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Preparation and characterization of graft copolymers of methyl methacrylate and poly(*n*-hexyl isocyanate) macromonomers

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Abstract

Living poly(*n*-hexyl isocyanate) (PHIC) was deactivated with methacryloyl chloride to produce methacryl-terminated poly(*n*-hexyl isocyanate) (PHIC-MA) rodlike macromonomers. Radical copolymerization of methyl methacrylate (MMA) with PHIC-MA was performed using 2,2′-azobis(isobutyronitrile) as an initiator in benzene at 60 °C to prepare poly(methyl methacrylate)-*graft*-poly(*n*-hexyl isocyanate) (PMMA-*graft*-PHIC) graft copolymers. The monomer reactivity ratios of MMA (M_1) and PHIC-MA (M_2) were evaluated as $r_1 = 11.5$ and $r_2 = \sim 0$, exhibiting remarkably lower reactivity of PHIC-MA macromonomer than that of common macromonomers. The resultant graft copolymers were characterized using gel permeation chromatography equipped with low-angle laser light-scattering to determine the molecular weights, and equipped with a refractive index detector and an ultraviolet light detector to estimate a PHIC weight fraction of PMMA-*graft*-PHIC at the *i*th elution volume of the GPC chromatogram. There are 2–3 PHIC grafts per PMMA molecule, and the PHIC rodlike chains might be difficult to introduce into the PMMA main chains having higher molecular weights. A specific dimension of PMMA-*graft*-PHIC in solution was discussed in detail.
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1. Introduction

Rodlike polymers have shown some unique physical properties such as liquid crystallinity [1], anisotropic solution and dielectric [2] and rheological behaviors due to their asymmetric shape [3,4]. Rod–Coil diblock copolymers consisting of a rodlike block and a flexible block have been reported to show a new morphology and phase behavior [5]. Thus, the rodlike polymers might be applied to new polymeric devices [6–8]. In the application of rodlike polymers, the next target is nonlinear block copolymers (such as star polymers and graft copolymers) [9–11] that consist of the rodlike polymers [12]. For this purpose, a synthetic route through macromonomers [13–15] is worthy of further study.

Recently, we succeeded in synthesizing methacryl-terminated poly(*n*-hexyl isocyanate) (PHIC-MA) rodlike macromonomers as a preliminary experiment [16] by living

titanium catalyzed coordination polymerization as reported by Novac and Patten [17]. The synthetic route is different from that reported in an early study by Novac and Patten [18]. The resultant PHIC-MAs have the desired molecular weights, and their molecular weight distributions are narrow. Yokota has reported that *N,N*-dialkylacrylamides, which are similar to a polymerizable vinyl group of PHIC-MA, could not be polymerized due to the steric effect [19]. However, a NMR study of PHIC-MA suggests that a symmetrical displacement or rotation about a C–CO bond of the methacryl group can be performed above 70 °C [16]. Hence, a small amount of PHIC-MA can be polymerized.

The present paper describes the preparation of PHIC-MA macromonomers having a 100% coupling efficiency. Radical copolymerization of methyl methacrylate (MMA) with PHIC-MA was carried out to determine the monomer reactivity ratios. The resultant poly(methyl methacrylate)-*graft*-poly(*n*-hexyl isocyanate) (PMMA-*graft*-PHIC) graft copolymers are characterized in detail so as to estimate their specific dimensions in solution.

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2. Experimental

2.1. Reagents

n-Hexyl isocyanate (HIC), $N(C_6H_{13})=C=O$ was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan) and distilled under 20 mmHg, then dried with calcium hydride (CaH_2) under high vacuum (10^{-6} mmHg), and then was distilled into ampules with breakable seals. Just before polymerization, HIC was distilled into an ampule after being dried with an octylzenzophenone–sodium complex [20,21]. A titanium catalyst, $TiCl_3OCH_2CF_3$, was prepared according to Novac and Patten [17] under high vacuum using a breakable-seal technique. MMA and all reagents, as well as the solvents employed in polymerization, were purified by the same methods used in the anionic living polymerization technique [20,21].

2.2. Polymerization

HIC was polymerized by $TiCl_3OCH_2CF_3$ under high vacuum using a breakable-seal technique to produce poly(*n*-hexyl isocyanate) (PHIC), $-[N(C_6H_{13})-C(O)]-$. The living end of PHIC was deactivated with methacryloyl chloride (MACl), $CH_2=C(CH_3)COCl$ to produce methacryl-terminated poly(*n*-hexyl isocyanate) (PHIC-MA) macromonomers [16]. The desired amounts of PHIC-MA, MMA, 2,2′-azobis(isobutyronitrile) (AIBN), and benzene (Bz) were weighed in a glass tube, degassed three times by freeze–thawing, sealed off by flame, and placed in a bath of 60 °C. Radical copolymerization of MMA with PHIC-MA macromonomers was performed using AIBN as an initiator in Bz at 60 °C to prepare poly(methyl methacrylate)-*graft*-poly(*n*-hexyl isocyanate) (PMMA-*graft*-PHIC) graft copolymers. The copolymerization mixture was poured into methanol and dried under reduced pressure.

2.3. Molecular characterization

Number average molecular weights (M_n^{VPO}) of PHIC with less than $M_n = 10^4$ were determined by vapor pressure osmometry (VPO; Model 117, Hitachi, Tokyo, Japan) in Bz at 30 °C. Molecular characterization of all the samples was carried out in tetrahydrofuran (THF) using gel permeation chromatography (GPC; Model CCPD, Tosoh Co., Tokyo, Japan) equipped with a low-angle laser light-scattering (LALLS) detector (Model LS-8000, Tosoh Co.) and new analytical equations we have presented elsewhere [22].

The ratio of the number average-molecular weight determined by VPO to that determined by NMR measurements (end-group analysis) for the PHIC-MA macromonomer, M_n^{VPO}/M_n^{NMR} is defined as the coupling efficiency (f_c) that indicates the number of MA groups per PHIC molecule. On the other hand, the PHIC weight fraction of PMMA-*graft*-PHIC at the *i*th elution volume of the GPC chromatogram is defined as

$$w_i^{PHIC} = \frac{c_i^{PHIC}}{c_i^{PHIC} + c_i^{PMMA}} \qquad (1)$$

where c_i^{PHIC} and c_i^{PMMA} are concentrations of PHIC and PMMA for the resultant PMMA-*graft*-PHIC graft copolymers at the *i*th elution volume, respectively. The ultraviolet light (UV) signal (H_i^{UV}) and refractive index (RI) signal (H_i^{RI}) of PMMA-*graft*-PHIC at the *i*th elution volume can be, respectively, described as $H_i^{UV} = k_{PHIC}^{UV}c_i^{PHIC}$ and $H_i^{RI} = k_{PMMA}^{RI}c_i^{PMMA} + k_{PHIC}^{RI}c_i^{PHIC}$, because the molar absorptivity of PHIC (4.1×10^4 mol^{-1} l cm^{-1}) at 254 nm is much larger than that of PMMA (~ 0). Therefore, w_i^{PHIC} can be determined as follows

$$w_i^{PHIC} = \frac{H_i^{UV}}{H_i^{UV} + [H_i^{RI} - H_i^{UV}(k_{PHIC}^{RI}/k_{PHIC}^{UV})](k_{PHIC}^{UV}/k_{PMMA}^{RI})} \qquad (2)$$

where k_{PHIC}^{UV}, k_{PHIC}^{RI} and k_{PMMA}^{RI} are instrumental constants that were previously determined by the GPC measurements of PHIC and PMMA using an UV detector (UV-8011, Tosoh Co.) and RI detector (RI-8010, Tosoh Co.). High resolution columns (7.8 mm i.d. × 60 cm; Tosoh Co.) were used for the GPC measurements. The PHIC weight fractions ($w_{PHIC}^{copolymer}$) of the graft copolymers can also be determined as follows

$$w_{PHIC}^{copolymer} =$$

$$\frac{\sum H_i^{UV}}{\sum H_i^{UV} + [\sum H_i^{RI} - \sum H_i^{UV}(k_{PHIC}^{RI}/k_{PHIC}^{UV})](k_{PHIC}^{UV}/k_{PMMA}^{RI})} \qquad (3)$$

3. Results and discussion

3.1. Synthesis of PHIC-MA macromonomers

The toluene solution of the HIC monomer was introduced into the toluene solution containing $TiCl_3OCH_2CF_3$, whose polymerization rate has been found to be very fast. After the initiation was finished in 30 min, a few percent of THF was added to the polymerization solution to introduce the living end to be solvated by coordination with THF. This small amount of THF was found to slow the propagation rate to a few hundredths of the initial rate. After 40–60 h, the residual monomer in the toluene/THF mixture was then added to the oligomeric living PHIC solution to propagate the polymer slowly at -5 °C for 142–245 h under high vacuum (10^{-6} mmHg). The details for preparing PHIC-MA are shown in Table 1. By this seed polymerization technique, we have prepared living PHIC with desired molecular weights and narrow molecular weight distributions.

The toluene-rich solvent was exchanged for a THF-rich

Table 1
Preparation and characterization of PHIC-MA macromonomers

PHIC-MA	HIC (g)	Initiation[a]			Propagation[a]							Coupling[a]			
		HIC (g)	Tol (ml)	t (h)	HIC (g)	Tol (ml)	THF (ml)	t (h)	$10^{-3}M_k$[b]	$10^{-3}M_n^{VPO}$[c]	M_w^{LALLS}/M_n^{LALLS}[c]	Exchange of solvent Tol/THF Before / After	[MACl]/[PHIC][d]	t (day)	f_c^e (%)
PHIC-MA/1	9.8_3	1.6_9	110	60	8.1_4	140	7	245	5.1_5	5.3_6	1.0_9	95/5 13/87	71	72	70_2
PHIC-MA/2	24.4	3.9	260	40	20.5	150	2	166	6.0_3	6.1_6	1.0_8	97/3 15/85	30	36	77_8
PHIC-MA/3	10.6	0.8_2	130	50	9.7_9	150	2	150	5.9_7	6.3_5	1.1_2	99/1 5/95	72	70	75_6
PHIC-MA/4	26.2	3.1	260	40	23.1	150	2	142	9.8_8	10.4	1.1_0	99/1 5/95	86	33	76_5

[a] Initiation, propagation and coupling reactions were carried out at −5°C under high vacuum.
[b] Determined from the amounts of monomer and initiator by considering polymer yield.
[c] Determined by VPO and GPC-LALLS using new analytical equations [22].
[d] Molar ratio of MACl to the living PHIC.
[e] Coupling efficiency determined by M_n^{VPO}/M_n^{NMR}.

solvent under high vacuum, and then MACl were added to the living PHIC solution to produce PHIC-MA macromonomer. The precursor was taken out of the glass apparatus at a given time by the same methods as for the anionic living polymerization technique [20,21], so as to determine the coupling efficiency (f_c). The details for the coupling reaction and the molecular characteristics of the resultant PHICs are shown in Table 1. Fig. 1 shows the second-order plots of the time-conversion curves for the living PHIC's coupling reactions with MACl. As shown in Fig. 1, the four coupling reactions show the different time conversion behaviors, which depend on the molecular weights of PHIC and the polarity (dielectric constants) of the toluene (Tol)/THF mixed solvents. The apparent rate constants (k_{ap}) for the second-order reaction were determined from the slopes for the lower reaction times to give 1×10^{-6}–2.4×10^{-6} l mol^{-1} s^{-1}. These k_{ap} values are probably the same as those of the living PHIC with p-phenylazobenzoyl chloride and 4-bromomethyl azobenzene [16].

The f_c values increased as the coupling time increased. As shown in Table 1, PHIC-MA macromonomer could be prepared at a high coupling efficiency (70–78%), but this efficiency would remain below 100%, even after a long coupling time (~740 h). As a PHIC chain forms a helical conformation and the resonance structure of the main chain, a ceiling temperature of 43 °C appears [17]. Therefore, the solution of the coupling reaction was left standing above the ceiling temperature under high vacuum for 2 days. The living PHIC unreacted with MACl was depolymerized to yield the corresponding monomer and/or trimer, and the PHIC-MA macromonomers were transferred intact due to the fact that they were not living. Therefore, the f_c value became 100%, as shown in Table 2. This technique to depolymerize the living PHIC is a remarkable method for preparing a macromonomer with a 100% coupling efficiency and it should be useful for other applications.
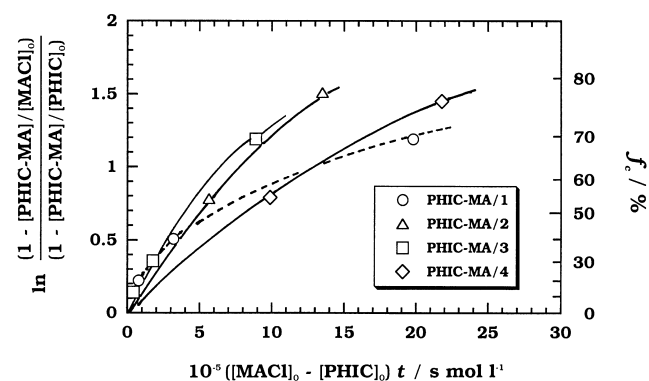

Fig. 1. Second-order plots of the coupling reaction for the living PHIC with methacryloyl chloride (MACl). [MACl]$_0$ and [PHIC]$_0$ are initial concentrations of MACl and living PHIC, respectively. [PHIC-MA] is a concentration of the resultant macromonomer at a given coupling time.

Table 2
Preparation of PHIC-MA macromonomers via an equilibrium polymerization technique

Polymer	Coupling			Depolymerization[a]				
	HIC (g)	Coupling time (day)	Polymer yield (%)	$10^{-3} M_n^{VPO}$[b]	f_c[c]		Polymer yield (%)	f_c[c] (%)
PHIC-MA/3	10.6	70	89.5	6.35	75.6		68.3	100
PHIC-MA/4	26.2	33	75.6	10.4	76.5		64.9	100

[a] A mixture of HIC monomer, the living PHIC, and PHIC-MA was first prepared. After the depolymerization was carried out at 50 °C for 2 days under high vacuum, PHIC-MA was isolated as precipitate when the resultant product was poured into methanol.
[b] Determined by VPO and GPC-LALLS using new analytical equations [22].
[c] Coupling efficiency determined by M_n^{VPO}/M_n^{NMR}.

3.2. Radical copolymerization of MMA with PHIC-MA macromonomer

Copolymerizations were carried out simultaneously in six ampules of Bz solution of MMA (10 w/v%), PHIC-MA/3 (10 w/v%) and AIBN (1.5×10^{-3} w/v%) to obtain the time conversion curve of PMMA-*graft*-PHIC. As shown in Fig. 2, the polymer yields increased with an increase of copolymerization time and then attained a certain value of 20% after 24 h. The molecular weights (M_n^{LALLS}) and PHIC weight fractions of PMMA-*graft*-PHIC ($w_{PHIC}^{copolymer}$) estimated from Eq. (3) were probably constant during the copolymerization time. These results suggest that the copolymerization did not proceed after 24 h due to the
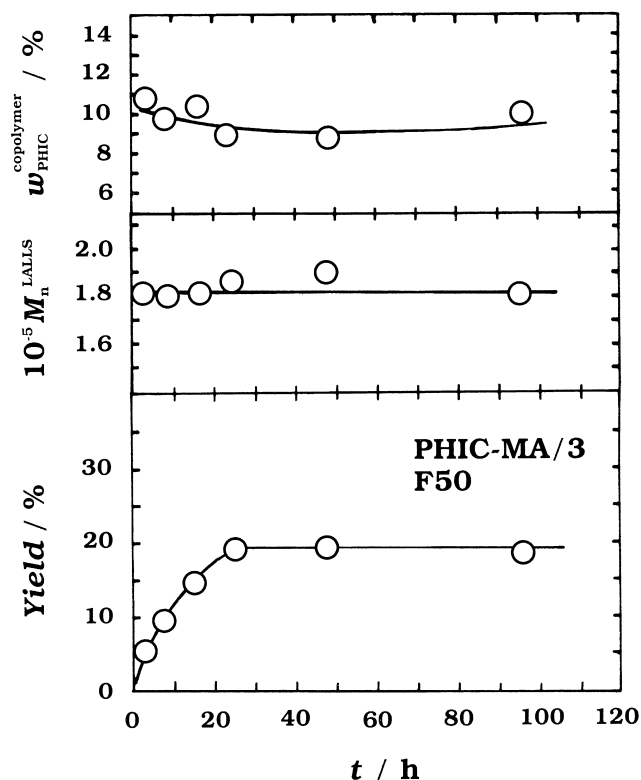
consumption of AIBN. Therefore, to obtain a plot of monomer feed (w_{PHIC}^{feed}) versus copolymer composition ($w_{PHIC}^{copolymer}$), the copolymerization of MMA with PHIC-MA was carried out in Bz (total concentration of $\sim$20 w/v%) at 60 °C for 24 h. The results are shown in Table 3. Although a mole fraction is used when plotting monomer feed against copolymer composition, a weight fraction is used in the present results because the mole fractions were too small for PHIC macromonomers. As shown in Fig. 3, the $w_{PHIC}^{copolymer}$ values of the resultant PMMA-*graft*-PHIC graft copolymers were less than 25 wt%, even with an 85 wt% PHIC-MA in the feed.

For binary copolymerization, which follows the terminal model, the instantaneous copolymer composition equation may be expressed as follows [23]

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \quad (4)$$

where M_1 is MMA and M_2 is PHIC-MA macromonomer. The well-known monomer–copolymer composition equation was linearized by Fineman and Ross as follows [24,25]

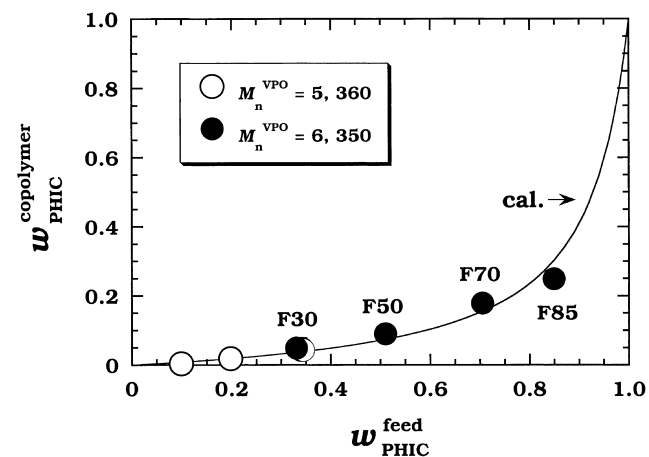$$F(f - 1)/f = (F^2/f)r_1 - r_2 \quad (5)$$

Fig. 2. Plots of the polymer yield, the molecular weight (M_n^{LALLS}) and the PHIC weight fraction ($w_{PHIC}^{copolymer}$) of the resultant PMMA-*graft*-PHIC versus the copolymerization time for copolymerization of MMA with PHIC-MA/3 in Bz at 60 °C under high vacuum.

Fig. 3. Plots of the PHIC feed (w_{PHIC}^{feed}) versus copolymer composition ($w_{PHIC}^{copolymer}$) described not using a mole fraction but using a weight fraction, and the calculated curve for copolymerization of MMA (M_1) with PHIC-MA/3 (M_2) in Bz ($r_1 = 11.5$ and $r_2 = 0$).

Table 3
Radical copolymerization (radical copolymerization was carried out in degassed glass ampules at 60 °C for 24 h) of MMA with PHIC-MA/3 and molecular characteristics of PMMA-*graft*-PHIC graft copolymers

Polymer	PHIC (g)	MMA (g)	w_{PHIC}^{feed} (%)	AIBN (mg)	Bz (g)	$10^{-4}M_k^a$	Yield (%)	$10^{-4}M_n^{PSt\,b}$	$10^{-4}M_n^{LALLS\,c}$	M_w^{LALLS}/M_n^{LALLS}	$w_{PHIC}^{copolymer}$ (%)	Number of grafts[d]
F0	0	0.24_6	0	0.022	0.97	$33._4$	$20._7$	$37._9$	$61._4$	2.0_1	0	0
F30	0.08_0	0.16_2	$33._1$	0.021	0.93	$23._8$	$17._3$	$16._9$	$24._2$	1.5_1	4.9_2	1.9
F50	0.13_4	0.12_9	$51._0$	0.019	0.98	$19._7$	$18._6$	$14._4$	$17._3$	1.6_8	9.0_6	2.5
F70	0.18_0	0.075_3	$70._5$	0.019	0.96	$11._9$	8.2_6	8.7_0	$11._3$	1.4_1	$17._9$	3.2
F85	0.23_6	0.042_1	$84._9$	0.019	0.96	6.9_0	3.8_9	4.3_2	4.6_8	1.5_1	$24._9$	1.8

[a] Kinetic molecular weights were calculated as follows: by an equation of radical polymerization using $P_k^{-1} = [k_p[M]/2(fk_dk_t[M])^{0.5}]^{-1} + C_S[S]/[M] + C_I[I]/[M] + C_M$ for a disproportionation model assuming $[M] = [M]_{MMA} + [M]_{PHIC}$, where all symbols are common meaning used in text books.

[b] PSt reduced molecular weights determined by the GPC measurement using a PSt calibration curve.

[c] Determined by GPC-LALLS using new analytical equations [22].

[d] The number of PHIC grafts per PMMA molecule was calculated by $M_n^{LALLS}w_{PHIC}^{copolymer}/M_n^{VPO}$ of PHIC-MA/3 (6350).

where

$$f = d[M_1]/d[M_2]; \qquad F = d[M_2]/[M_2] \qquad (6)$$

As shown in Fig. 4, graphical plotting of Eq. (5) gives a good straight line. The correlation coefficient between experiments and the graphical straight line is $R = 0.999$. The monomer reactivity ratios were evaluated as $r_1 = 11.5$ and $r_2 = \sim 0$. The PHIC-MA macromonomer showed a very low reactivity in radical copolymerization compared with that of MMA [26–28]. By using the resultant r_1 and r_2 values, a calculated curve was also plotted in Fig. 3. The calculated curve is in harmony with the experimental points.

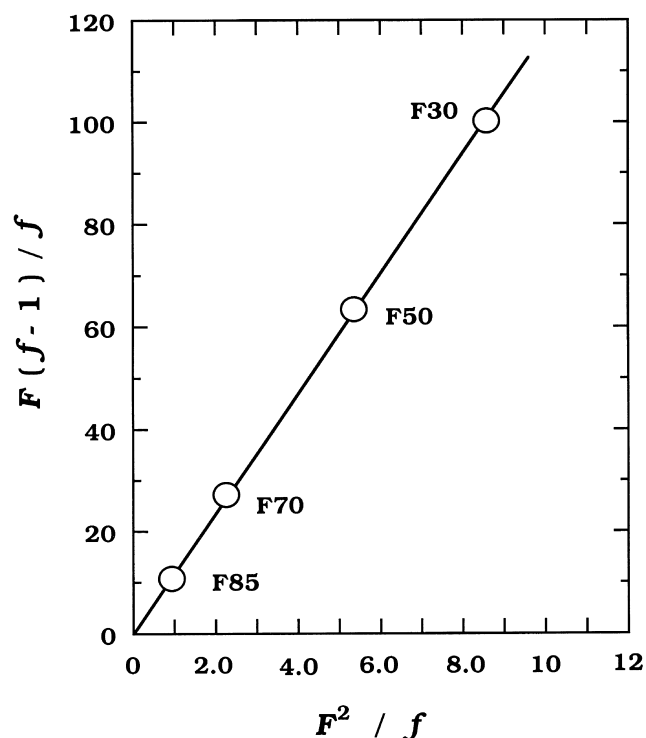The PHIC-MA/1 macromonomer with $M_n = 5360$ was

Fig. 4. Plots of $F(f-1)/f$ versus F^2/f for copolymerization of MMA with PHIC-MA/3. $r_1 = 11.5$ and $r_2 = 0$ (Fineman-Ross graphical method). Correlation coefficient $R = 0.999$.

also copolymerized with MMA under the same copolymerization condition as that of the PHIC-MA/3 macromonomer with $M_n = 6350$. The r_1 and r_2 values for $M_n = 5360$ were the same as those for $M_n = 6350$. Although the molecular weight dependence of r_1 and r_2 was not systematically studied in the present study, no difference in the r_1 and r_2 values between $M_n = 6350$ and $M_n = 5360$ was confirmed.

A NMR study of PHIC-MA suggests that a symmetrical displacement or rotation about the C–CO bond of the methacryl group of PHIC-MA can be performed above 70 °C [16]. We expect that the higher the copolymerization temperatures are, the higher the r_2 values are due to the lower steric hindrance of the *N,N*-di-substituted methacryl amide group of PHIC-MA. So, the copolymerization of MMA with PHIC-MA was also performed using di-*tert*-butyl peroxide as an initiator at 110 °C. The resultant r_1 and r_2 values were approximately the same as those for the copolymerization performed at 60 °C. The solvent effect of the copolymerization on the r_1 and r_2 values was not studied in the present paper.

GPC measurements were carried out to determine a distribution of w_i^{PHIC} for PMMA-*graft*-PHIC using Eq. (2). As shown in Fig. 5, for the samples having the lower PHIC contents (F30 and F50), the w_i^{PHIC} values are probably not correlated with the elution volume. In contrast, for the samples having the higher PHIC content (F85 and F 70), the w_i^{PHIC} values depend on the elution volume; namely, the PHIC rodlike chains might be difficult to introduce into the PMMA main chains having higher molecular weights. The reason for this may be bulkiness of the rodlike graft chains for the graft copolymer and/or a thermodynamic effect such as demixing of the PHIC macromonomers from the growing PMMA main chains. The latter effect shows strong molecular weight dependence [29], corresponding to that of w_i^{PHIC} observed in Fig. 5.

The absolute molecular weights of M_n^{LALLS} and M_w^{LALLS} of the resultant PMMA-*graft*-PHIC graft copolymers were determined using GPC-LALLS and new analytical equations we have presented elsewhere [22]. The $w_{PHIC}^{copolymer}$ values were estimated from Eq. (3). Therefore,

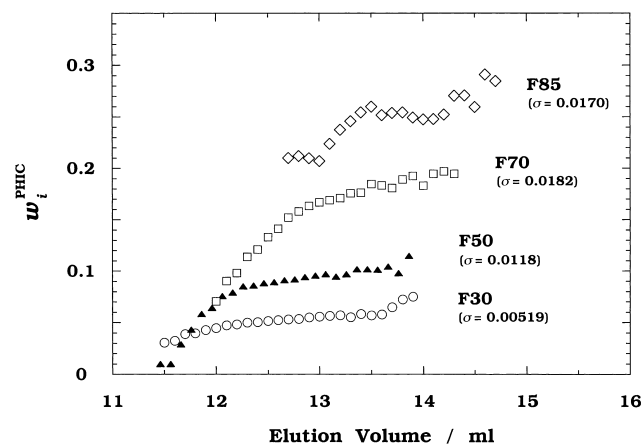Fig. 5. Distributions of the PHIC weight fraction (w_i^{PHIC}) of PMMA-*graft*-PHIC at the *i*th elution volume of the GPC chromatogram. The σ indicates the standard deviation of the w_i^{PHIC} for the corresponding samples.
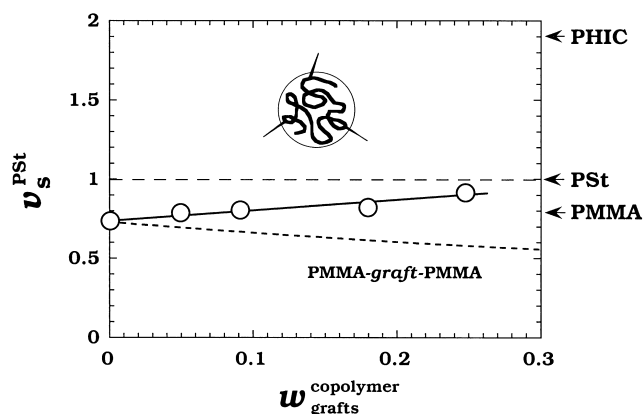

Fig. 6. Plots of v_s^{PSt} versus $w_{grafts}^{copolymer}$ for the PMMA-*graft*-PHIC graft copolymer. The observed v_s^{PSt} values of PHIC, PSt, and PMMA are indicated at a right side of the vertical axis. The calculated v_s^{PSt} curve of the PMMA-*graft*-PMMA graft copolymer using Eq. (8) is also plotted in the figure.

the number of PHIC grafts can be calculated as M_n^{LALLS} $w_{PHIC}^{copolymer}/M_n^{PHIC}$, where M_n^{PHIC} is the molecular weight of the PHIC macromonomer determined by VPO. There were 2–3 PHIC grafts per molecule in a graft copolymer. The methacryl group of PHIC-MA does not seem to be quantitatively polymerized due to steric hindrance of the *N*,*N*-di-substituted methacryl amide [19]. So as to increase the $w_{PHIC}^{copolymer}$ values and the number of PHIC grafts of PMMA-*graft*-PHIC, *N*,*N*-di-substituted acryl-terminated poly(*n*-hexyl isocyanate) macromonomers might be copolymerized with MMA. The coupling of living PHIC with acryloyl chloride, CH$_2$=CHCOCl, is in progress.

3.3. The specific dimensions of the PMMA-graft-PHIC graft copolymers

Attention should be directed to a unique molecular structure or a specific dimension of PMMA-*graft*-PHIC in THF. For this purpose, light scattering measurements using more than three different solvents must be performed [30, 31] to determine relationship between M_w and the radius of gyration ($\langle s^2 \rangle$) of PMMA-*graft*-PHIC. Though that study will be carried out in the future, a brief discussion of a specific dimension of PMMA-*graft*-PHIC in THF follows.

Polystyrene-reduced molecular weights (M_w^{PSt}) of the resultant PMMA-*graft*-PHIC graft copolymers were also determined by a common GPC technique. The M_w^{PSt} values of the graft copolymers correspond to the dimensions of the graft copolymers in THF as a result of the mechanism of the GPC measurements. Hence, the M_w^{LALLS}/M_w^{PSt} ratios might correspond to specific densities. Therefore, the specific volumes of the PMMA-*graft*-PHIC graft copolymers in THF (v_s^{PSt}) might be estimated simultaneously by GPC measurements as follows

$$v_s^{PSt} = (M_w^{LALLS}/M_w^{PSt})^{-1} \tag{7}$$

In the case of linear polystyrenes, linear PMMAs, and linear PHICs, the v_s^{PSt} values were estimated to be 1.0, 0.8, and 1.9, respectively. The higher value for the PHICs reflects the bulkiness of the rodlike polymer. In the case of simple graft copolymers, which consist of a PMMA main chain and PMMA graft chains, we can calculate the dependence of v_s^{PSt} on a weight fraction of grafts ($w_{grafts}^{copolymer}$) using the theoretical g values of the graft copolymers [32,33].

$$g = \frac{1 + 2fr + (2f + f^2)r^2 + (3f^2 - 2f)r^2}{(1 + fr)^3} \tag{8}$$

where *f* and *r* are the number of grafts and the molecular weight ratio of the grafts to the main chain, respectively. The molecular weights of the PMMA graft and PMMA-*graft*-PMMA are assumed to be equal to those of the PHIC graft and PMMA-*graft*-PHIC, respectively. The calculated curve of v_s^{PSt} for PMMA-*graft*-PMMA decreases with an increase in $w_{grafts}^{copolymer}$ and/or in the number of graft chains, as shown in Fig. 6. This finding represents a common behavior for the graft copolymers. The three linear polymers show no dependence of v_s^{PSt} on $w_{grafts}^{copolymer}$.

In contrast, PMMA-*graft*-PHIC with rodlike grafts shows an inverse dependence of v_s^{PSt} on $w_{grafts}^{copolymer}$, which is contrary to that of PMMA-*graft*-PMMA with flexible graft chains. In other words, v_s^{PSt} increases with an increase of $w_{grafts}^{copolymer}$. This is a remarkable feature of PMMA-*graft*-PHIC graft copolymer [34], which should show a behavior of the specific dimension that is the inverse of that of the common graft copolymers.

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