Synthesis of Methacrylate-Ended Poly(*n*-hexyl isocyanate) Rodlike Macromonomers and Their Radical Copolymerization Behavior

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ABSTRACT: Methacrylate-ended rodlike macromonomers consisting of poly(*n*-hexyl isocyanate) (MA-HIC-*n*(**2**), where *n* is a degree of polymerization of *n*-hexyl isocyanate (HIC)) with narrow molecular weight distribution have successfully been synthesized in CH_2Cl_2 at room temperature by living coordination polymerization of HIC using 2-methacrylate ethyloxydichloro(cyclopentadienyl)titanium (IV) (**1**) as an initiator. The rodlike macromonomers prepared have carefully been characterized by size exclusion chromatography fitted with a multiangle laser light scattering (SEC−MALS) and ^{1}H NMR spectroscopy. The radical copolymerization behavior of the rodlike macromonomers (M_2) with methyl methacrylate (MMA) (M_1) or styrene (ST) (M_1) in benzene at 60 °C has thoroughly been studied and rationalized with a function of degree of polymerization of HIC. In region of degree of polymerization (*n*) higher than 26, the macromonomer's apparent reactivity ($1/r_1$) relative to MMA was found to be almost independent of *n* and macromonomer concentration but lower than MMA ($1/r_1$ is ca. 0.6). On the other hand, in the macromonomers with *n* less than 26, the reactivity appeared to steeply increase with decreasing *n*, because of weak aggregation due to hydrogen bond formation between terminal amide groups in benzene. In the copolymerization with ST (M_1), the apparent reactivities ($1/r_1$) were also lower the reference value reported in the copolymerization of MMA with ST. The copolymerization behavior of MA-HIC-*n* macromonomers was compared with that of styryl-ended (VB-HIC-*n*, $1/r_1 \approx 1.0$) and methacryloyl-ended (Bz-HIC-*n*-MA, $1/r_1 \approx 0.1$) macromonomers and discussed from the structural point of views. The methacrylate functional group was thought to be much more subject to steric hindrance effects than the styrenic group.

Introduction

Macromonomers are usually defined as a polymeric or an oligomeric monomer with a polymerizable or copolymerizable functional group at one end that are capable of further co- and homopolymerization.[1−9] During polymerization, macromonomers serve as a convenient building block to design a variety of branched homo- and copolymers including comb, star, brush, and graft types. For each of these architectures, the identity of the branches is directly dependent on characteristics of the macromonomers. Therefore, adequate control of molecular weight, composition, and molecular topology of the macromonomer chain impart a well-defined nature to the resulting branched (co-)polymers. An essential, fundamental, and important point to be considered in the macromonomer method is to clarify the reactivity in co- or homopolymerization, because it is a key factor for controlling and designing the graft copolymers.

Over the past two decades, a large number of macromonomers, differing in the type of the repeating monomer unit and the end group have been prepared, thereby offering the possibility of construction of an enormous number of branched polymers in a variety of architectures, combinations, and compositions. Fundamental understandings in co- and homopolymerizabilities of the macromonomers, solution properties of the resulting branched co- and homopolymers, and their successful application to polymeric microsphere syntheses have been reviewed by Ito and his co-workers.[1−3] In general, the reactivity of macromonomer has been known to decrease or to be similar to that of low molecular weight momonomer at least in apparently homogeneous solution. Some feasible explanations for lowering of the reactivity have been proposed, including thermodynamic repulsions between macromonomer and propagating chains, kinetic excluded volume effects, and decrease in mobility of reactive species. The macromonomers which have so far been studied, however, are limited to those consisting of flexible polymer chain in solution, such as polymethacrylates,[10] polystyrene,[11] poly(ethylene oxide),[12] poly(dimethylsiloxane),[13] and so on. Little is known about macromonomers consisting of semiflexible, or rodlike polymer chain.[14]

Recently, we have become interested in the synthesis of rodlike macromonomers, their radical (co-)polymerizabilities, and dimensional properties of branched polymers including comb, star, and cylindrical brush, consisting of rod side chains.[15] Polyisocyanates are known to be typical semiflexible polymers in solution. Their main chain rigidities may come from the resonance delocalization in the amide linkage. Because of their unique structural properties, which are remarkably different from conventional vinylic flexible polymers, polyisocyanates have widely been studied in various fields such as chiral recognition materials, optical switches and liquid crystal materials. Among others, poly(*n*-hexyl isocyanate) (PHIC) is one of the most characterized polyisocyanates. It assumes a dynamic 8_3 helical conformation with a persistent length $q = 42$ nm and a molar mass per unit contour length of $M_L = 730$ nm^{-1} in hexane at 25 °C.[16] Thus, the PHIC chain with weight-averaged molecular weight (M_w) lower than $M = 6.1 \times 10^4$ may be considered in hexane as a rigid rod molecule.

Whereas there have been many reports on the polymerization of HIC, the controlled synthesis of HIC was first established by Novak et al.[17] with titanium-catalyzed coordination living

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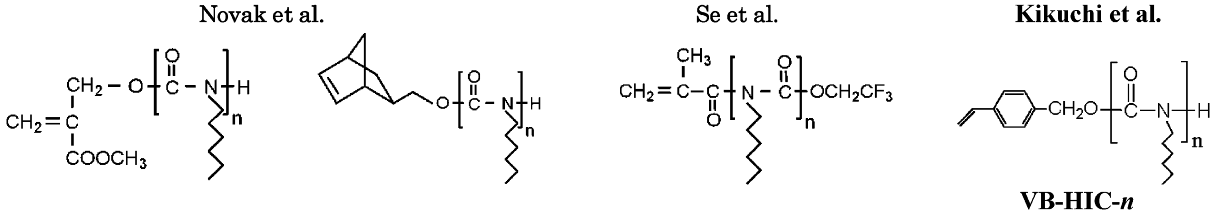
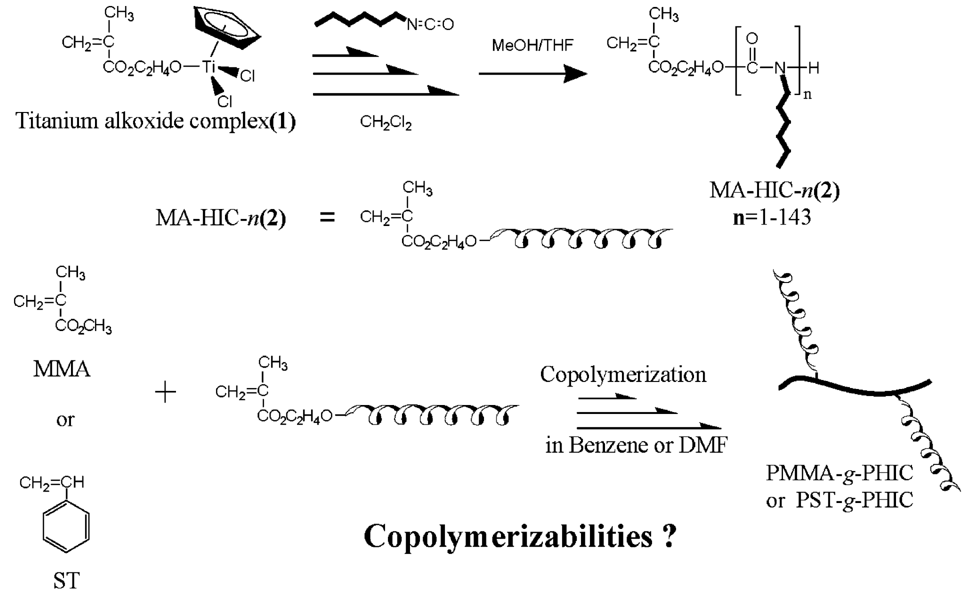
Scheme 1. Molecular Structures of Poly(*n*-hexyl isocyanate) Macromonomers Which Have So Far Been Prepared



Scheme 2. Reaction Schemes of MA-HIC-*n* Macromonomers and Their Copolymerization in This Study



polymerization and more recently Lee et al.[18] with anionic living polymerization using sodium tetraphenylborate ($NaBPh_4$) as a common salt. As shown in Scheme 1, Novak et al. have reported preparation of PHIC macromonomers with α-substituted acrylate or norbornene group by initiator method using corresponding titanium alkoxide initiators, but not reported their (co-)polymerizability. Quite recently, Se et al.[19] have synthesized PHIC macromonomers (PHIC-MA) with a methacryloyl group by titanium-catalyzed polymerization of HIC followed by termination reaction with methacryloyl chloride, as shown in Scheme 1. They also studied radical copolymerization of methyl methacrylate (MMA) (M_1) with PHIC-MA (M_2) and found that their reactivities were $r_1 = 11.5$ and $r_2 =$ approximately 0, implying extremely low (co-)polymerizabilities of the rodlike macromonomer. In remarkable contrast, Kikuchi et al. have reported the preparation of styryl-ended PHIC macromonomers (VB-HIC-*n*) and apparent reactivities of VB-HIC-*n* relative to styrene (ST), which are almost equivalent to that of ST.[15]

Herein, we report preparation of novel methacrylate ended rodlike PHIC macromonomers (MA-HIC-*n*) (**2**) by initiator method with 2-methacrylate ethyloxydichloro(cyclopentadienyl)-titanium(IV) (**1**) as an initiator and radical copolymerization behavior of MA-HIC-*n* with MMA or styrene (ST), as shown in Scheme 2. For comparison, PHIC macromonomer (Bz-HIC-*n*-MA) with a benzyloxy and a methacryloyl group at each end is also prepared by termination reaction of living chain end with methacrylic anhydride in the presence of Lewis acid. Copolymerization behavior of Bz-HIC-*n*-MA with MMA is also studied and compared. The results have been rationalized as a function of degree of polymerization of HIC (*n*) and discussed those previously reported, as shown in Scheme 2.

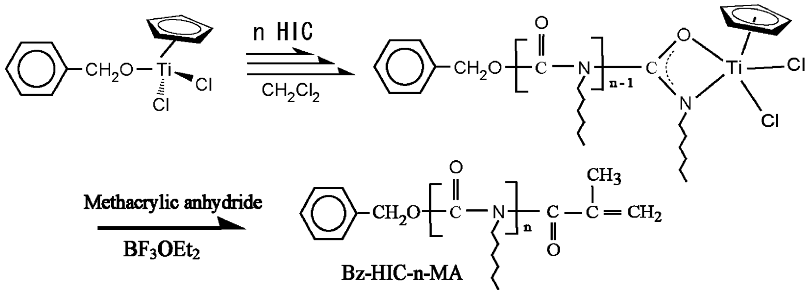
Experimental Section

Materials. Benzene (Kanto Kagaku Co., Ltd., Japan) was washed with concentrated H_2SO_4 to remove thiophene, 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. HIC and *n*-butyl isocyanate (BIC) monomers (Tokyo Kasei, Japan), dichloromethane (Kanto Kagaku Co., Ltd., Japan), MMA (Wako, Japan), benzyl alcohol (Bz) (Wako Co., Ltd., Japan), and methacrylic anhydride (Kanto Kagaku Co., Ltd., Japan) were distilled from calcium hydride under reduced pressure just before use. 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. Trichlorocyclopentadienyl titanium ($CpTiCl_3$) (Kanto Kagaku Co., Ltd., Japan) and BF_3OEt_2 (Kanto Kagaku Co., Ltd., Japan) were used as received. The radical initiator, 2,2′-azobis(isobutyronitrile) (AIBN) (Wako, Japan) was purified by recrystallization three times from methanol. Unless otherwise specified, all other reagents were purchased from commercially available sources and used as received.

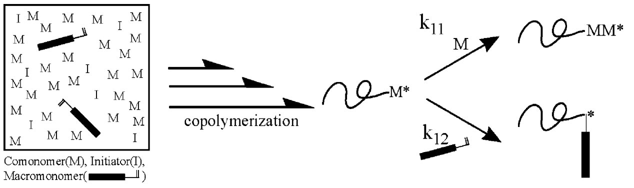
Synthesis of 2-Methacrylate Ethyloxydichloro(cyclopentadienyl)titanium(IV) (1). The titanium alkoxide complex (**1**) was synthesized according to Novak et al.[17] In a drybox, a solution of HEMA (1.2 g, 9.1 mmol) in 10 mL of dry THF was slowly added to a solution of $CpTiCl_3$ (2.0 g, 9.1 mmol) and 10 mL dry THF in three-necked 50 mL flask with a magnetic stir bar. The reaction was carried out at room temperature for 3 h and then the reaction mixture was evaporated to remove THF. Finally, the product dissolved in 30 mL of dry benzene was freeze-dried.[15] Benzyloxydichloro(cyclopentadienyl)titanium(IV) was prepared according to the same procedures.

Preparation of MA-HIC-*n* Using the Titanium Alkoxide Complex (1). The polymerization reaction scheme is also shown in Scheme 2. In a drybox, to a 20 mL flask with a magnetic stir bar were added titanium alkoxide complex and dichloromethane.

Scheme 3. Reaction Schemes of Bz-HIC-*n*-MA Macromonomers by the Termination Method



Scheme 4. Schematic Pictures of Copolymerization of Comonomer (M_1) with Macromonomer (M_2)



After the titanium alkoxide complex had completely dissolved, the desired amount of HIC was added, the flask was capped, and it was taken out of drybox. The polymerization was carried out at room temperature. After polymerization was complete, the polymer was dissolved into THF containing 5% methanol to terminate and precipitated into methanol to afford a white solid. The reprecipitation procedure from THF to methanol was done three times. Finally, the polymer dissolved in 50 mL of dry benzene was freeze-dried.

Preparation of Bz-HIC-*n*-MA Macromonomer by Termination Method. The polymerization reaction scheme is also shown in Scheme 3. The experimental procedures are the same as mentioned above, except for benzyloxydichloro(cyclopentadienyl)-titanium(IV) as an initiator. In the termination reaction, solution of excess amount of methacrylic anhydride and BF_3OEt_2 are added to the polymerization flask in a drybox and vigorously stirred for 24 h at room temperature. After reaction, the polymer dispersion was dissolved into THF containing methanol and poured into methanol. The reprecipitation procedure from THF to methanol was done three times and finally freeze-dried from benzene solution.

Synthesis of 2-Methacrylate Ethyl Butyl Urethane (BUEMA). The low molecular weight analogue of MA-HIC-*n*, 2-methacrylate ethyl butyl urethane (BUEMA) as a unimer was synthesized in a 20 mL flask with a magnetic stir bar by reacting HEMA (5.0 g, 38.5 mmol) with a 1.5-fold excess of BIC (5.7 g, 57.5 mmol) for 24 h at 40 °C. The reaction mixture was evaporated to remove unreacted BIC followed by distillation under reduced pressure to remove unreacted HEMA. Finally, the crude product was purified by distillation under reduced pressure.

Radical Copolymerization of MA-HIC-*n* with MMA or ST. The radical copolymerization of MMA or ST with MA-HIC-*n* macromonomers were conducted with AIBN as an initiator in benzene at 60 °C. The desired amounts of MA-HIC-*n*, MMA, and AIBN (1 mol % to total monomers) were weighed in the 20 mL flask and degassed by three times freeze-thawing. After copolymerization, the reaction mixture was poured into methanol, filtered, and dried under reduced pressure. The MMA conversion was then determined by the weight method using[20]

$$\text{conversion(MMA) (\%)} = \frac{W(t) - W_0(\text{macromonomer})}{W_0(\text{MMA})} \times 100 \tag{1}$$

where $W_0(i)$ is the weight of component i after polymerization time t. Unreacted macromonomer from the reaction mixtures was completely removed by 10-times reprecipitation from THF into *n*-hexane. This procedure was especially important for the determination of reactivity in the copolymerization. The complete removal of unreacted macromonomers without missing the resulting graft copolymers (less than 2%) was confirmed by ^{1}H NMR and SEC−UV−MALS−RI measurements of the *n*-hexane-soluble part and precipitates. Copolymerizations of ST with MA-HIC-*n* or MMA with Bz-HIC-*n*-MA were conducted by the same procedures.

Determination of Copolymerization Parameters. Copolymerization behaviors of conventional monomer (M_1) with macromonomer (M_2) are usually discussed on the basis of the well-known copolymerization equation, the Mayo−Lewis equation, using the experimental data obtained at very low conversion

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2](r_2[M_2] + [M_1])} \tag{2}$$

where $[M_i]$ is the monomer concentration of component i in the feed, r_i is monomer reactivity ratio of M_i, and k_{ij} is the propagating rate constant of a propagating chain ending in M_i reacting with M_j, with i or $j = 1$ or 2. With the condition $[M_1]/[M_2] \gg 1$, the r_1 determined should approximate most simply the relative reactivities

Table 1. Polymerization Results of MA-HIC-*n* Macromonomers Prepared by Living Coordination Polymerization of HIC[a]

sample	$[HIC]_0/[initiator]_0$	CH_2Cl_2 (g)	time (h)	convn (%)	Dp[c]	$M_n \times 10^{-3}$ calcd[d]	$M_n \times 10^{-3}$ NMR[e]	$M_w \times 10^{-3}$ (SEC)[f]	M_w/M_n (SEC)[f]	d*n*/d*c*[g] (mL/g)
MA-HIC-26	23.4	0.80	12	71.5	26	2.26	3.43	4.08	1.0_6	0.085_0
MA-HIC-34	25.0	0.80	12	76.7	34	2.57	4.44	4.06	1.2_0	0.084_0
MA-HIC-42	45.6	0.80	12	88.5	42	5.26	5.46	7.55	1.0_9	
MA-HIC-43	37.1	0.51	24	91.8	43	5.43	5.91	7.55	1.0_9	0.086_9
MA-HIC-50	47.2	0.06	36	93.4	50	5.73	6.48	10.2	1.1_8	0.084_4
MA-HIC-91	102	0.80	24	87.6	91	11.5	11.7	14.6	1.1_2	
MA-HIC-95	75.0	0.80	18	95.6	95	12.2	12.2	12.3	1.4_0	0.087_1
MA-HIC-120	134	0.20	36	95.4	120	16.4	15.4	17.7	1.1_5	0.086_8
MA-HIC-141	150	0.80	36	75.6	141	18.0	18.0	18.7	1.1_6	
MA-HIC-143	131	0.25	36	96.4	143	18.3	18.3	20.2	1.0_9	0.087_8
Bz-HIC-90-MA[b]	50.0	0.30	18	89.6	90	5.89	12.0	12.5	1.3_9	

[a] Carried out under N_2 atmosphere at room temperature. [b] Methacryloyl-terminated macromonomer. [c] Determined by ^{1}H NMR intensity ratio of methyl protons of poly(*n*-hexyl isocyanate) (PHIC) (g) to vinyl protons of double bond (a) in Figure 2. [d] $M_n(\text{calcd}) = M_{\text{HEMA}} + [\text{HIC}]_0/[\text{initiator}]_0 \times M_{\text{HIC}} \times$ conversion (HIC), where M_{HIC} is the molecular weight of HIC. [e] $M_n(\text{NMR}) = M_{\text{HEMA}} + \text{Dp} \times M_{\text{HIC}}$. [f] Determined from SEC calibrated using a series of poly(*n*-hexyl isocyanate) (PHIC). [g] In THF at 25.0 °C. The value of (d*n*/d*c*) of 2-hydroxyethyl methacrylate (HEMA) in THF at 25 °C is also determined to be 0.0470 mL/g.

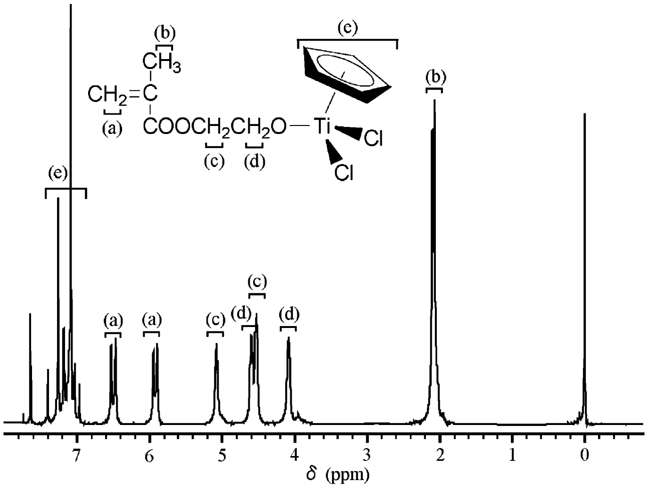


Figure 1. ^{1}H NMR spectrum of titanium alkoxide complex (**1**) in $CDCl_3$.

of M_1 and M_2 in competition reaction with the M_1-ended radical which should also approximate a homopoly(M_1) radical, as shown in Scheme 4. Therefore, the relative reactivity of macromonomer can be regarded as the reciprocal of r_1, $1/r_1$. Accordingly, eq 2 may be approximated to a simplified form:[12]

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]},\ r_1 = \frac{k_{11}}{k_{12}} \qquad (3)$$

Measurements. ^{1}H NMR spectra were recorded on JEOL 270 MHz instrument using $CDCl_3$ and C_6D_6 as a solvent. Fourier transformation infrared spectra (FT−IR) were obtained with a HORIBA FT-270 spectrophotometer under nitrogen atmosphere. The benzene solution of BUEMA was held between two NaCl plates separated by a spacer of 25 μm thickness. Recording conditions were 16 of accumulation times and 2 cm^{-1} of resolution, and concentration of BUEMA is ranged from 1 to 20 wt %. Net IR spectra of BUEMA were obtained by subtracting a spectrum of benzene. The elemental analysis data were obtained from a Perkin-Elmer 2400 II CHN analyzer.

The molecular weight and molecular weight distribution of the macromonomers and graft copolymers were determined by size exclusion chromatography (SEC; THF, 40 °C, columns: Shodex KF802 + KF806L + KF806L, RI; Shodex RI-101, UV; Tosoh UV-8020) fitted with a multiangle laser light scattering detector (Dawn-DSP; wavelength, 632.8 nm, Wyatt Technology) (SEC−UV−MALS−RI). Elution volume in SEC was calibrated with a series of PHICs whose molecular weight are predetermined by SEC−MALS. Excess refractive index increments (dn/dc) of macromonomers were measured using a differential refractometer (DRM-1021, Otsuka Electronics) in THF at 25 °C and are given in Table 1.

Results and Discussion

Synthesis of Initiator. The ^{1}H NMR spectrum of 2-methacrylate ethyloxydichloro(cyclopentadienyl)titanium(IV)(**1**) synthesized is shown in Figure 1. Two peaks of methylene (c and d) are shifted to low magnetic field, likely due to ring-current effects of cyclopentadiene. Integral peak ratio supports the assumption that the titanium alkoxide complex (**1**) is successfully synthesized. Yields were ca. 80 ∼ 95%. The preparation of benzyloxydichloro(cyclopentadienyl)titanium(IV) is also confirmed.

Preparation of MA-HIC-*n* Macromonomers (2). Living coordination polymerization of HIC was carried out using titanium alkoxide complex (**1**) as an initiator in CH_2Cl_2. Figure 2 shows a typical ^{1}H NMR spectrum of MA-HIC-*26* in $CDCl_3$.

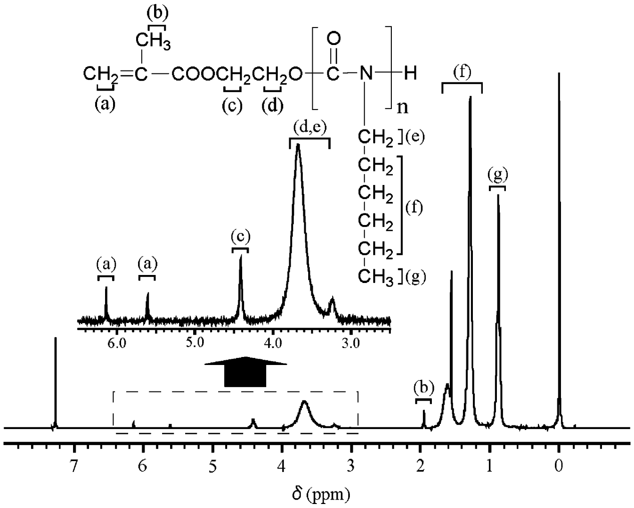


Figure 2. ^{1}H NMR spectrum of PHIC macromonomer (MA-HIC-*26*) in $CDCl_3$.

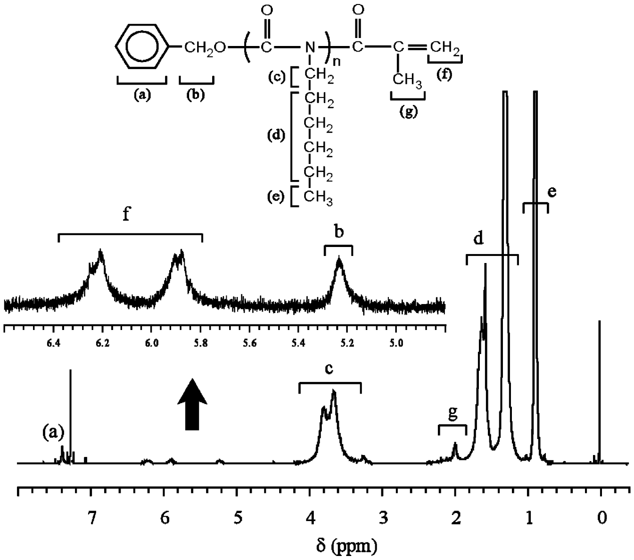


Figure 3. ^{1}H NMR spectrum of PHIC macromonomer (Bz-HIC-*90*-MA) in $CDCl_3$.

It shows ^{1}H NMR peaks due to a methacryloyloxy-ended group, as well as due to PHIC chain. The number-averaged molecular weight, M_n(NMR) is determined by ^{1}H NMR peak intensity ratio of methyl protons (g) of PHIC chain to a terminal methacrylate group (a) using the equation,

$$M_n(\mathrm{NMR}) = \frac{(g)}{3(a)} \times M_{\mathrm{HIC}} + 130 \qquad (4)$$

where M_{HIC} is the molecular weight of HIC. In Table 1, the polymerization results and characteristics of the resulting MA-HIC-*n* are listed. It is clearly seen that PHIC macromonomers with relatively narrow molecular weight distribution are successfully prepared with quantitative yield, except for those with degree of polymerization (Dp) less than 40. The low yield may be due to low reprecipitation efficiency into methanol. It should be noted in this table that the values of M_n determined from ^{1}H NMR peak intensities based on methacrylate terminal group are almost consistent with weight-averaged molecular weight (M_w) determined by SEC calibrated with a series of PHICs. The result clearly demonstrates a successful preparation of PHIC macromonomers with a methacrylate functional group at an end by the present initiator method.

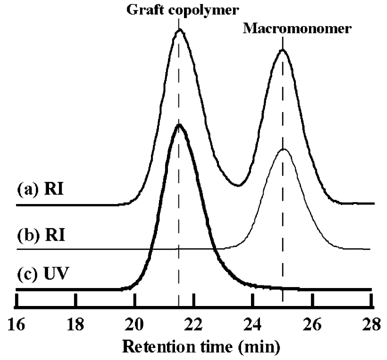


Figure 4. SEC−UV−MALS−RI curves of (a) RI signals of a mixture of PMMA-*g*-PHIC and unpolymerized PHIC macromonomer, (b) RI signals of PHIC macromonomer, and (c) UV signals of PMMA-*g*-PHIC.

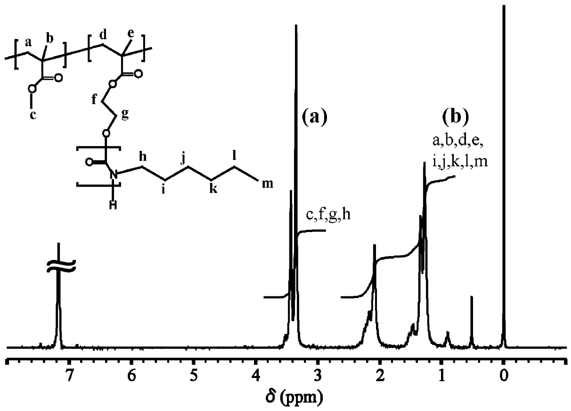


Figure 5. ^{1}H NMR spectrum of PMMA-*g*-PHIC in C_6D_6.

Preparation of Bz-HIC-*n*-MA Macromonomers. The ^{1}H NMR spectrum of Bz-HIC-*90*-MA macromonomer is presented in Figure 3. Characteristics of the macromonomer are also presented in Table 1. One sees clearly peak signals due to methacryloyl and benzyloxy groups as well as PHIC to imply successful synthesis of macromonomer by the present termination method. The functionality of methacryloyl group determined by the ratio of peak signals of peak f to peak a in Figure 3 is almost 100%. One interesting observation to be noted in this figure is that the peaks of double bond significantly broaden, when compared to those of the methacrylate-ended macromonomer as shown in Figure 2, implying strictly restricted mobilities in the former. Similar features in ^{1}H NMR were also pointed out by Se et al.[21]

Radical Copolymerization of MMA with MA-HIC-*n*. As mentioned in the experimental part, the most important point in estimating radical copolymerizability of the macromonomer is to establish the method to remove completely only unreacted macromonomer from the resulting graft copolymer mixtures, because contamination of the macromonomer significantly affects the result. The complete removal has been established by ten times reprecipitation from THF into hexane, which is a good solvent for PHIC but a nonsolvent for the graft polymers. The complete removal of unreacted PHIC macromonomer from the graft copolymer is finally confirmed using a UV detector in SEC−MALS because PHIC side chain has UV absorption but the PMMA chain does not. One example of the SEC−UV−MALS−RI curve is presented in Figure 4 in which part a is the RI curve of reaction mixture of graft copolymer and macromonomer, part b is the RI curve of PHIC macromonomer only, and part c is the UV curve of the isolated graft copolymer. Figure 4c clearly demonstrates the complete removal of unreacted PHIC macromonomer. The ^{1}H NMR spectrum of the isolated PMMA-*g*-PHIC in C_6D_6 is presented in Figure 5. The composition ratio, d[M$_1$]/d[M$_2$] is estimated by the equation

$$\frac{d[M_1]}{d[M_2]} = \frac{2(n+2)\alpha - (11n+5)}{5-3\alpha} \tag{5}$$

where n is the degree of polymerization of HIC and α is the ratio of curve b to curve a (α = b/a) in Figure 5.

First, we studied the dependence of the total monomer concentration ([M$_1$] + [M$_2$]) at constant monomer ratio, [M$_1$]/[M$_2$] = 443, on the relative reactivity of PHIC macromonomer in benzene. The copolymerization results are listed in Table 2. It is seen that the value of $1/r_1$ is independent of the total monomer concentration and the average value is 0.66 ± 0.05, showing that the PHIC macromonomer can be fairly copolymerized. Apparent M_n(app) of graft copolymers determined by SEC−MALS with dn/dc = 0.085 mL/g both for PMMA and PHIC macromonomer is also listed in Table 2. The apparent degree of polymerization of main chain (Dp(app)) and the apparent number of branched chains (*f*(app)) of the graft copolymers are listed in Table 2, in which they are calculated by the equations

$$\mathrm{Dp(app)} = \frac{M_n(\mathrm{app})(y+1)}{M_1(y+k)} \tag{6}$$

$$f(\mathrm{app}) = \frac{\mathrm{Dp(app)}}{y+1} \tag{7}$$

where y = d[M$_1$]/d[M$_2$], $k = M_2/M_1$, and M_i is a monomer molecular weight of species i. In the present experimental condition of [M$_1$]/[M$_2$] = 443, the graft copolymers with PHIC chain from 0.13 to 1.2 are prepared, depending on Dp(app).

Secondary, the molecular weight dependence of the relative reactivities of PHIC macromonomer was studied at various monomer concentrations. The copolymerization results of MMA (M$_1$) with MA-HIC-*n* (M$_2$) are summarized in Table 3. In $n \geq 26$, the molecular weight dependence of $1/r_1$ value is not clearly observed within experimental error and the average value of $1/r_1$ for each macromonomer ranges from 0.46 to 0.82. Since the experimental values slightly scatter, it may be concluded that the apparent relative reactivity of MA-HIC-*n* with $n \geq 26$ is lower than that of MMA.

Table 2. Copolymerization Results of MMA (M$_1$) with MA-HIC-34 (M$_2$) at Various Total Monomer Concentrations[a]

run	$[M_1]_0 + [M_2]_0$[b] (mol/L)	benzene (mL)	convn (M_1) (%)	$d[M_1]$[c]/ $d[M_2]$	$1/r_1$	$M_{n(app)}$[d] ($\times10^{-4}$)	$Dp_{(app)}$[e] ($\times10^{-2}$)	$f_{(app)}$[e]
1	10.1	2.0	10.2	625	0.71	8.11	7.58	1.21
2	2.01	10	11.5	693	0.64	3.98	3.74	0.54
3	1.01	20	10.7	706	0.61	5.00	4.70	0.67
4	0.402	50	4.56	657	0.68	0.936	0.878	0.13

[a] Copolymerizations of MMA with MA-HIC-34($[M_1]_0/[M_2]_0$ = 443) were carried out at 60 °C using AIBN (1 mol % to total monomer) in benzene. [b] Total initial concentration of MMA and MA-HIC-34. [c] Determined by ^{1}H NMR peak intensity ratio of a to b in Figure 5. [d] Determined by SEC-MALS. [e] Calculated with eqs 6 and 7.

Table 3. Copolymerization Results of MMA (M_1) with MA-HIC-*n* (M_2)[a]

sample run	$[M_1]/[M_2]$	convn (M_1) (%)	$d[M_1]/d[M_2]$	$1/r_1$	$1/r_1$(av)	$M_{n(app)}$[c] ($\times 10^{-4}$)	$Dp_{(app)}$[d] ($\times 10^{-2}$)	$f_{(app)}$[d]
MA-HIC-26								
1	861	10.4	1741	0.49		20.1	19.7	1.1
2	540	10.9	867	0.62	0.64 ± 0.14	14.1	13.6	1.6
3	229	19.6	301	0.76		6.71	6.04	2.0
4	177	19.2	261	0.68		7.39	6.55	2.5
MA-HIC-34								
1	443	10.2	625	0.71		8.65	8.09	1.3
2	673	11.2	1228	0.55	0.67 ± 0.20	9.63	9.63	0.8
3	894	12.1	1880	0.48		10.3	10.1	0.5
MA-HIC-42								
1	545	10.1	843	0.65		9.74	9.16	1.1
2	366	9.45	488	0.75	0.64 ± 0.12	10.3	9.28	1.9
3	272	8.75	519	0.52		10.1	9.15	1.8
4	532	10.1	915	0.58		13.9	13.1	1.4
MA-HIC-50								
1	982	9.01	1116	0.88		20.0	18.9	1.7
2	641	10.1	915	0.70	0.75 ± 0.13	14.8	13.9	1.5
3	637	26.8	882	0.72		4.7	4.38	0.5
MA-HIC-91								
1	469	21.0	710	0.66		7.79	6.69	0.94
2	1869	14.5	3500	0.53		13.5	13.0	0.37
3	1170	11.4	2007	0.58	0.55 ± 0.11	8.92	8.43	0.42
4	778	11.9	1611	0.48		9.19	8.57	0.53
5	584	11.5	1199	0.49		10.9	9.94	0.83
MA-HIC-95								
1	1189	9.18	2347	0.51		8.54	8.1	0.35
2	1810	10.6	2808	0.64	0.60 ± 0.09	9.54	9.15	0.33
3	2427	11.9	3724	0.65		11.2	10.9	0.29
MA-HIC-141								
1	903	24.9	2180	0.41		6.36	5.87	0.27
2	1198	25.3	2530	0.47	0.46 ± 0.05	6.28	5.86	0.23
3	1805	26.1	3639	0.50		9.71	9.25	0.25
MA-HIC-143	1798	9.88	2496	0.72		8.45	7.87	0.32
1	2662	9.41	2855	0.93	0.82 ± 0.11	12.5	11.7	0.41
2	3633	7.98	4446	0.82		14.4	13.8	0.31
3								
Bz-HIC-90-MA[b]								
1	1005	7.66	10 351	0.097		-	-	-

[a] Copolymerization of MMA with MA-HIC-*n* were carried out at 60 °C using AIBN (1 mol % to total monomer) in benzene. [b] Methacryloyl-terminated macromonomer. [c] Determined by SEC-MALS. [d] Calculated using eqs 6 and 7.

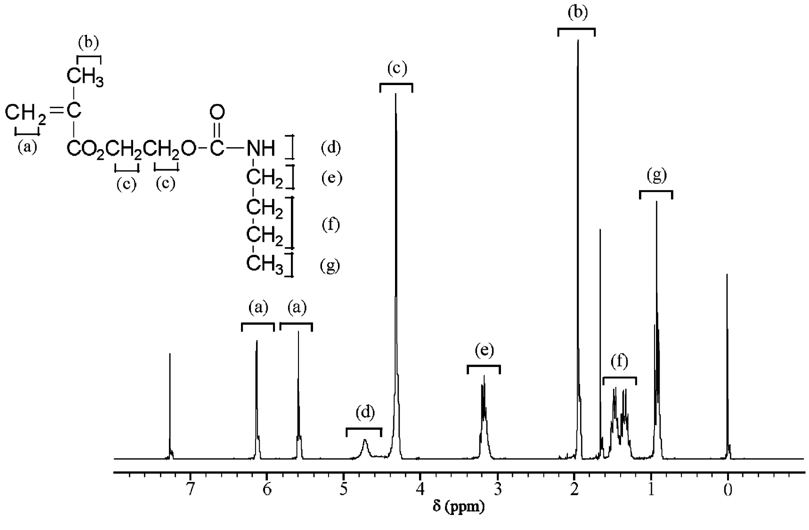


Figure 6. ^{1}H NMR spectrum of 2-methacrylate ethyl butyl urethane (BUEMA) in $CDCl_3$.

The copolymerization result of MMA (M_1) with Bz-HIC-90-MA (M_2) is also presented in Table 3. The value of $1/r_1$ is remarkably low (0.097), consistent with that reported by Se et al.[19] This is most likely due to the fact of less reactivity in the disubstituted methacrylamide. The remarkable broadening of ^{1}H NMR peaks of methacryloyl group as seen in Figure 3 may also correspond to the low polymerizability. It may be fairly concluded here that an introduction of an oxyethylene unit between methacryloyl group and PHIC chain as a spacer greatly enhances the copolymerizabilities of PHIC macromonomer.

Synthesis of BUEMA and the Radical Copolymerization of MMA with BUEMA. To discuss more deeply reactivity of MA-HIC-*n* in the radical copolymerization with MMA, the macromonomer model compound of MA-HIC-*n*, 2-methacrylate

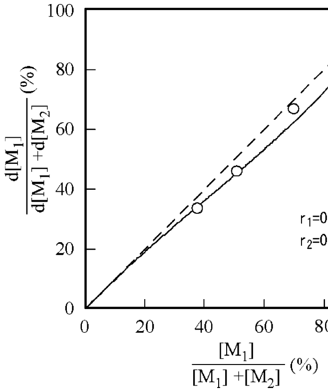


Figure 7. Compositional curve in the copolymerization of MMA (M_1) and BUEMA (M_2). The solid line is calculated using the values of $r_1 = 0.593$ and $r_2 = 0.969$.

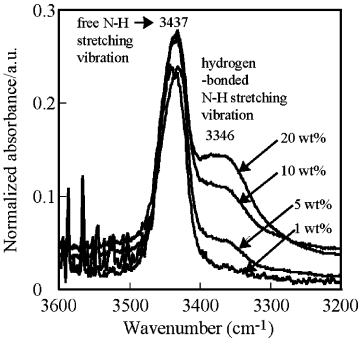


Figure 8. Normalized FT−IR spectra of BUEMA in benzene at different concentrations.

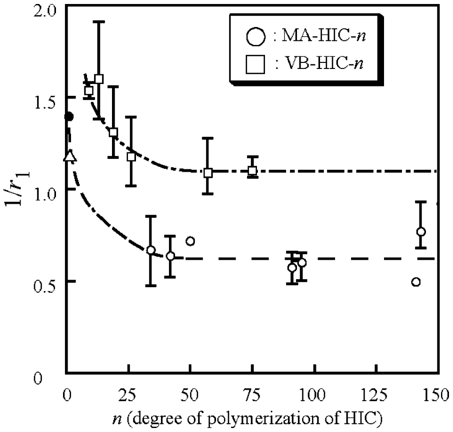


Figure 9. Plots of apparent relative reactivities ($1/r_1$) in the copolymerization of MMA (M_1) with MA-HIC-*n* (M_2)(○) against degree of polymerization of HIC: (△) BUEMA in DMF; (●) BUEMA in benzene. The data (□)[15] in the copolymerization of styrene (M_1) with VB-HIC-*n* (M_2) are also shown for comparison.

ethyl butyl urethane (BUEMA), is synthesized and the radical copolymerizability with MMA was studied. The ^{1}H NMR spectrum of the BUEMA prepared is presented in Figure 6 in which one sees successful synthesis of VBBU. The compositional curve in the copolymerization of MMA (M_1) and BUEMA (M_2) carried out in benzene is presented in Figure 7. The conversions in the copolymerizations were less than 10%. One determines $r_1 = 0.59$ and $r_2 = 0.97$ by the Fineman−Ross plot, and the theoretical curve (denoted by solid line) with these values is also shown in the figure. This compositional curve seems unusual, when compared to the conventional binary copolymerization, most likely due to hydrogen bonding between urethane groups, and/or between urethane and carbonyl group of MMA. The carbonyl group on MMA terminal radical ($k_1^\bullet$) can form a hydrogen bond with BUEMA (M_2) but not with MMA (M_1) to increase the consumption rate of BUEMA (apparent decrease of r_1). On the other hand, BUEMA terminal radical ($k_2^\bullet$) may form a hydrogen bond both with MMA (M_1) and with BUEMA (M_2) ($r_2 \approx 1$). This qualitative explanation is also thought to hold in the copolymerization of ST (M_1) with *p*-vinylbenzyloxy butyl urethane (VBBU) (M_2), previously reported.[15] One obtained $r_1 = 0.80$ and $r_2 = 1.93$ in benzene. The large value of r_2 may come from that fact that the VBBU terminal chain ($k_2^\bullet$) end can form a hydrogen bond to VBBU (M_2) but not to ST (M_1), to apparently increase the r_2 value. On the other hand, since the ST terminal end ($k_1^\bullet$) cannot form a hydrogen bond to both ST and VBBU, the r_1 value was not significantly affected.

FT−IR spectra of BUEMA in benzene at various concentrations are shown in Figure 8 where spectra are normalized with peaks due to CH_2 stretching vibration. One sees clearly two peaks due to free N−H stretching vibration around 3437 cm^{-1} and a hydrogen-bonded N−H one around 3346 cm^{-1}. The absorption intensities due to the hydrogen-bonded N−H increase with an increase of [BUEMA]. This result supports that BUEMA molecules tend to form a hydrogen bond in benzene, to apparently enhance the local concentration.

Copolymerizations of MMA (M_1) with BUEMA (M_2) were further studied in benzene and DMF under the condition $[M_1]/[M_2] \gg 1$ for direct comparison with those of macromonomer systems. The copolymerization results obtained are summarized in Table 4, in which the monomer compositions of the copolymer were determined by elemental analysis for C and N. The higher average value of $1/r_1 = 1.43 \pm 0.10$ than unity in benzene and that of $1/r_1 = 1.19 \pm 0.11$, close to unity in DMF, are obtained. In the latter solvent, the effects of hydrogen bonding are reasonably thought to decrease.

Molecular Weight Dependence of Apparent Relative Reactivity of MA-HIC-*n*. Figure 9 shows plots of apparent

Table 4. Copolymerization Results of MMA (M_1) with BUEMA (M_2)[a]

run	$[M_1]/[M_2]$	solvent (amt (mL))	convn (%)	$d[M_1]/d[M_2]$[b]	$1/r_1$	$1/r_1$(av)
1	100	benezene (2.0)	10.1	71.5	1.40	
2	125	benezene (2.0)	9.98	91.0	1.38	
3	150	benezene (2.0)	9.83	97.9	1.53	1.43 ± 0.10
4	175	benezene (2.0)	12.4	125	1.40	
5	200	benezene (2.0)	10.6	138	1.46	
6	101	DMF (26)	10.1	84.7	1.19	
7	126	DMF (24)	10.5	114	1.10	
8	151	DMF (29)	10.2	125	1.21	
9	173	DMF (34)	10.7	153	1.13	1.19 ± 0.11
10	201	DMF (25)	10.6	155	1.30	

[a] Copolymerization of MMA with BUEMA was carried out at 60 °C using AIBN (1 mol % to total monomer). [b] Determined by elemental analysis for C to N.

Table 5. Copolymerization Results of ST (M_1) with MA-HIC-*n* (M_2)[a]

sample run	$[M_1]/[M_2]$	convn (M_1) (%)	$d[M_1]^b/d[M_2]$	$1/r_1$	M_n(app)[c] ($\times 10^{-4}$)	Dp(app)[d] ($\times 10^{-2}$)	*f*(app)[e]
MA-HIC-26							
1	0330	11.5	318	1.0_4	2.23	2.03	0.58
2	0218	11.3	184	1.1_8	2.29	1.94	1.05
3	0164	09.10	132	1.2_5	2.44	1.95	1.47
				av = 1.2 + 0.1			
MA-HIC-34							
1	0434	6.64	294	1.4_8	4.97	4.27	1.21
2	0636	6.75	460	1.3_8	4.11	3.56	0.93
3	0855	7.00	625	1.3_7	4.23	3.82	0.60
				av = 1.4 + 0.1			
MA-HIC-95							
1	0498	9.15	354	1.4_1	8.00	6.15	1.33
2	2289	4.10	2250	1.0_2	7.66	7.30	0.30
				av = 1.2 + 0.1			

[a] Copolymerization of styrene with MA-HIC-*n* was carried out at 60 °C in benzene. AIBN is 0.063 mol % to styrene for MA-HIC-26, 1.0 mol % for MA-HIC-34, and 0.50 mol% for MA-HIC-95. [b] Determined by ^{1}H NMR peak intensity ratio of a to b in Figure 10. [c] Determined by SEC-MALS with d*n*/d*c* = 0.185 mL/g. [d] Calculated using eqs 6 and 7.

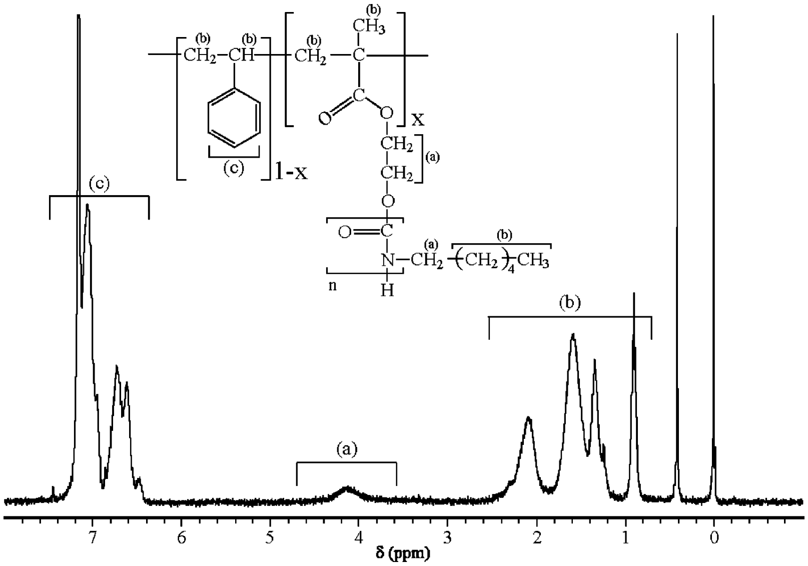


Figure 10. ^{1}H NMR spectrum of polystyrene-*g*-PHIC in C_6D_6.

relative reactivity of MA-HIC-*n* to MMA as a function of *n*. The results[15] in the copolymerization of ST (M_1) with VB-HIC-*n* (M_2) are also shown for comparison. One sees that in region of degree of polymerization (*n*) higher than 26, apparent reactivities ($1/r_1$) of MA-HIC-*n* relative to MMA are almost independent of *n* but lower than MMA ($1/r_1$ is ca. 0.6). On the other hand, in the macromonomers with *n* less than 26, the reactivities seem to increase with decreasing *n*. This increase may be reasonably explained by hydrogen bond formation between terminal amide groups in benzene, as discussed above. The terminal amide effects on the reactivities may reasonably decrease with increasing *n*. In addition, whereas DMF is thought to be a proper solvent for estimation of true reactivities of methacrylate functional group with a long rod chain, unfortunately, the PHIC chain does not dissolve in DMF.

It should be stressed in this figure that for *n* higher than 30 there exists a large difference in $1/r_1$ values between MA-HIC-*n* and VB-HIC-*n*. That is, the apparent reactivities of the latter macromonomer relative to ST are almost equivalent to that of the styrene, implying that the reactivity is mainly determined in the chemical reactivity of the double bond. On the other hand, those of MA-HIC-*n* are lower than those of MMA, as mentioned above. Three feasible explanations for the low reactivities are solubility of the monomer to PHIC chain, incompatibilities of PMMA propagating chain and PHIC chain, and steric hindrance around a polymerizable functional group.

First is the solubility difference between ST and MMA to PHIC chain. In fact, ST can dissolve the PHIC chain but MMA cannot. Whereas the copolymerizations were carried out in benzene, the repulsion between MMA and the MA-HIC-*n* chain may result in the increase of microscopic concentration of MMA around a propagating PMMA chain. The second is based on the incompatibilities. Character of the monomers is thought to be parallel to that of polymer. Thus, the PMMA propagating chain is more incompatible with the PHIC chain than the PST one, which results in larger thermodynamic repulsion between PMMA and PHIC chains than between PST and PHIC chains. To support these ideas, we further carried out the copolymerization of ST with MA-HIC-*n* in benzene as follows.

Radical Copolymerization of ST with MA-HIC-*n*. Table 5 shows the copolymerization results of ST (M_1) and MA-HIC-*n* (M_2) in benzene at 60 °C. Figure 10 shows the ^{1}H NMR spectrum of the resulting PST-*g*-PHIC in C_6D_6. The values of $1/r_1$ are ranged from 1.2 to 1.4. Their values are, however, considerably lower than the reference value of $1/r_1 = 1.92$ in the copolymerization of ST (M_1) and MMA (M_2).[22] This result may imply that incompatibilities of monomer and propagating chain with macromonomer chain are not responsible for lower reactivity of MA-HIC-*n* than VB-HIC-*n*. Our current feasible explanation is that the methacrylate functional group is much more subject to steric hindrance effects than the styrenic group.

Conclusions

Methacryloyloxy-ended rodlike poly(*n*-hexyl isocyanate) macromonomers (MA-HIC-*n*, *n* is from 26 to 143) with relatively narrow molecular weight distributions were successfully prepared by living coordination polymerization of HIC. Their radical copolymerization behavior with methyl methacrylate or styrene was studied and rationalized with a function of degree of polymerization of HIC. In *n* higher than 26, the macromonomer's apparent reactivity relative to MMA was almost independent of *n* but lower than MMA ($1/r_1$ is ca. 0.6). On the other hand, in *n* less than 26, the reactivity increased with decreasing *n*, because of weak aggregation due to hydrogen bond formation between terminal amide groups in benzene. In the copolymerization with ST (M_1), the apparent reactivities ($1/r_1$) were also lower than the reference values. The low copolymerizabilities of methacrylate functional group with a long rodlike molecule are most likely due to steric hindrance around the double bond.

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