and MMA with various feed ratios was also conducted to provide poly{[2-(4-cyanatophenyl)ethyl methacrylate]-*stat*-(methyl methacrylate)}, and the results are summarized in Table 1. The unit ratios of **1** to MMA in the copolymers were estimated by ^{1}H NMR spectra, and found to be almost same as feed ratios. This indicates that the content of cyanate-containing unit in the copolymers can be tuned for requirements in their application. No spectral change in the NMR spectra of PCPMA and the copolymers was observed after settled under the air for several months, indicating that the cyanate-containing polymers can be easily preserved even under the moist condition.

TABLE 2 Model Reaction of **2** with Various Nucleophiles[a]

Nucleophiles	Temp. (°C)	Time (h)	Conv.[b] (%)
H_2O	r. t.	24	0
H_2O	60	24	0
n-Propanol	r. t.	24	0
n-Propanol	60	24	0
Phenol	r. t.	24	0
n-Propylamine	r. t.	0.5	91
n-Propylamine[c]	r. t.	0.5	90
Diethylamine	r. t.	1	95
Diisopropylamine	r. t.	12	92
Aniline	r. t.	24	0
Acetic acid	r. t.	24	0
Tricyclohexylphosphine	r. t.	0.5	>99
Triphenylphosphine	r. t.	6	94
1-Octadecanethiol	r. t.	12	0

[a] Reaction was carried out using **2** (1.0 mmol) and a nucleophile (1.0 mmol) in THF (0.5 M).
[b] Conversion of **2** determined by ^{1}H NMR.
[c] Using 0.5 mmol.



SCHEME 3 Nucleophilic addition to **2** using amines and phosphines.

To investigate the reactivity of a cyanate group, a model reaction with various nucleophiles was carried out using 4-cyanatotoluene (**2**) as a model compound. The reaction was examined by mixing **2** and an equimolar nucleophile in THF at room temperature or 60 °C. The conversion was monitored by the consumption of **2**, which was estimated by the decrease in a signal at 7.23 ppm derived from the aromatic proton in ^{1}H NMR spectra. The results are summarized in Table 2. No spectral change was observed when water was added to the solution of **2** at both room temperature and 60 °C. In addition, the cyanate group does not react with nucleophiles containing a hydroxy group such as *n*-propanol and phenol even at 60 °C. This indicates that the polymer containing cyanate groups can be stored and used in the presence of water and/or alcohols. On the other hand, the consumption of **2** rapidly proceeded within 1 h on the addition of aliphatic amines such as *n*-propylamine and diethylamine. Nucleophilic addition to the cyanate group immediately took place using an aliphatic amine to generate an isourea compound. However, aromatic amines such as aniline gave no adduct with **2**. In the case of primary amines such as *n*-propylamine, using 0.5 equiv of the amine to **2** resulted in high conversion up to 90%, which revealed that the 1:2 adduct **3** was generated by the reaction of the primary amine with 2 equiv of **2** as shown in Scheme 3 (not isolated owing to the instability). The reaction with secondary amines provided the 1:1 adduct, and the reaction rate was significantly influenced by the bulkiness of the amines. Figure 4 shows the conversion curves of the reactions with diethylamine and diisopropylamine. Because of the bulky structure of diisopropylamine, the reaction rate decreased

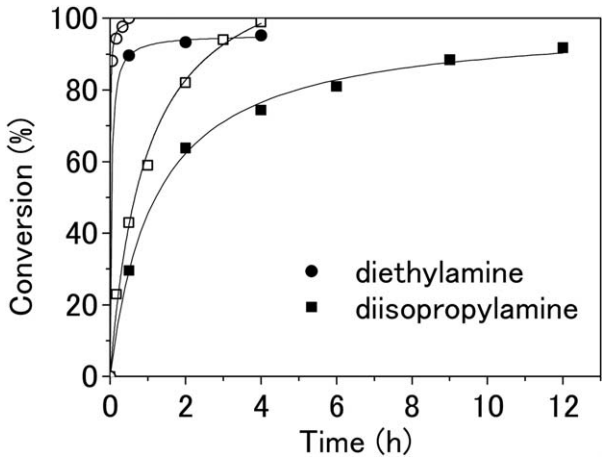


FIGURE 4 Conversion curves of the model reaction with diethylamine and diisopropylamine using **2** (filled symbol) and PCPMA (open symbol).

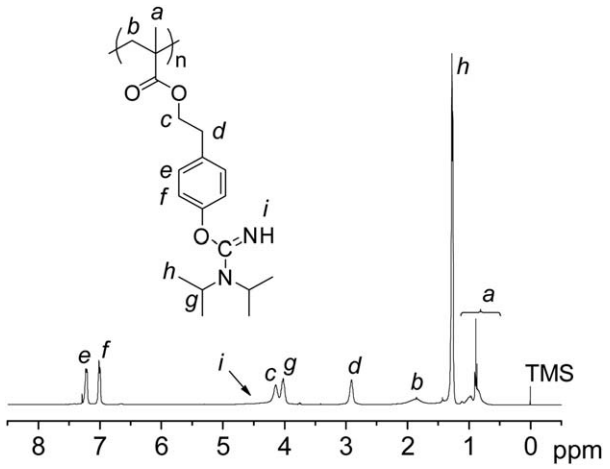
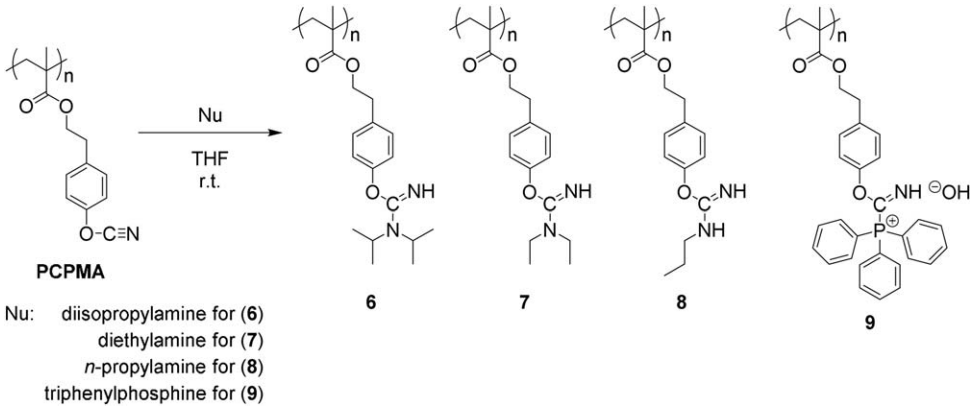


FIGURE 5 ^{1}H NMR spectrum of **6** in $CDCl_3$.

and the conversion moderately increased up to 92% for 12 h. The adduct of **2** with diisopropylamine was isolated and the formation of the isourea compound **4** was confirmed by NMR and IR spectra. Phosphines are other reactants giving high conversions for the reaction with **2**. However, the following decyanation occurred to give *p*-cresol as a main product, especially for the reaction with tricyclohexylphosphine. In the case of triphenylphosphine, the adduct could be isolated after precipitation in hexane in low yield (21%). Characterization of the crude product by NMR revealed that the hydrated phosphonium salt **5** was obtained (Scheme 3). Finally, carboxylic acid and thiol compounds do not react with the cyanate group at room temperature.

Based on the results of the model reaction, the structural modification of PCPMA was performed by the reactions with various nucleophiles in THF at room temperature (Scheme 4). By the reaction with diisopropylamine, the polymer bearing isourea groups in the side chain (**6**) was obtained in a high yield (88%). The reaction proceeded faster than using the model compound **2** as shown in Figure 4, which is probably due to the neighboring effect. In the ^{1}H NMR spectrum (Fig. 5), all the signals were clearly assigned to the polymer structure of **6**, and the transformation of cyanate into isourea was found to be quantitative. Figure 6 shows IR spectra of PCPMA and **6**. The peaks assignable to cyanate at 2264 and 2237 cm^{-1} completely disappeared for **6**, and a new strong peak arose at 1628 cm^{-1} according to the generation of the isourea group. The reaction of PCPMA with diethylamine was carried out to provide an isourea polymer (**7**), and the reaction proceeded in a very fast rate as shown in Figure 4. The isourea structure of **7** was confirmed by the assignment of all the signals in ^{1}H NMR spectrum (Supporting Information Fig. S1). When *n*-propylamine was used instead of these secondary amines, the resulting polymer (**8**) was almost insoluble in common solvents because of the crosslinking reaction. The structure of **8** was confirmed by IR spectrum (Supporting Information Fig. S2). Although the peak at 1651 cm^{-1} derived from C=N bond in isourea group can be observed, the cyanate group partially remained in spite of the excess use of *n*-propylamine. This is due to the steric hindrance of the cyanate group left in the networked structure. Triphenylphosphine also reacted with PCPMA, and the pale yellow polymer (**9**) was obtained. The polymer **9** was insoluble in any common solvent. By the IR spectrum of **9** (Supporting Information



SCHEME 4 Functionalization of PCPMA with various nucleophiles.

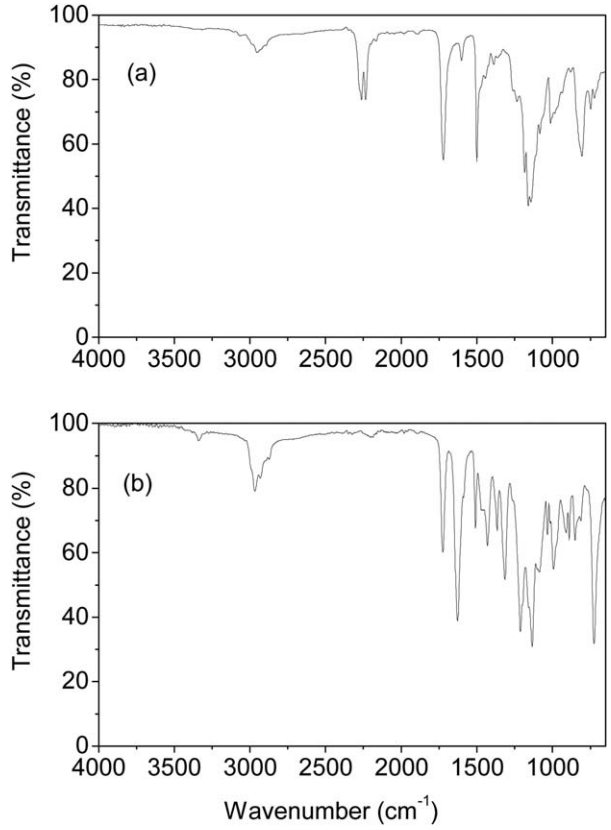


FIGURE 6 IR spectra of (a) PCPMA and (b) **6**.

Fig. S3), the transformation of cyanate group was assumed to be complete according to the disappearance of the peak at 2264 and 2237 cm^{-1}. However, **9** showed a very weak peak corresponding to C═N bond compared to isourea polymers. This result suggests that the elimination of phosphonium moiety partially occurred to afford phenol group as indicated by the model reaction.

On the other hand, water and *n*-propanol were also used as a nucleophile for the reaction of PCPMA in THF at room temperature. These nucleophiles do not react with PCPMA, even when fivefold excess of water or *n*-propanol was used, which resulted in the recovery of PCPMA.

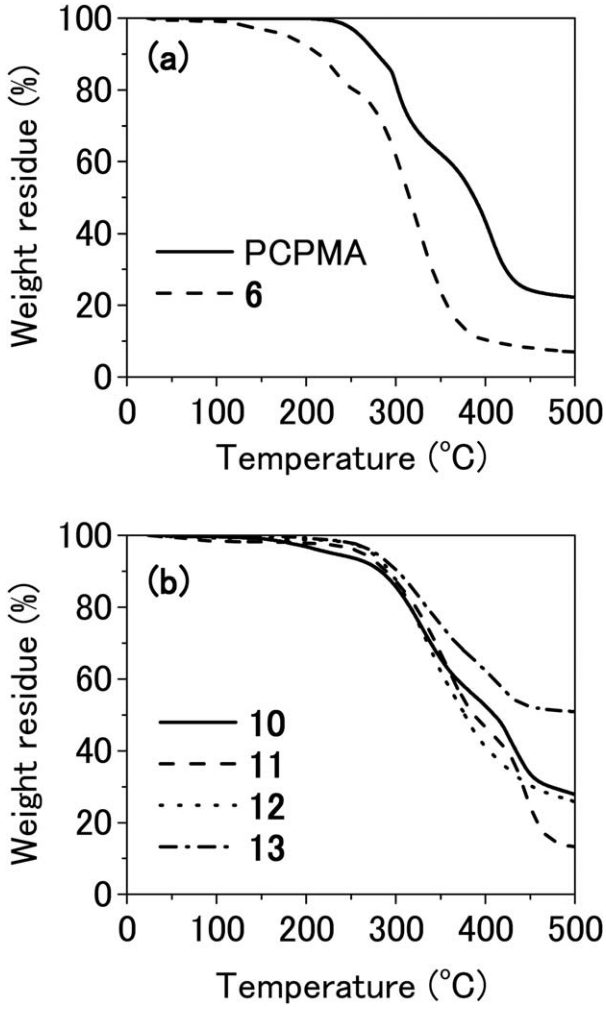
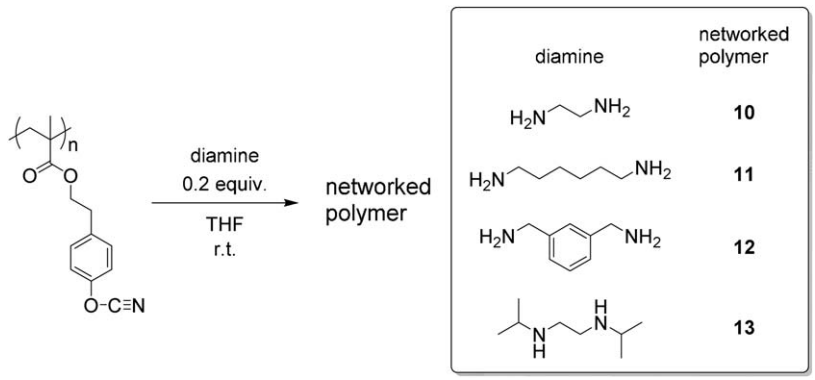


FIGURE 7 TGA profiles of (a) PCPMA and **6**, and (b) networked polymers; the crosslinker for **10**: ethylenediamine, **11**: hexamethylenediamine, **12**: *m*-xylylenediamine, and **13**: *N,N′*-diisopropylethylenediamine.

The formation of isourea polymers **6** and **7** was also evidenced by GPC measurement eluted by DMF. The chromatograms of **6** and **7** were similar profiles to that of PCPMA with a slight increase of M_n (Supporting Information Fig. S4).



SCHEME 5 Synthesis of networked polymers based on PCPMA using diamines.

The M_ns of PCPMA, **6**, and **7** were 13,500, 15,200, and 14,200, respectively. Therefore, it is assumed that the transformation of the cyanate into isourea proceeded without any undesired crosslinking and/or branching reactions.

As another example of functionalization using cyanate group, the formation of networked polymers based on PCPMA by crosslinking with aliphatic diamines was examined (Scheme 5). Ethylenediamine, hexamethylenediamine, *m*-xylylenediamine, and *N*,*N*′-diisopropylethylenediamine were used as a diamine crosslinker. On adding the primary diamines (0.2 equiv to the cyanate group) to the solution of PCPMA in THF, the gelation immediately occurred within 1 min. Using *N*,*N*′-diisopropylethylenediamine, a secondary diamine with a bulky structure, retarded the gelation time over 1 h as expected by the result of the model reaction. All the networked polymers were quantitatively obtained after reprecipitation into hexane. Thermal property of these networked polymers was investigated by TGA under nitrogen atmosphere, and the profiles are shown in Figure 7. PCPMA showed 5% weight loss temperature (T_d) of 261 °C, whereas the decomposition of **6** began at lower temperature ($T_d = 180$ °C). The formation of network slightly increased the T_ds compared to PCPMA except for **10** (**11**: 263 °C, **12**: 274 °C, and **13**: 278 °C). The T_d of **7** was observed at 230 °C. In the case that ethylenediamine was used as a crosslinker, the reaction proceeded too quickly to form a homogeneous network. The heterogeneity in the network structure probably caused a decrease in the decomposition temperature of **10**.

CONCLUSIONS

A novel reactive polymer PCPMA containing cyanate groups in the side chain was successfully prepared by free radical polymerization of methacrylate monomer **1**. The composition of cyanate-bearing unit was able to be controlled in the copolymers with MMA. The model reaction using 4-cyanatotoluene revealed that the reaction of the cyanate ester with aliphatic amines gives an isourea group quantitatively, whereas the cyanate group remains unreactive in the presence of water, alcohols, or aromatic amines under moderate conditions. By post-functionalization with aliphatic amines, PCPMA was quantitatively converted to isourea-containing polymers. The networked polymers based on PCPMA were also prepared by the reaction with diamines as the crosslinkers. These results indicate that PCPMA can be used as a reactive polymer with long storage stability, which is easily modified by the reaction with functionalized amine agents.

REFERENCES AND NOTES

1 M. A. Gauthier, M. I. Gibson, H.-A. Klok, *Angew. Chem. Int. Ed.* **2009**, *48*, 48–58.

2 G. Tillet, B. Boutevin, B. Ameduri, *Prog. Polym. Sci.* **2011**, *36*, 191–217.

3 J. B. Beck, K. L. Killops, T. Kang, K. Sivanandan, A. Bayles, M. E. Mackay, K. L. Wooley, C. J. Hawker, *Macromolecules* **2009**, *42*, 5629–5635.

4 J. D. Flores, J. Shin, C. E. Hoyle, C. L. McCormick, *Polym. Chem.* **2010**, *1*, 213–220.

5 R. M. Hensarling, S. B. Rahane, A. P. LeBlanc, B. J. Sparks, E. M. White, J. Locklin, D. L. Patton, *Polym. Chem.* **2011**, *2*, 88–90.

6 X. Piao, X. Zhang, Y. Mori, M. Koishi, A. Nakaya, S. Inoue, I. Aoki, A. Otomo, S. Yokoyama, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 47–54.

7 Y. Itagaki, A. Sudo, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 681–685.

8 Y. Kamimura, O. Haba, T. Endo, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 2448–2453.

9 I. Hamerton, J. N. Hay, *Polym. Int.* **1998**, *47*, 465–473.

10 C. A. Fyee, J. Niu, S. J. Retting, D. W. Wang, M. D. Poliks, *J. Polym. Sci. Part A: Polym. Chem.* **1994**, *32*, 2203–2221.

11 C. A. Fyfe, J. Niu, K. Mok, *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 1191–1202.

12 C. H. Lin, K. Z. Yang, T. S. Leu, C. H. Lin, J. W. Sie, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 3487–3502.

13 K. S. Santhosh Kumar, C. P. Reghunadhan Nair, K. N. Ninan, *Eur. Polym. J.* **2009**, *45*, 494–502.

14 X. Li, Y. Gu, *Polym. Chem.* **2011**, *2*, 2778–2781.

15 W. Kern, M. Cifrain, R. Schroder, K. Hummel, C. Mayer, M. Hofstotter, *Eur. Polym. J.* **1998**, *34*, 987–995.

16 D. Mathew, C. P. R. Mair, K. N. Ninan, *Eur. Polym. J.* **2000**, *36*, 1195–1208.

17 E. Grigat, R. Pütter, *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 206–218.

18 K. Ohno, T. Akashi, Y. Tsujii, M. Yamamoto, Y. Tabata, *Biomacromolecules* **2012**, *13*, 927–936.

19 K. Fukumoto, A. A. Dahy, T. Oya, K. Hayasaka, M. Itazaki, N. Koga, H. Nakazawa, *Organometallics* **2012**, *31*, 787–790.