

# Preparation of $\alpha$ -, $\omega$ -End-Functionalized Poly(*n*-hexyl isocyanate) Heterotelechelic

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$\alpha$ - and  $\omega$ -End-functionalized heterotelechelic poly(*n*-hexyl isocyanate) (PHIC) has been prepared by living coordination polymerization of HIC using benzyloxydichloro(cyclopentadienyl)titanium(IV) (BzCpTiCl<sub>2</sub>) (1) or 2-methacryloyloxyethoxydichloro(cyclopentadienyl)titanium(IV) (HEMACpTiCl<sub>2</sub>) (2) as an initiator, followed by heterogeneous termination with carboxylic anhydrides in the presence of a Lewis acid. The use of acetic (AAn), methacrylic (MAAn), butyric, *n*-hexanoic, and maleic anhydrides as a terminator, and trialkyl aluminum compounds, including trimethyl, triethyl, and triisobutyl, and boron trifluoride-diethyl etherate (BF<sub>3</sub>OEt<sub>2</sub>) as a Lewis acid were examined in the termination reaction. The effect of experimental conditions in the termination reaction on the yield of recovered polymer and  $\omega$ -end-functionality have been examined and optimized. Using BF<sub>3</sub>OEt<sub>2</sub> as a Lewis acid and AAn or MAAn as a terminator, several  $\alpha$ - and  $\omega$ -PHIC heterotelechelic having  $\alpha$ -benzyloxy- $\omega$ -acetyl (Bz-HIC-*n*-Ac, where *n* is the degree of polymerization of HIC),  $\alpha$ -benzyloxy- $\omega$ -methacryloyl (Bz-HIC-*n*-MA), and  $\alpha$ -2-methacryloyloxyethoxy- $\omega$ -acetyl (MA-HIC-*n*-Ac) groups could be successfully prepared with quantitative recovery (>98%) and functionality (~100%). The thermal stability of the end-functionalized heterotelechelic PHICs in benzene were found to be remarkably enhanced, when compared to that of the corresponding  $\omega$ -hydrogen-terminated compound (Bz-HIC-*n*-H).

KEY WORDS: Poly(*n*-hexyl isocyanate) / Macromonomer / Heterotelechelic / Termination Method / End-capping / Living Polymerization / Thermal Stability / Back Biting / Cyclic Trimer /

The presence of successive backbone amide groups makes polyisocyanates good examples of semi-flexible polymers. They have a dynamic 8<sub>3</sub> helical conformation in solution. Because of their unique structural properties, polyisocyanates have received much attention in various fields such as chiral recognition materials, optical switches, liquid crystal materials, and etc.<sup>1–3</sup> Among them, poly(*n*-hexyl isocyanate) (PHIC) is the best characterized polyisocyanate in solution.<sup>4</sup>

We have recently reported the preparation of 4-vinylbenzyloxy- and 2-methacryloyloxyethoxy-ended rodlike PHIC macromonomers and their fundamental radical copolymerization behavior.<sup>5,6</sup> We have also given many details of the molecular characterizations of the rodlike macromonomers and cylindrical rod brushes found in THF at 25 °C by small-angle X-ray scattering (SAXS), size exclusion chromatography-multi-angle laser light scattering (SEC-MALS), and viscometry.<sup>7,8</sup> When we carried out the fractionation of the cylindrical rod brushes consisting of a polystyrene main chain and PHIC side chains, however, we happened to meet a serious problem of degradation of the PHIC side chains. In general, the fractionation of PHIC chain is carried out with a solvent mixture of benzene as a good solvent, and methanol as a precipitant.<sup>4</sup> As will be presented in a forthcoming publication,<sup>9</sup> when PHIC was allowed to stand in a benzene-methanol mixture (70:30) at 40 °C, depolymerization occurred very rapidly to afford cyclic trimers (isocyanurates) (45% after 12 h).

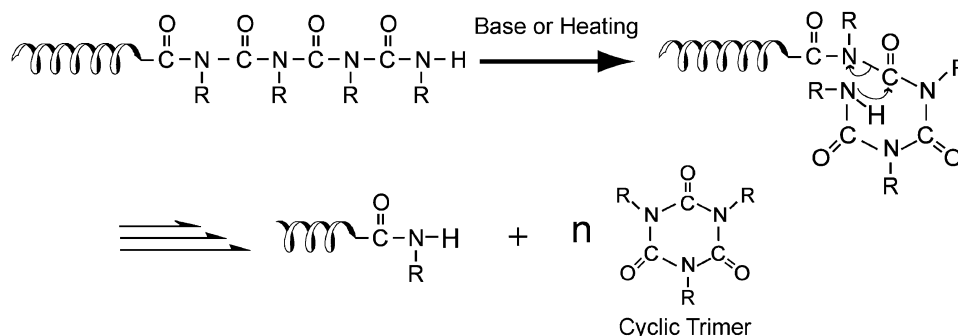
The chemical and thermal instabilities of polyisocyanates have been pointed out since the discovery of these polymers by Shashoua *et al.*<sup>10</sup> When polyisocyanates stand at room temperature in *N,N*-dimethylformamide containing sodium cyanide, the polymer undergoes depolymerization to give cyclic trimers.<sup>10</sup> The unfavorable stabilities of polyisocyanates restrict their utilization, in spite their interesting characteristics. One mechanism<sup>11</sup> proposed for the depolymerization of the PHIC is the back-biting reaction, shown in Scheme 1. The depolymerization is initiated by the abstraction of the proton at the terminal –NH by base or by heating.

The stability of polyisocyanates is expected to be increased by end-capping of the terminal –NH group. Basically, four methods are available for introducing a functional group into a polymer chain end:<sup>12</sup> (1) end-capping (termination) of a living polymer by a functional terminator, (2) initiation of living polymerization by a functional initiator, (3) transformation of an end-functional group, and (4) polyaddition. Of these,  $\alpha$ - and  $\omega$ -end functionalized PHIC can be prepared using both initiation and termination methods. There are two types of living polymerizations available for the polymerization of HIC. The first is an anionic living polymerization, developed recently by Lee *et al.*, which has to be conducted at a very low temperature (–98 °C) using demanding experimental techniques.<sup>13</sup> Quite recently, they have success-

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**Scheme 1.** A proposed reaction mechanism for depolymerization of polyisocyanates by base or heating.

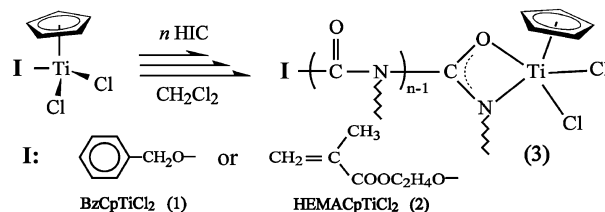
fully prepared  $\alpha$ - and  $\omega$ -functionalized PHIC with chiral residues at both ends using initiation and termination methods.<sup>14</sup>

The second type of controlled living polymerization of HIC is a polymerization initiated by a titanium alkoxide complex as an initiator at room temperature, developed by Novak in 1991.<sup>15–17</sup> This method is very versatile and convenient for the preparation of  $\alpha$ -end-functionalized PHIC using a functional initiator. We have actually used this method to prepare the PHIC macromonomers described in previous papers.<sup>5,6</sup> However, the polymerization has to be carried out at a very high monomer concentration, usually without solvents, to obtain a high conversion to the polymer at room temperature. As a result, after the polymerization the viscosity of the reaction mixture dramatically increases and in some cases the reaction mixture solidifies. When a good solvent for the PHIC chain, such as toluene is added to the reaction mixture to promote the termination reaction, depolymerization rapidly occurs at room temperature, resulting in a significant decrease in the amount of recovered polymer. Some research groups have studied the  $\omega$ -end-functionalization of the living polyisocyanate chain initiated with an titanium alkoxide initiator by the termination method, but the end-functionality and yield of recovered polymer were unsatisfactory low (*ca.* 60%).<sup>18,19</sup> To the best of our knowledge, no quantitative preparation method of  $\alpha$ - and  $\omega$ -end-functionalized PHIC with a titanium alkoxide initiator has so far been reported.

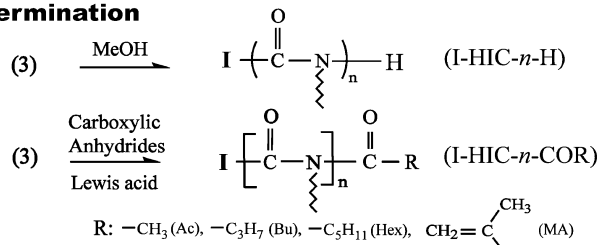
Based on our knowledge of heterogeneous polymerizations, such as dispersion polymerizations, we have successfully used a heterogeneous reaction in order to prevent the depolymerization of a PHIC living chain by dissolution.<sup>20,21</sup> Anionic living polymerizations are known to proceed quantitatively even in a heterogeneous polymerization system consisting of submicron-sized polymer particles and continuous phase.<sup>22,23</sup>

In the present study, we report the quantitative method shown in Scheme 2 to introduce an  $\omega$ -functional group to a PHIC living chain end, using a heterogeneous termination reaction, with anhydrides as a terminator and a Lewis acid as a catalyst. In addition, the thermal stabilities of PHIC heterotelechelic are also studied in benzene and in the solid state, and compared with those of the corresponding  $\omega$ -hydrogen(H)-terminated compounds.

### Living Coordination Polymerization of HIC



### Termination



**Scheme 2.** Reaction schemes for polymerization of HIC and termination in this study.

## EXPERIMENTAL

### Materials

Benzyl alcohol (Bz) (Wako Co., Ltd., Japan), HIC (Tokyo Kasei, Japan), dichloromethane (Kanto Kagaku Co., Ltd., Japan), acetonitrile (Tokyo Kasei, Japan) and various carboxylic anhydrides, such as acetic anhydride (AAn) (Kanto Kagaku Co., Ltd., Japan), methacrylic anhydride (MAAn) (Kanto Kagaku Co., Ltd., Japan), butyric anhydride (C4) (Kanto Kagaku Co., Ltd., Japan), *n*-hexanoic anhydride (C6) (Kanto Kagaku Co., Ltd., Japan), and methacryloyl chloride (MACl) (Kanto Kagaku Co., Ltd., Japan), were distilled from calcium hydride under reduced pressure just before use. Maleic anhydride (Kanto Kagaku Co., Ltd., Japan) was dried under vacuum.  $\text{AlMe}_3$  (1.0 M in toluene, Aldrich, USA),  $\text{AlEt}_3$  (0.95 M in toluene, Kanto Kagaku Co., Ltd., Japan),  $\text{Al}i\text{Bu}_3$  (1.0 M in toluene, Aldrich, USA),  $\text{BF}_3\text{OEt}_2$  (Kanto Kagaku Co., Ltd., Japan) and trichlorocyclopentadienyl titanium ( $\text{CpTiCl}_3$ ) (Kanto Kagaku Co., Ltd., Japan) were used as received. Benzene (Kanto Kagaku Co., Ltd., Japan) was

washed with concentrated  $\text{H}_2\text{SO}_4$ , neutralized with sodium hydroxide solution, dried with calcium chloride and finally distilled from Na/benzophenone. Tetrahydrofuran (THF) (Kanto Kagaku Co., Ltd., Japan) was distilled from Na/benzophenone. Methanol (Tokyo Kasei, Japan) was distilled in the presence of Mg. 2-Hydroxyethyl methacrylate (HEMA) (Tokyo Kasei, Japan) was distilled under reduced pressure just before use. The initiator, 2-2'-azobis(isobutyronitrile) (AIBN) (Wako, Japan) was purified by recrystallization three times from methanol.

### Synthesis of $\text{BzCpTiCl}_2$ (1) and $\text{HEMACpTiCl}_2$ (2)

The titanium alkoxide complex  $\text{BzCpTiCl}_2$  (1) was synthesized according to the method of Novak *et al.*<sup>15–17</sup> The details have been described in previous paper.<sup>5</sup> In a drybox, a solution of sodium benzyl alkoxide (4.99 mmol) in dry benzene was slowly added to a solution of trichloro(cyclopentadienyl) titanium (IV) ( $\text{CpTiCl}_3$ ) (4.96 mmol, 10 mL dry benzene). This reaction was carried out at room temperature for 1 h, and then the mixture was filtered through a G4 glass filter to remove sodium chloride. The filtrate was evaporated until dryness, producing a yellow solid. The product was dissolved again in dry benzene, and freeze-dried under reduced pressure. 2-Methacryloyloxyethoxydichloro(cyclopentadienyl)titanium-IV)  $\text{HEMACpTiCl}_2$  (2) was prepared according to the reported procedures,<sup>6</sup> except for the use of a flask equipped with a tube containing dry triethylamine to trap HCl gas.

**$\text{BzCpTiCl}_2$ :**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.38 (m, 5H,  $\text{C}_6\text{H}_5$ -), 6.59 (s, 4H,  $-\text{C}_5\text{H}_4-$ ), 5.61 (s, 2H,  $\text{C}_6\text{H}_5-\text{CH}_2-\text{O}-$ ).

**$\text{HEMACpTiCl}_2$ :**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 6.62 (s, 4H,  $-\text{C}_5\text{H}_4-$ ), 6.20 (s, 1H,  $\text{CH}_a\text{H}_b=\text{C}-$ ), 5.65 (s, 1H,  $\text{CH}_a\text{H}_b=\text{C}-$ ), 4.77 (t,  $J = 8.25$  Hz, 2H,  $-\text{OCO}-\text{CH}_2-\text{CH}_2-\text{O}-$ ), 4.31 (t,  $J = 8.25$  Hz, 2H,  $-\text{OCO}-\text{CH}_2-\text{CH}_2-\text{O}-$ ) and 1.93 (s, 3H,  $\text{CH}_2=\text{C}(\text{CH}_3)-$ ).

### Polymerization of HIC Using Initiator (1) and (2)

The polymerization of HIC was carried out in a drybox; details of the procedure are described in previous papers.<sup>5,6</sup> In brief, the initiator and dichloromethane were added to a 20 mL flask fitted with a magnetic stirrer bar. After the initiator was completely dissolved, a desired amount of HIC was added and the flask was sealed off and taken out of the drybox. The reaction was carried out for 18 h at room temperature to afford a PHIC living chain as a solid material. Then, one part of the reaction mixture was separately transferred to other flask in a dry-box and terminated with methanol to determine the conversion and polymer characteristics. To this end, a solution of THF and methanol (90/10 w/w) was added to the reaction mixture to dissolve and concurrently terminate the PHIC living chain to give rise to hydrogen (H)-terminated PHIC. The product was isolated by precipitation into a large amount of methanol, filtered off, and then dried under reduced pressure at room temperature for 24 h. The polymer was redissolved into THF containing 5% methanol and reprecipitated into methanol. This procedure was done three times. The white solid polymer was dissolved in 50 mL dry-benzene and freeze-dried under

vacuum for 24 h. The product was characterized by NMR and SEC-MALS measurements.

**$\text{Bz-HIC-43-H}$ :**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.38 (m, 5H,  $\text{C}_6\text{H}_5$ -), 5.23 (broad, 2H,  $-\text{CH}_2-\text{O}-$ ), 4.1–3.0 (broad, 86H,  $-\text{N}-\text{CH}_2-\text{CH}_2-$ ), 1.92–1.0 (broad, 344H,  $-\text{CH}_2-\text{C}_4\text{H}_8-\text{CH}_3$ ), 0.88 (broad, 129H,  $-\text{CH}_2-\text{CH}_3$ ).

### $\omega$ -End-functionalization of PHIC Living Chain by Termination Method

The  $\omega$ -end-functionalization of a PHIC living chain by carboxylic anhydrides was carried out in a heterogeneous reaction to avoid the back-biting reaction during the termination. Accordingly, the solution containing of a large excess amount of anhydride terminator and a Lewis acid catalyst was added to the solid reaction mixtures prepared as above in a dry-box. The solid body was pulverized in the reaction mixture to disperse it. It is worthwhile to note that the anhydride functions not only as a terminator but also acts as a reaction medium. The dispersion was vigorously stirred at room temperature for 24 h at room temperature. After the reaction, the polymer dispersion was slowly poured into methanol at  $-5^\circ\text{C}$ . The polymer was redissolved into THF containing 5% methanol and reprecipitated into methanol. This procedure was done three times and the final polymer was finally freeze-dried from benzene solution. Terminators examined in this study include acetic (AAn), methacrylic (MAAn), butyric, *n*-hexanoic, and maleic anhydrides and methacryloyl chloride, and Lewis acids include trimethyl, triethyl, and triisobutyl aluminium and boron trifluoride-diethyl etherate ( $\text{BF}_3\text{OEt}_2$ ). The products were characterized by NMR, FT-IR, and SEC-MALS measurements.

**$\text{Bz-HIC-40-Ac}$ :**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.39 (m, 5H,  $\text{C}_6\text{H}_5$ -), 5.23 (broad, 2H,  $-\text{CH}_2-\text{O}-$ ), 4.12–2.95 (broad, 80H,  $-\text{N}-\text{CH}_2-\text{CH}_2-$ ), 2.30 (s, 3H,  $-\text{CO}-\text{CH}_3$ ), 1.95–1.0 (broad, 320H,  $-\text{CH}_2-\text{C}_4\text{H}_8-\text{CH}_3$ ), 0.88 (broad, 120H,  $-\text{CH}_2-\text{CH}_3$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 156.8 (main chain,  $-\text{CO}-\text{N}-$ ), 149.0 ( $-\text{CO}-\text{CH}_3$ ), 128.8 ( $\text{C}_6\text{H}_5$ -; Aromatic carbons should be appeared as four peaks, but the signals were too small to be distinguished.), 48.7 ( $\text{Bz}-\text{CH}_2-\text{O}-$ ), 42.8 (side chain,  $\text{N}-\text{C}^1\text{H}_2-$ ), 31.4 (side chain,  $\text{N}-\text{C}^2\text{H}_2-$ ), 28.2 (side chain,  $\text{N}-\text{C}^3\text{H}_2-$ ), 26.2 (side chain,  $\text{N}-\text{C}^4\text{H}_2-$ ), 24.3 ( $-\text{CO}-\text{CH}_3$ ), 22.6 (side chain,  $\text{N}-\text{C}^5\text{H}_2-$ ), and 13.8 (side chain,  $\text{N}-\text{C}^6\text{H}_3$ ). **FT-IR:** 2956(m), 2858(m), 1700(s), 1653(sh), 1457(m), 1347(m), 1246(w), 1092(w), 999(w), 890(w)  $\text{cm}^{-1}$ .

**$\text{Bz-HIC-73-MA}$ :**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.39 (m, 5H,  $\text{C}_6\text{H}_5$ -), 6.40–6.08 (broad, 1H,  $\text{CH}_a\text{H}_b=\text{CCH}_3-$ ), 6.04–5.72 (broad, 1H,  $\text{CH}_a\text{H}_b=\text{CCH}_3-$ ), 5.23 (broad, 2H,  $-\text{CH}_2-\text{O}-$ ), 4.2–3.0 (broad, 146H,  $-\text{N}-\text{CH}_2-\text{CH}_2-$ ), 1.96 (broad, 3H,  $\text{CH}_2=\text{C}-\text{CH}_3$ ), 1.9–1.0 (broad, 584H,  $-\text{CH}_2-\text{C}_4\text{H}_8-\text{CH}_3$ ), 0.88 (broad, 219H,  $-\text{CH}_2-\text{CH}_3$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 156.7 (main chain,  $-\text{CO}-\text{N}-$ ), 149.1 ( $-\text{N}-\text{CO}-\text{CCH}_3=\text{CH}_2$ ), 145.1 ( $-\text{CO}-\text{CCH}_3=\text{CH}_2$ ), 128.4 ( $\text{C}_6\text{H}_5$ -; Aromatic carbons should be appeared as four peaks, but the signals were too small to be distinguished.), 112.6 ( $-\text{CO}-\text{CCH}_3=\text{CH}_2$ ), 48.4 ( $\text{Bz}-\text{CH}_2-\text{O}-$ ), 43.1 (side chain,  $\text{N}-\text{C}^1\text{H}_2-$ ), 31.4 (side chain,  $\text{N}-\text{C}^2\text{H}_2-$ ), 28.2 (side chain,  $\text{N}-\text{C}^3\text{H}_2-$ ), 26.4 (side chain,  $\text{N}-\text{C}^4\text{H}_2-$ ), 22.6 (side chain,  $\text{N}-\text{C}^5\text{H}_2-$ ), 18.1 ( $-\text{CO}-\text{CCH}_3=\text{CH}_2$ ),

and 14.0 (side chain, N-C<sup>6</sup>H<sub>3</sub>). **FT-IR:** 2956(m), 2859(m), 1695(s), 1653(sh), 1457(m), 1347(m), 1247(w), 1093(m), 999(w), 891(w) cm<sup>-1</sup>.

**MA-HIC-31-Ac:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 6.13 (s, 1H, CH<sub>a</sub>H<sub>b</sub>=CCH<sub>3</sub>-), 5.60 (s, 1H, CH<sub>a</sub>H<sub>b</sub>=CCH<sub>3</sub>-), 4.41 (broad, 2H, -COO-CH<sub>2</sub>-CH<sub>2</sub>-), 4.0-3.2 (broad, 64H, -COO-CH<sub>2</sub>-CH<sub>2</sub>- and -N-CH<sub>2</sub>-CH<sub>2</sub>-), 2.30 (s, 3H, -CO-CH<sub>3</sub>), 1.95 (s, 3H, CH<sub>2</sub>=C-CH<sub>3</sub>), 1.9-1.0 (broad, 248H, -CH<sub>2</sub>-C<sub>4</sub>H<sub>8</sub>-CH<sub>3</sub>), 0.88 (broad, 93H, -CH<sub>2</sub>-CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ (ppm): 166.6 (CH<sub>2</sub>=CCH<sub>3</sub>-COO-CH<sub>2</sub>-), 156.6 (main chain, -CO-N-), 153.0 (-CO-CH<sub>3</sub>), 135.8 (CH<sub>2</sub>=CCH<sub>3</sub>-COO-), 126.1 (CH<sub>2</sub>=CCH<sub>3</sub>-), 62.1 (-O-CH<sub>2</sub>-CH<sub>2</sub>-), 48.6 (-CH<sub>2</sub>-CH<sub>2</sub>-O-), 42.1 (side chain, N-C<sup>1</sup>H<sub>2</sub>-), 31.6 (side chain, N-C<sup>2</sup>H<sub>2</sub>-), 28.3 (side chain, N-C<sup>3</sup>H<sub>2</sub>-), 26.3 (side chain, N-C<sup>4</sup>H<sub>2</sub>-), 24.3 (-CO-CH<sub>3</sub>), 22.6 (side chain, N-C<sup>5</sup>H<sub>2</sub>-), 18.3 (CH<sub>2</sub>=CCH<sub>3</sub>-COO-), and 14.0 (side chain, N-C<sup>6</sup>H<sub>3</sub>). **FT-IR:** 2956(m), 2859(m), 1700(s), 1653(sh), 1559(w), 1457(m), 1347(m), 1247(w), 1093(m), 999(w), 890(w) cm<sup>-1</sup>.

### Thermal Stability of Bz-HIC-66-Ac in Benzene

The thermal stability of Bz-HIC-66-Ac ( $M_n = 6.64 \times 10^3$ ,  $M_w/M_n = 1.18$ , functionality of  $\omega$ -acetyl group,  $f = 100\%$ ) was studied in dry-benzene at different temperatures (60–80 °C) and compared to that of Bz-HIC-68-H ( $M_n = 7.14 \times 10^3$ ,  $M_w/M_n = 1.18$ ). A 5 mL of sample solution (5.0 wt %) was degassed by three freeze-thaw cycles, sealed off and put into an oil bath. After a certain time, the reaction mixture was quenched with liquid nitrogen. The reaction mixture was freeze-dried from benzene and used for a SEC-MALS measurement.

### Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Varian INOVA500 NMR instrument using CDCl<sub>3</sub> and C<sub>6</sub>D<sub>6</sub> as a solvent. FT-IR spectra were obtained with a HORIBA FT-270 spectrophotometer. The spectra were measured using a NaCl plate. Recording conditions were 16 accumulation cycles at a resolution of 2 cm<sup>-1</sup> of. Band intensities are assigned as weak (w), medium (m), shoulder (sh), and strong (s).

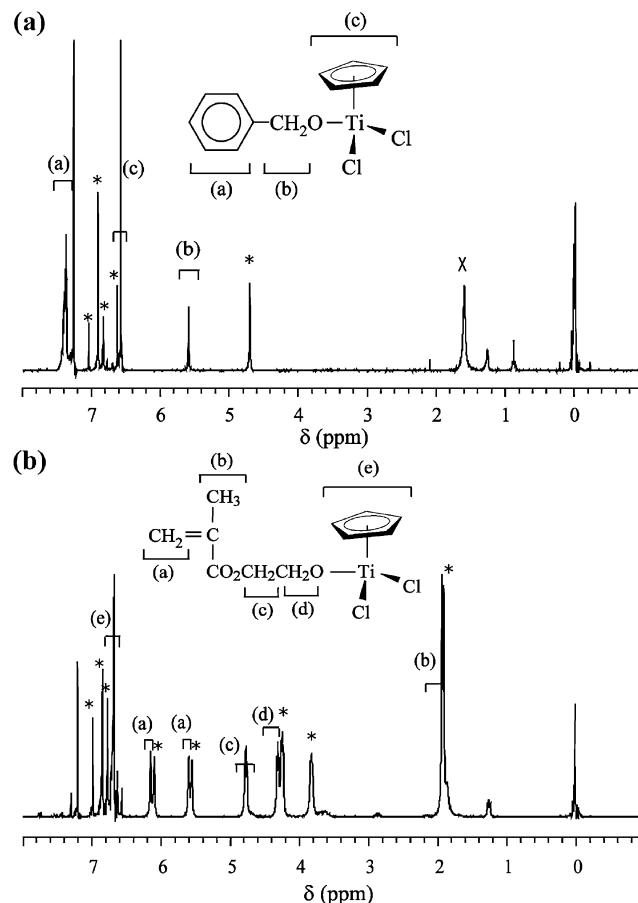
Size exclusion chromatography (SEC) measurements were carried out with an instrument (pump: Tosoh DP-8020, eluent: THF, Temp: 40 °C, columns: Shodex KF802 + KF806L + KF806L, RI; Shodex RI-101, UV; Tosoh UV-8020) fitted with a multi-angle laser light scattering detector (DAWN-DSP; wavelength, 632.8 nm, Wyatt Technology) (SEC-UV-MALS-RI). For the characterization of the PHIC, the elution volume in the SEC was calibrated with a series of PHICs whose molecular weight are predetermined by SEC-MALS.<sup>7</sup>

Differential thermal analysis (DTA) of Bz-HIC-64-Ac was carried out with a TG/DTA6200 (SEIKO instrument Inc., Japan) in a nitrogen atmosphere at a heating rate of 10 °C/min and was compared to that of Bz-HIC-63-H.

## RESULTS AND DISCUSSION

### Synthesis of Initiators (1) and (2)

The syntheses of initiator (1) and (2) were confirmed by



**Figure 1.** <sup>1</sup>H NMR spectra of (a) BzCpTiCl<sub>2</sub> and (b) HEMACpTiCl<sub>2</sub> in CDCl<sub>3</sub>. The asterisks indicate <sup>1</sup>H NMR peak signals due to the decomposed materials by reacting with water in CDCl<sub>3</sub>.

<sup>1</sup>H NMR spectroscopy, as shown in Figure 1(a) and 1(b).<sup>24</sup> Although the initiators are considerably decomposed by reacting with water in CDCl<sub>3</sub>, the assignments for each peak signal are listed in the Experimental section. The <sup>1</sup>H NMR signals from the decomposed compounds are indicated using asterisks. The yield is 87–90%, for use as an initiator in the polymerization of HIC.<sup>6</sup>

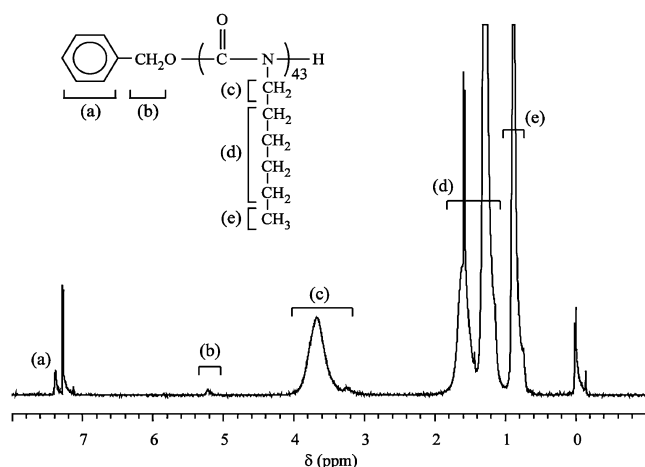
### Preparation of Bz-HIC-*n*-Ac by Termination with Acetic Anhydride (AAn)

Table I shows the time-evolution of the recovered polymer yield and end-functionality of Bz-HIC-*n*-Ac during termination using acetic anhydride as a terminator and AlMe<sub>3</sub> as a Lewis acid at room temperature. At the reaction time = 0, when the PHIC living chain was directly terminated with methanol,  $\omega$ -H-terminated PHIC (Bz-HIC-43-H) with a relatively narrow molecular weight distribution of  $M_w/M_n = 1.19$  was prepared at relatively high conversion (87%) (run 1-1). The <sup>1</sup>H NMR spectrum of Bz-HIC-43-H (run 1-1) is shown in Figure 2. It shows <sup>1</sup>H NMR peaks due to the  $\alpha$ -benzyloxy-ended group as well as due to the PHIC chain. The number-averaged degree of polymerization ( $n$ ) of HIC was calculated from the ratio of the <sup>1</sup>H NMR peak intensity of methyl protons (e) of PHIC to benzyl protons (a + b) using the equation

**Table I.** Time evolution of the polymer recovery and end-functionality of Bz-HIC-*n*-Ac during termination using acetic anhydride as a terminator and AlMe<sub>3</sub> as a catalyst<sup>a)</sup>

Run	Reaction Time (h)	Recovery (%)	$M_n \times 10^{-3}$ <sup>c)</sup> (NMR)	$M_n \times 10^{-3}$ <sup>d)</sup> (SEC)	$M_w/M_n$ <sup>d)</sup> (SEC)	$f$ <sup>e)</sup> (%)
1-1 <sup>b)</sup>	0	86.8	5.21	4.70	1.1 <sub>9</sub>	—
1-2	1	16.4	4.99	4.63	1.2 <sub>2</sub>	81.8
1-3	3	14.7	4.97	4.73	1.2 <sub>2</sub>	82.0
1-4	6	14.0	5.14	4.62	1.2 <sub>0</sub>	88.8
1-5	12	14.2	4.82	4.59	1.2 <sub>0</sub>	88.6
1-6	24	12.2	5.24	4.59	1.2 <sub>0</sub>	100

<sup>a)</sup> Polymerization was carried out for 18 h at room temperature with [HIC]/[Ini] = 52, [HIC] = 19.66 mmol and CH<sub>2</sub>Cl<sub>2</sub> = 0.083 mL. Termination reaction was carried out with [AAn]/[AlMe<sub>3</sub>]/[Ini] = 1000/1500/1 at room temperature. <sup>b)</sup> Terminated with methanol. <sup>c)</sup> Determined by <sup>1</sup>H NMR using eq (1). <sup>d)</sup> Determined by SEC using a series of PHICs as a calibration. <sup>e)</sup>  $f$  is the end-functionality of acetyl group, determined by <sup>1</sup>H NMR using eq (2).

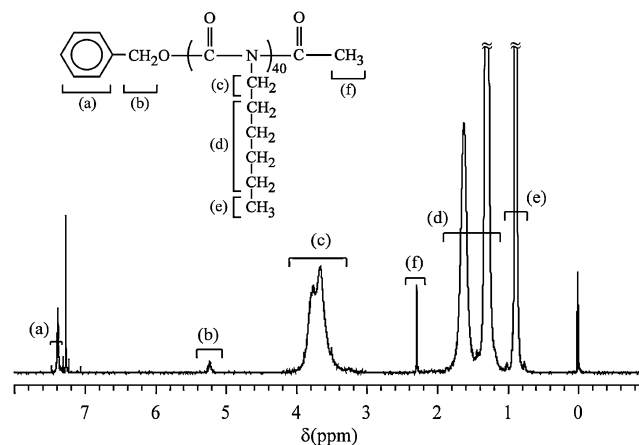

**Figure 2.** <sup>1</sup>H NMR spectrum of (Bz-HIC-43-H) in CDCl<sub>3</sub> (Table I, Run 1-1).

$$n = \frac{7(e)}{3(a+b)} \quad (1)$$

The recovered polymer yield, however, markedly decreases down to 16% after a one hour termination reaction (run 1-2), implying that significant depolymerization occurs concurrently during the termination reaction under the condition that [AAn]/[AlMe<sub>3</sub>]/[Ini] = 1000/1500/1. The <sup>1</sup>H NMR spectrum of recovered Bz-HIC-40-Ac (run 1-6) is presented in Figure 3. One sees <sup>1</sup>H NMR signals due to the ω-acetyl end group at 2.30 ppm. The ω-end-functionality,  $f$  was determined by the ratio of the <sup>1</sup>H NMR peak intensity of the methyl protons of acetyl group ( $f$ ) to those of benzyl protons ( $a+b$ ) using the equation,

$$f = \frac{7(f)}{3(a+b)} \times 100 \quad (2)$$

ω-Acetylated PHIC with an end-functionality higher than 80% can be prepared by the present heterogeneous termination reaction but the recovered polymer yield is very low because side reactions such as backbiting occur competitively. An excess amount of AlMe<sub>3</sub> relative to AAn might interact with the titanium active site on a PHIC living end and/or be


**Figure 3.** <sup>1</sup>H NMR spectrum of (Bz-HIC-40-Ac) in CDCl<sub>3</sub> (Table I, Run 1-6).

**Table II.** Influence of molar ratio of acetic anhydride to AlMe<sub>3</sub> on end-functionality of Bz-HIC-*n*-Ac<sup>a)</sup>

Run	[AAn]/[AlMe <sub>3</sub> ]	Recovery (%)	$M_n \times 10^{-3}$ <sup>b)</sup> (NMR)	$M_n \times 10^{-3}$ <sup>c)</sup> (SEC)	$M_w/M_n$ <sup>c)</sup> (SEC)	$f$ <sup>d)</sup> (%)
2-1	1000/0	83.8	5.52	5.32	1.1 <sub>5</sub>	37.7
2-2	1000/10	76.6	5.63	5.34	1.1 <sub>2</sub>	60.3
2-3	1000/20	76.3	3.75	3.22	1.0 <sub>9</sub>	62.0
2-4	1000/30	70.1	4.02	3.24	1.0 <sub>8</sub>	81.1
2-5	1000/40	66.1	3.93	3.27	1.0 <sub>8</sub>	77.0
2-6	1000/50	66.6	3.86	3.24	1.0 <sub>8</sub>	62.4

<sup>a)</sup> Polymerization was carried out for 18 h at room temperature with [HIC]/[Ini] = 50, [HIC] = 14.23 mmol and CH<sub>2</sub>Cl<sub>2</sub> = 0.16 mL. Termination reaction was carried out for 48 h at room temperature. <sup>b)</sup> Determined by <sup>1</sup>H NMR using eq (1). <sup>c)</sup> Determined by SEC using a series of PHICs as a calibration. <sup>d)</sup>  $f$  is the end-functionality of acetyl group, determined by <sup>1</sup>H NMR using eq (2).

replaced resulting depolymerization before end capping. Interestingly, the molecular weight of the recovered products is not as low as might be expected from the drastic decrease of their recovery, implying an “all or nothing” mechanism for the depolymerization.

The influence of the ratio of AAn to AlMe<sub>3</sub> on the polymer recovery and end-functionality was investigated and the results are summarized in Table II. In the absence of AlMe<sub>3</sub>, a polymer with relatively high recovery (84%) but with very low end-functionality (38%) (run 2-1) was obtained. One sees in Table II that the recovered polymer yield slowly decreases but the end-functionality steeply increases with increasing the amount of AlMe<sub>3</sub> added. This suggests that AlMe<sub>3</sub> forms a complex with AAn to promote the reactivity. The highest end-functionality was obtained at the molar ratio of AAn/AlMe<sub>3</sub>/initiator of 1000/30/1.

### Influence of Lewis Acids Species on the End-functionality

The influence of the Lewis acids species on the end-functionality was studied at a constant molar ratio of AAn/Lewis acid/initiator of 1000/30/1, and the results are listed in Table III. Irrespective of the Lewis acid species used, α-benzyloxy- and ω-acetyl-heterotelechelic PHIC was obtained with fairly high polymer recovery (>85%) and high end-

**Table III.** Influence of Lewis acids species on end-functionality<sup>a)</sup>

Lewis acid	Recovery (%)	$M_n \times 10^{-3}$ <sup>b)</sup> (NMR)	$M_n \times 10^{-3}$ <sup>c)</sup> (SEC)	$M_w/M_n$ <sup>c)</sup> (SEC)	$f$ <sup>d)</sup> (%)
AlMe <sub>3</sub>	85.7	8.68	8.12	1.2 <sub>1</sub>	73.8
AlEt <sub>3</sub>	87.7	9.01	8.15	1.2 <sub>1</sub>	81.4
Al( <i>i</i> Bu) <sub>3</sub>	95.0	9.18	8.02	1.2 <sub>0</sub>	88.4
BF <sub>3</sub> OEt <sub>2</sub>	85.4	8.59	7.71	1.2 <sub>0</sub>	99.3

<sup>a)</sup>Polymerization was carried out for 18 h at room temperature with [HIC]/[Ini] = 55, [HIC] = 7.53 mmol and CH<sub>2</sub>Cl<sub>2</sub> = 0.075 mL. Termination reaction was carried out for 48 h at room temperature with [AAn]/[Lewis acid]/[Ini] = 1000/30/1. <sup>b)</sup>Determined by <sup>1</sup>H NMR using eq (1). <sup>c)</sup>Determined by SEC using a series of PHICs as a calibration. <sup>d)</sup> $f$  is the end-functionality of acetyl group, determined by <sup>1</sup>H NMR using eq (2).

**Table IV.** Effect of molar ratio of terminator, BF<sub>3</sub>OEt<sub>2</sub> and initiator on end-functionality<sup>a)</sup>

Run	[AAn]/[BF <sub>3</sub> OEt <sub>2</sub> ]/[Ini]	Recovery (%)	$M_n \times 10^{-3}$ <sup>b)</sup> (NMR)	$M_n \times 10^{-3}$ <sup>c)</sup> (SEC)	$M_w/M_n$ <sup>c)</sup> (SEC)	$f$ <sup>d)</sup> (%)
4-1	500/5/1	98.1	7.31	7.46	1.1 <sub>6</sub>	98.1
4-2	500/10/1	91.3	8.06	7.47	1.1 <sub>5</sub>	94.7
4-3	500/20/1	96.5	7.88	7.50	1.1 <sub>5</sub>	100
4-4	250/20/1	97.1	7.69	7.44	1.1 <sub>5</sub>	97.6

<sup>a)</sup>Polymerization was carried out for 18 h at room temperature with [HIC]/[Ini] = 50, [HIC] = 7.55 mmol and CH<sub>2</sub>Cl<sub>2</sub> = 0.083 mL. Termination reaction was carried out for 48 h at room temperature. <sup>b)</sup>Determined by <sup>1</sup>H NMR using eq (1). <sup>c)</sup>Determined by SEC using a series of PHICs as a calibration. <sup>d)</sup> $f$  is the end-functionality of acetyl group, determined by <sup>1</sup>H NMR using eq (2).

functionality (>81%) by the heterogeneous reaction. One sees in Table III that the weaker the acidity of the Lewis acids, the higher is the end-functionality, although the reason for this is not clearly understood. To optimize the termination reaction, the reaction conditions were further studied with BF<sub>3</sub>OEt<sub>2</sub> as a catalyst.

### Influence of Ratio of AAn/BF<sub>3</sub>OEt<sub>2</sub> and Reaction Time on the End-functionality

Since the present termination reaction proceeds in a dispersion, the terminator activated by BF<sub>3</sub> may diffuse into the polymeric dispersed phase from the continuous phase and react with the PHIC living end. Therefore, the recovered polymer yield and end-functionality may strongly depend on the experimental conditions. The influence of the molar ratio of AAn to BF<sub>3</sub>OEt<sub>2</sub> on the end-functionality was studied and the results are listed in Table IV. The heterotelechelic PHIC can be prepared with quantitative end-functionality ( $f > 95\%$ ) and recovery (>91%) using BF<sub>3</sub>OEt<sub>2</sub> as a catalyst. The optimal condition found within those examined is ([AAn]/[BF<sub>3</sub>OEt<sub>2</sub>]/[Ini] = 500/20/1).

The time-evolution of the end-functionality during the termination reaction was also studied at the optimal condition and listed in Table V. The reaction rate is relatively high (>85% at 3 h), despite the system being heterogeneous.

### Termination by Various Anhydrides Using BF<sub>3</sub>OEt<sub>2</sub> as Catalyst

A variety of terminators other than AAn, including

**Table V.** Time evolution of end-functionality during termination with BF<sub>3</sub>OEt<sub>2</sub> as a Lewis Acid<sup>a)</sup>

Run	Time (h)	Recovery (%)	$M_n \times 10^{-3}$ <sup>c)</sup> (NMR)	$M_n \times 10^{-3}$ <sup>d)</sup> (SEC)	$M_w/M_n$ <sup>d)</sup> (SEC)	$f$ <sup>e)</sup> (%)
5-1 <sup>b)</sup>	0	85.1	8.75	7.14	1.1 <sub>8</sub>	—
5-2	3	81.8	7.92	7.08	1.1 <sub>8</sub>	85.0
5-3	6	94.8	8.02	7.12	1.1 <sub>8</sub>	91.4
5-4	12	96.5	7.68	7.23	1.1 <sub>8</sub>	100
5-5	24	89.8	8.56	7.15	1.1 <sub>8</sub>	100

<sup>a)</sup>Polymerization was carried out for 18 h at room temperature with [HIC]/[Ini] = 50, [HIC] = 9.20 mmol and CH<sub>2</sub>Cl<sub>2</sub> = 0.128 mL. Termination reaction was carried out at 0 °C with [AAn]/[BF<sub>3</sub>OEt<sub>2</sub>]/[Ini] = 500/20/1. <sup>b)</sup>Terminated with methanol as a terminator. <sup>c)</sup>Determined by <sup>1</sup>H NMR using eq (1). <sup>d)</sup>Determined by SEC using a series of PHICs as a calibration. <sup>e)</sup> $f$  is the end-functionality of acetyl group, determined by <sup>1</sup>H NMR using eq (2).

**Table VI.** End-functionalization with various anhydrides<sup>a)</sup>

Run	Time (h)	Recovery (%)	$M_n \times 10^{-3}$ <sup>e)</sup> (NMR)	$M_n \times 10^{-3}$ <sup>f)</sup> (SEC)	$M_w/M_n$ <sup>f)</sup> (SEC)	$f$ <sup>g)</sup> (%)
6-1	Methacrylic	76.1	9.34	6.90	1.1 <sub>9</sub>	100
6-2	MAC <sup>b)</sup>	57.4	8.64	6.30	1.2 <sub>2</sub>	0
6-3	Maleic <sup>c)</sup>	83.9	7.49	5.94	1.1 <sub>7</sub>	0
6-4	<i>n</i> -butyric (C4)	92.4	12.2	8.74	1.2 <sub>5</sub>	39.3
6-5	<i>n</i> -butyric (C4) <sup>d)</sup>	83.2	16.6	13.8	1.2 <sub>8</sub>	60.0
6-6	<i>n</i> -hexanoic (C6)	83.7	8.29	7.36	1.1 <sub>8</sub>	19.2
6-7	<i>n</i> -hexanoic (C6) <sup>d)</sup>	74.4	9.19	8.44	1.2 <sub>1</sub>	22.5

<sup>a)</sup>Polymerization was carried out for 18 h at room temperature with [HIC]/[Ini] = 50, [HIC] = 9.20 mmol and CH<sub>2</sub>Cl<sub>2</sub> = 0.128 mL. Termination reaction was carried out at 0 °C for 24 h with [Anhydrides]/[BF<sub>3</sub>OEt<sub>2</sub>]/[Ini] = 500/20/1. <sup>b)</sup>Methacryloyl chloride. <sup>c)</sup>Maleic anhydride (solid) was dissolved in dry acetone and then added to the reaction mixture. <sup>d)</sup>Termination reaction was carried out in acetonitrile. <sup>e)</sup>Determined by the <sup>1</sup>H NMR using eq (1). <sup>f)</sup>Determined by SEC using a series of PHICs as a calibration. <sup>g)</sup> $f$  is the end-functionality of end-group, determined by <sup>1</sup>H NMR using eq (2).

methacrylic anhydride, methacryloyl chloride, maleic anhydride, *n*-butyric anhydride and *n*-hexanoic anhydride were examined in the presence of BF<sub>3</sub>OEt<sub>2</sub>. The results are summarized in Table VI. Unfortunately, the end-functionality for anhydrides other than methacrylic anhydride is unsatisfactory. The heterogeneous system may be responsible for the low functionality in the case of these large anhydrides. The <sup>1</sup>H NMR spectrum of the  $\alpha$ -benzyloxy- and  $\omega$ -methacryloyl-functionalized heterotelechelic PHIC is shown in Figure 4 to clearly demonstrate the successful synthesis by the termination reaction using methacrylic anhydride.

The PHIC macromonomer with  $\alpha$ -2-methacryloyloxyethoxy and  $\omega$ -acetyl groups (MA-HIC-31-Ac,  $M_w/M_n = 1.17$ ,  $f = 100\%$ ) could be successfully prepared by coordination polymerization of HIC using HEMACpTiCl<sub>2</sub> (**2**) as an initiator, followed by termination using [AAn]/BF<sub>3</sub>OEt<sub>2</sub>/[Ini] = 500/20/1 at 0 °C. The <sup>1</sup>H NMR spectrum of MA-HIC-31-Ac is also shown in Figure 5.

### Influence of $\alpha$ - and $\omega$ -End-functionalization on Thermal Stability of PHIC

The thermal stability of the  $\alpha$ -benzyloxy- and  $\omega$ -acetyl-functionalized PHIC (Bz-HIC-64-Ac) was studied in benzene

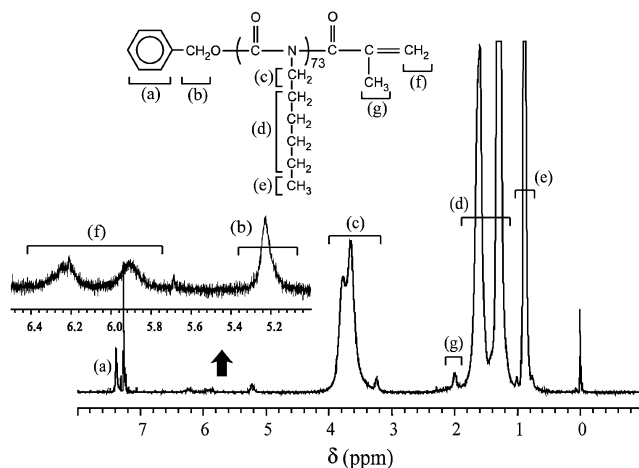


Figure 4.  $^1\text{H}$  NMR spectrum of Bz-HIC-73-MA in  $\text{CDCl}_3$ .

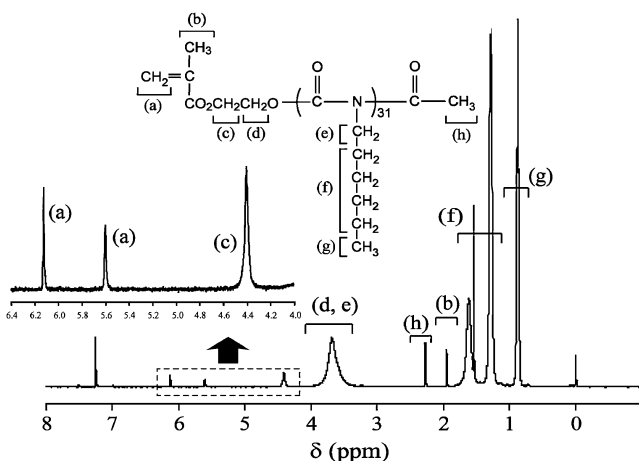


Figure 5.  $^1\text{H}$  NMR spectrum of MA-HIC-31-Ac in  $\text{CDCl}_3$ .

(5.0 wt %) at 60 °C, 70 °C and 80 °C. Figure 6 shows the time-conversion curve to the cyclic trimer for Bz-HIC-64-Ac at different temperatures. The data for the  $\alpha$ -benzyloxy- and  $\omega$ -H-terminated PHIC (Bz-HIC-63-H) at the same concentration are shown for comparison. The content of the cyclic trimer was determined from the ratio of RI signal intensities of the parent PHIC to the cyclic trimer in the SEC chromatogram. It is apparent that the thermal stability of Bz-HIC-64-Ac is greatly enhanced, in comparison to that of Bz-HIC-63-H. This experimental result partly supports the idea shown in Scheme 1 that proton abstraction from the terminal NH initiates the depolymerization at least in an inert solvent.

The thermal stability of Bz-HIC-64-Ac and Bz-HIC-63-H in their solid states was also investigated by differential thermal analysis (DTA) measurement and the results are shown in Figure 7. Temperatures corresponding to the initial 5%, 10% and 90% decomposition of the polymer are listed in Table VII. Both polymers decomposed in two different stages as reported by Durairaj *et al.*<sup>25</sup> The value of  $T_5$  of Bz-HIC-64-Ac increases by 7.4 °C, when compared to that of Bz-HIC-63-H. This

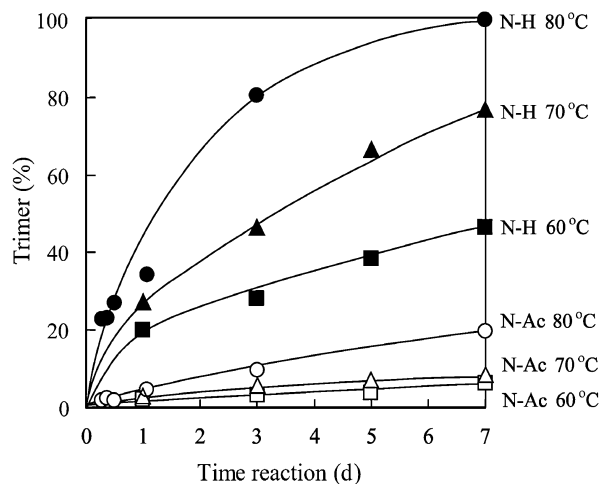


Figure 6. Time-conversion curve of trimer by depolymerization of Bz-HIC-64-Ac and Bz-HIC-63-H in benzene at various temperatures.

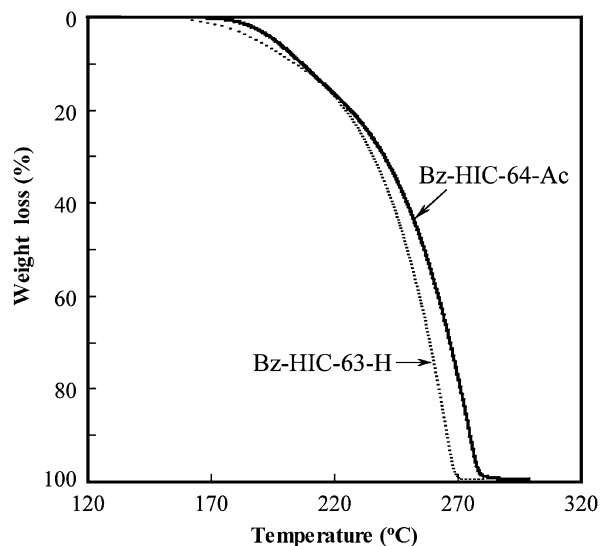


Figure 7. DTA curves of Bz-HIC-64-Ac and Bz-HIC-63-H.

Table VII. Influence of  $\omega$ -end group on thermal stability of PHIC in solid state

Sample	$T_5^c$ (°C)	$T_{10}^d$ (°C)	$T_{90}^e$ (°C)
Bz-HIC-63-H <sup>a)</sup>	188.5	204.2	265.6
Bz-HIC-64-Ac <sup>b)</sup>	195.9	206.8	275.0

<sup>a)</sup>  $M_n(\text{SEC}) = 6.99 \times 10^3$ ;  $M_w/M_n(\text{SEC}) = 1.2_2$ . <sup>b)</sup>  $M_n(\text{SEC}) = 7.51 \times 10^3$ ;  $M_w/M_n(\text{SEC}) = 1.1_4$ . <sup>c), d), e)</sup> Temperature at which weight loss reached 5%, 10% and 90%, respectively.

difference is small but yet is noteworthy, when taking into account that the chemical structure of the two compounds differs only by an  $\omega$ -end group. While the mechanism for thermal decomposition of PHIC in the solid state is complex and not well understood, we can conclude that  $\alpha$ - and  $\omega$ -end-capping both ends of a PHIC chain enhances the thermal stability in the solid state.

## CONCLUSIONS

$\alpha$ - and  $\omega$ -End-functionalized poly(*n*-hexyl isocyanate) was prepared by living coordination polymerization of HIC, followed by heterogeneous termination with carboxylic anhydrides in the presence of Lewis acid. With BF<sub>3</sub>OEt<sub>2</sub> as a Lewis acid and AAn and MAAn as a terminator,  $\alpha$ - and  $\omega$ -PHIC heterotelechelic having  $\alpha$ -benzyloxy- $\omega$ -acetyl (Bz-HIC-*n*-Ac),  $\alpha$ -benzyloxy- $\omega$ -methacryloyl (Bz-HIC-*n*-MA), and  $\alpha$ -2-methacryloyloxyethoxy- $\omega$ -acetyl (MA-HIC-*n*-Ac) functional groups were successfully prepared with a quantitative recovery (>98%) and functionality (~100%). The thermal stability of the heterotelechelic was markedly enhanced in benzene and in the solid state.

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## REFERENCES AND NOTES

1. M. Goodman and S. Chen, *Macromolecules*, **3**, 398 (1970).
2. M. M. Green, C. Andreola, B. Munoz, M. P. Reidy, and K. J. Zero, *J. Am. Chem. Soc.*, **110**, 4063 (1988).
3. S. M. Aharoni, *Macromolecules*, **12**, 94 (1979).
4. T. Norisuye, A. Tsuboi, and A. Teramoto, *Polym. J.*, **28**, 357 (1996).
5. M. Kikuchi, S. Kawaguchi, and K. Nagai, *Des. Monomers. Polym.*, **7**, 603 (2004).
6. S. Kawaguchi, T. Mihara, M. Kikuchi, L. T. N. Lien, and K. Nagai, *Macromolecules*, **40**, 950 (2007).
7. M. Kikuchi, T. Mihara, Y. Jinbo, Y. Izumi, K. Nagai, and S. Kawaguchi, *Polym. J.*, **39**, 330 (2007).
8. M. Kikuchi, L. T. N. Lien, A. Narumi, Y. Jinbo, Y. Izumi, K. Nagai, and S. Kawaguchi, *Macromolecules*, in press.
9. M. Kikuchi, S. Kawaguchi, and K. Nagai, *Polym. Prepr. Jpn.*, **55**, 182 (2006).
10. V. E. Shashoua, W. Sweeny, and R. F. Tietz, *J. Am. Chem. Soc.*, **82**, 866 (1960).
11. Y. Iwakura, K. Uno, and N. Kobayashi, *J. Polym. Sci., Part A-1*, **6**, 1087 (1968).
12. K. Ito, *Prog. Polym. Sci.*, **23**, 581 (1998).
13. J.-S. Lee and S. W. Ryu, *Macromolecules*, **32**, 2085 (1999).
14. G. Y. Nath, S. Samal, S.-Y. Park, C. N. Murthy, J.-S. Lee, and S. W. Ryu, *Macromolecules*, **39**, 5965 (2006).
15. T. E. Patten and B. M. Novak, *J. Am. Chem. Soc.*, **113**, 5065 (1991).
16. T. E. Patten and B. M. Novak, *Macromolecules*, **26**, 436 (1993).
17. S. H. Goodson and B. M. Novak, *Macromolecules*, **34**, 3849 (2001).
18. K. Ute, T. Asai, Y. Fukunishi, and K. Hatada, *Polym. J.*, **27**, 445 (1995).
19. K. Se, K. Aoyama, J. Aoyama, and M. Donkai, *Macromolecules*, **36**, 5878 (2003).
20. K. Ito and S. Kawaguchi, *Adv. Polym. Sci.*, **142**, 129 (1999).
21. S. Kawaguchi and K. Ito, *Adv. Polym. Sci.*, **175**, 299 (2005).
22. M. A. Awan, V. L. Dimonie, and M. S. El-Aasser, *J. Polym. Sci., Polym. Chem. Ed.*, **34**, 2633 (1996).
23. M. A. Awan, V. L. Dimonie, and M. S. El-Aasser, *J. Polym. Sci., Polym. Chem. Ed.*, **34**, 2651 (1996).
24. Note: the <sup>1</sup>H NMR spectrum of HEMACpTiCl<sub>2</sub> was presented in Figure 1 of Ref. 6. Since the spectrum was plotted with incorrect chemical shift values, the authors replace it by Figure 1(b) of this paper.
25. B. Durairaj, A. W. Dimock, and E. T. Samulski, *J. Polym. Sci., Part A: Polym. Chem.*, **27**, 3211 (1989).