Synthesis of Graft Polymer^{*1} with Controlled Stereoregularities in the Main Chain and in the Side Chains by Stereospecific Copolymerization of Isotactic Poly(methyl methacrylate) Macromonomer with Methacrylate Monomer

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(Received May 11, 1995)

ABSTRACT: Highly isotactic poly(methyl methacrylate) (PMMA) macromonomer having methacryloyl group as a polymerizable function was synthesized from PMMA living anion prepared with *t*-C₄H₉MgBr in toluene at -78°C . Anionic copolymerizations of the PMMA macromonomer with methyl or ethyl methacrylate were carried out to obtain stereoregular graft polymers.^{*1} Copolymerizations by 1,1-diphenylhexyllithium in tetrahydrofuran at -78°C and by *t*-C₄H₉MgBr in toluene at -78°C gave graft polymers with syndiotactic and isotactic main chains, respectively, as confirmed by ¹³C NMR spectroscopy. Some of solution properties of the stereoregular graft polymers were investigated. The graft polymers with isotactic and syndiotactic PMMA chains were found to exhibit peculiar viscosity behavior due to stereocomplex formation.

KEY WORDS Macromonomer / Graft Polymer / Stereoregularity / Anionic Copolymerization / Methacrylate Monomer / Poly(methyl methacrylate) / NMR / End Group / Stereocomplex /

Recent advances of living polymerization have made it possible to prepare polymers with controlled structure, such as end-functional polymer, block polymer, graft polymer, star-like polymer and so on. Among them, macromonomer is one of the most attractive end-functional polymers derived from living polymers, and has been proved to provide an effective way for the structural control of branched polymers such as graft polymers and comblike polymers.^{1–13} Utilizing our findings of stereospecific living polymerizations of methacrylate,^{14,15} we have prepared stereoregular poly(methyl methacrylate) (PMMA) macromonomers having styrene-type group^{6–10,13}; polymerization and copolymerization of these macromonomers could be used without doubt to control the stereoregularity of side chains

in comblike and graft polymers. Recently, we reported the synthesis of syndiotactic (*st*-) PMMA macromonomer with methacryloyl group, anionic copolymerizations of which with low-molecular-weight methacrylate monomers afforded graft polymers with controlled stereoregularities both in the main chain and in the side chains.^{12,13} The reason why methacryloyl group was selected as a polymerizable function is that methacrylate is one of the few monomers whose stereospecific polymerizations have been well surveyed.^{16,17} In the present work, an isotactic (*it*-) PMMA macromonomer with the same chemical structure as the *st*-macromonomer was prepared and copolymerized anionically with methyl (MMA) or ethyl (EMA) methacrylate to obtain stereoregular graft polymers with

^{*1} In this paper, "graft polymer" is used to describe the products from copolymerization of macromonomer and comonomer, although some can be termed graft copolymer and some branched polymer. See ref 12.

it-PMMA side chains. Some of solution properties of the stereoregular graft polymers with *it*-PMMA side chains were investigated and compared with those of graft polymer with *st*-PMMA side chains reported in the previous papers.^{12,13}

EXPERIMENTAL

Materials

Monomers and solvents used were purified by the same manners described in the previous paper.¹² 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purified by distillation. The details for other reagents were described in the previous paper.¹²

Preparation of *it*-PMMA Macromonomer

Isotactic PMMA macromonomer having methacryloyl function was prepared from *it*-PMMA anion as shown in Scheme 1. The procedure for the preparation of *it*-PMMA macromonomer is almost the same as that of *st*-macromonomer.¹²

To *it*-PMMA living anions formed with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -78°C ,¹⁴ 10 equivalents of allyl iodide were added slowly at -78°C to obtain *it*-PMMA with allyl end group (*it*-PMMA- $\text{CH}_2\text{CH}=\text{CH}_2$). After 1 h, 5 equivalents of DBU in toluene were added to this mixture, and the reaction was continued for 24 h at -78°C and then for further 3 h at 0°C . The reaction mixture was poured into a large amount of hexane. The precipitated polymer was collected by filtration, washed successively with hexane, diluted aqueous HCl and water, and dried under vacuum at room temperature. The polymer was redissolved in benzene and recovered by freeze-drying after removing undissolved materials by centrifugation.

The *it*-PMMA macromonomer was synthesized by the reaction between *it*-PMMA having hydroxyl end group (*it*-PMMA- $\text{CH}_2\text{CH}_2\text{-CH}_2\text{OH}$), which was derived from the *it*-PMMA- $\text{CH}_2\text{CH}=\text{CH}_2$ through hydrobo-

ration with 9-borabicyclo[3.3.1]nonane (9-BBN), and methacryloyl chloride in the presence of pyridine (Scheme 1). The procedures for the syntheses of *it*-PMMA- $\text{CH}_2\text{CH}_2\text{-CH}_2\text{OH}$ and *it*-PMMA macromonomer were similar to those of *st*-one as described in the previous paper.¹²

Anionic Copolymerization of *it*-PMMA Macromonomer

The detailed procedures for copolymerizations of PMMA macromonomer with MMA or EMA were described in the previous paper.¹² The copolymerizations of *it*-PMMA macromonomer were carried out in glass ampoules filled with dry nitrogen. After a certain polymerization time, a small amount of methanol containing HCl (1 mol l^{-1}) was added to the polymerization mixture to quench the polymerization reaction. The solvent was removed under vacuum, the residue was dissolved in benzene and centrifuged to remove insoluble materials, and then the product mixture was recovered by freeze-drying.

The graft polymer was separated from unreacted *it*-PMMA macromonomer and *it*-PMMA without methacryloyl function by repeated reprecipitation in toluene-hexane or in chloroform-hexane mixtures.

Measurements

^1H NMR spectra of the polymers were recorded on a JNM GSX270 NMR spectrometer (JEOL) at 270 MHz. ^{13}C NMR spectra of the polymers were measured on the JNM GSX270 NMR spectrometer at 67.8 MHz.

Gel permeation chromatography (GPC) was performed on a JASCO 880-PU chromatograph equipped with Shodex GPC columns KF-80M (30 cm $\times$ 0.80 cm) and KF-802.5 (30 cm $\times$ 0.80 cm) with maximum porosities of 2×10^7 and 2×10^4 , respectively, using tetrahydrofuran (THF) as an eluent at 40°C . The chromatograms were calibrated with standard polystyrene samples, without taking the branching factor into account as first approx-

imation. GPC-low angle laser light scattering (GPC-LALLS) experiments were run on the GPC system equipped with a TOSOH LS-8000 light scattering photometer as a detector.

Differential scanning calorimetric (DSC) analysis was performed on a Rigaku DSC 8230 calorimeter at a heating rate of $10^{\circ}\text{C min}^{-1}$.

Solution viscosities of the polymers were measured in chloroform and in acetone at 35°C using an Ubbelohde type viscometer.

RESULTS AND DISCUSSION

Preparation of *it*-PMMA Macromonomer

The *it*-PMMA macromonomer with methacryloyl function was synthesized from *it*-PMMA living anion, which was prepared with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene,¹⁴ by three-step reactions shown in Scheme 1. The results are summarized in Tables I–III.

The living polymerization of MMA with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene has been utilized in order to obtain highly isotactic PMMA macromonomer with styrene-type end group.⁸ From the experience in the synthesis of *it*-PMMA macromonomer with styrene-type end group, DBU was used to facilitate the coupling reaction between the *it*-PMMA living anion and allyl iodide as described in the Experimental section. The result is summarized in Table I. The functionality of allyl end group was determined as 0.95 from the ^1H NMR spectroscopic analysis for the $t\text{-C}_4\text{H}_9$ and olefinic proton signals of *it*-PMMA- $\text{CH}_2\text{CH}=\text{CH}_2$. Number-average molecular weight ($\bar{M}_n$) could be determined from the ^1H NMR spectra

by comparing signal intensities of OCH_3 and $t\text{-C}_4\text{H}_9$ protons.

The results of the syntheses of *it*-PMMA- $\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ and *it*-PMMA macromonomer are shown in Tables II and III, respectively. The values of functionality and $\bar{M}_n$ of these two *it*-polymers were determined by the ^1H NMR spectroscopic analysis in a similar manner to that for the corresponding *st*-polymers described in the previous papers.^{12,13} The *it*-PMMA macromonomer with methacryloyl function having the same chemical structure as the *st*-PMMA macromonomer was obtained with a good functionality.

Anionic Copolymerization of *it*-PMMA Macromonomer

Anionic copolymerizations of the *it*-PMMA macromonomer with MMA or EMA were carried out in toluene with $t\text{-C}_4\text{H}_9\text{MgBr}$ and in THF by 1,1-diphenylhexyllithium (DPHLi)

Scheme 1. Preparation of *it*-PMMA macromonomer.

Table I. Preparation of *it*-PMMA with allyl end group^a

MMA	$t\text{-C}_4\text{H}_9\text{MgBr}$	Iodide ^b	DBU ^c	Yield	$\bar{M}_n^d$	$\bar{M}_w^e$	Tacticity ^d (%)			f^f
mmol	mmol	mmol	mmol	%		$\bar{M}_n$	<i>mm</i>	<i>mr</i>	<i>rr</i>	%
103	4.0	42.0	21.0	94	2910	1.11	94	3	3	95

^a Polymerization was carried out in toluene at -78°C for 24 h. ^b Allyl iodide. ^c Added as a toluene solution. ^d Determined by ^1H NMR spectroscopy. ^e Determined by GPC. ^f Functionality of allyl group determined by ^1H NMR spectroscopy.

Table II. Preparation of *it*-PMMA with hydroxyl end group

THF	97 ml
<i>it</i> -PMMA-CH ₂ -CH=CH ₂ ^a	9.71 g
Allyl end group	3.17 mmol
9-BBN ^b	31.7 mmol
NaOH ^c	32 mmol
H ₂ O ₂ ^d	96 mmol
Conversion of allyl end group ^e	95%
Functionality of hydroxyl end group ^e	90%
$\bar{M}_n^e$ (DP)	3070 (29.5)

^a $\bar{M}_n$ = 2910 (DP = 28.1); functionality = 0.95. ^b 0.5 M THF solution. ^c 3N aqueous solution. ^d 30% aqueous solution. ^e Determined by ¹H NMR spectroscopy.

Table III. Preparation of *it*-PMMA macromonomer

Toluene	45 ml
<i>it</i> -PMMA-CH ₂ CH ₂ CH ₂ -OH ^a	4.55 g
Hydroxyl end group	1.33 mmol
Pyridine	14.1 mmol
Methacryloyl chloride	7.0 mmol
Conversion of hydroxyl end group ^b	99%
Functionality of methacryloyl end group ^b	89%
$\bar{M}_n^b$ (DP)	3140 (29.5)

^a $\bar{M}_n$ = 3070 (DP = 29.5); functionality = 0.90. ^b Determined by ¹H NMR spectroscopy.

at -78°C . The results are shown in Table IV. The conversions of methacrylate comonomers were determined from the yield of the polymerization mixture, and found to be 100% in all the cases. The conversion of the macromonomer was determined from the ¹H NMR spectroscopic analysis of the polymerization mixture for the vinylidene proton signals of the methacryloyl group. The NMR analyses indicated that the conversions in the polymerization with *t*-C₄H₉MgBr in toluene did not reach 100%, while those in the polymerization with DPHLi in THF were 100%. These results mean that the rate of the polymerization was smaller for the copolymerization with *t*-C₄H₉MgBr in toluene than for that with DPHLi in THF, as observed for polymerizations of low-molecular-weight methacrylate. Such phenomena were observed in the copolymerization of *st*-PMMA macromonomer with MMA or EMA.¹²

In the copolymerization with MMA by *t*-C₄H₉MgBr in toluene, the conversion of *it*-PMMA macromonomer was 89% (polymerization time: 14 days) and that of *st*-PMMA macromonomer was 65% (polymerization time: 16 days),¹² while the conversions of MMA were 100% in both cases. We have reported that *it*-PMMA macromonomer with styrene-type end group showed higher reactivity than the corresponding *st*-PMMA macromonomer in radical polymerization and radical copoly-

Table IV. Anionic copolymerization of *it*-PMMA macromonomer (Mac.) with *t*-C₄H₉MgBr in toluene [A] and with DPHLi in THF [B] at -78°C for 14 days

Polymn condition	Mac.	Comonomer (mmol)	RMA	Initiator	Conversion/%	
	mmol		Mac.	mmol	Mac. ^a	RMA ^b
[A]	0.15 ^c	MMA (1.50)	9.90	0.083	89	100
[A]	0.12 ^c	EMA (1.14)	9.40	0.063	83	100
[B]	0.12 ^d	MMA (1.20)	10.0	0.066	100	100
[B]	0.11 ^d	EMA (1.23)	11.2	0.061	100	100

^a Determined by ¹H NMR spectroscopy. ^b Determined from the yield. ^c $\bar{M}_n$ = 3000, DP = 28.1, *mm*:*mr*:*rr* = 94:3:3, *f* = 0.84, [Mac.]₀ = 0.036 (mol l⁻¹). ^d $\bar{M}_n$ = 3140, DP = 29.5, *mm*:*mr*:*rr* = 94:3:3, *f* = 0.89, [Mac.]₀ = 0.035 (mol l⁻¹).

Figure 1. GPC chromatograms of the reaction mixture of the copolymerization of *it*-PMMA macromonomer with EMA by DPHLi in THF at -78°C (a) and the graft polymer fractionated therefrom (b).

erization with styrene,^{8,10,13} and in Ziegler polymerization.¹³ The higher reactivity of the *it*-macromonomer was ascribed to the higher segmental mobility of *it*-PMMA chain.¹⁸ The present result for the methacrylate-type PMMA macromonomers confirmed the higher reactivity of *it*-PMMA macromonomer than *st*-PMMA macromonomer, irrespective of the type of polymerizable function.

Figure 1a shows a GPC chromatogram for the polymerization mixture of the copolymerization of *it*-PMMA macromonomer and EMA with DPHLi in THF as an example. The GPC curve shows a shoulder, indicating that the polymerization mixture contained a low-molecular-weight fraction besides a graft polymer. Since the conversion of the macromonomer reached 100% as mentioned above, the low-molecular-weight fraction should not be the starting macromonomer. Therefore, the fraction should be PMMA without methacryloyl function and the product from the macromonomer reacted but failed to propagate further. The graft polymer was isolated from the mixture by repeated precipitation in

toluene–hexane mixture. The GPC curve of the graft polymer thus fractionated is shown in Figure 1b.

Other graft polymers except for that prepared with MMA by DPHLi in THF were isolated successfully by the same procedure. For the fractionation of the graft polymer prepared with MMA in THF, which was expected to comprise *st*-PMMA main chain and *it*-PMMA side chains as described later, chloroform–hexane mixture was used for repeated precipitation since stereocomplex formation between *it*- and *st*-PMMA segments¹⁹ may occur in toluene but not in chloroform. The stereocomplex formation of graft polymers with *it*- and *st*-PMMA segments obtained in the present work is discussed in the last section of this paper.

Characterization of the Resulting Graft Polymer

The graft polymers thus fractionated were characterized in detail by ^1H and ^{13}C NMR spectroscopy. The results are shown in Table V.

Figure 2 shows ^1H NMR spectra of the graft polymers prepared with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene, together with that of the *it*-PMMA macromonomer. The spectrum of the *it*-macromonomer showed vinylidene proton signals due to the methacryloyl unit at 5.40 and 5.99 ppm (Figure 2a). The spectra of the graft polymers (Figures 2b and 2c) did not show these peaks, indicating that the graft polymers isolated from the polymerization mixtures did not contain the starting macromonomer.

Qualitative Determination of Main-Chain Tacticity In the spectrum of the graft polymer with MMA main chain (Figure 2b), the signal patterns in the regions of $\alpha\text{-CH}_3$ and CH_2 protons are almost the same as those of the *it*-PMMA macromonomer (Figure 2a), indicating that the main-chain tacticity is isotactic. The spectral patterns for the graft polymer with EMA main chain (Figure 2c) are more complicated, since the signals due to $\alpha\text{-CH}_3$ and CH_2 protons of EMA units show different chemical shifts from those of MMA units in

Table V. Characteristics of graft polymers of *it*-PMMA macromonomer (Mac.) and methacrylate comonomer (RMA) prepared with *t*-C₄H₉MgBr in toluene [A] and with DPHLi in THF [B]

Polymn condition	RMA	RMA ^a		$\bar{M}_n$		$\bar{M}_w$ ^b		N_{br} ^c	Main chain ^d				Side chain ^f			
		Mac.	GPC	NMR	Calcd	$\bar{M}_n$	DP ^e		<i>mm</i>	<i>mr</i>	<i>rr</i>	DP ^e	<i>mm</i>	<i>mr</i>	<i>rr</i>	
[A]	MMA	13.1	15500	23600	6690	1.69	5.47	77.1	100	0	0	28.1	94	3	3	
[A]	EMA	8.90	32700	—	6860	4.37	8.13 ^b	80.6	92	8	0	28.1	94	3	3	
[B]	MMA	9.41	9180	12000	7770	1.30	2.89	30.1	3	19	78	29.5	94	3	3	
[B]	EMA	7.70	11700	14600	8200	1.69	3.57	77.1	6	23	71	29.5	94	3	3	

^aComposition of graft polymer. ^bDetermined by GPC. ^cDetermined by ¹H NMR spectroscopy. ^dMain-chain tacticity determined by ¹³C NMR spectroscopy. ^eDP (main chain) = $N_{br} \times (RMA/Mac.) + N_{br}$. ^fSide-chain tacticity is that of the *it*-macromonomer determined by ¹H NMR spectroscopy.

Figure 2. 270 MHz ¹H NMR spectra measured in nitrobenzene-*d*₅ at 110°C of *it*-PMMA macromonomer (a), and graft polymers of the *it*-PMMA macromonomer with MMA (b) and with EMA (c) prepared by *t*-C₄H₉MgBr in toluene at -78°C. [‡] ¹³C satellite signal of OCH₃ signal.

Figure 3. 270 MHz ^1H NMR spectra measured in nitrobenzene- d_5 at 110°C of graft polymers of *it*-PMMA macromonomer with MMA (a) and with EMA (b) prepared by DPHLi in THF at -78°C . $^{\#}$ ^{13}C satellite signal of OCH_3 signal. * Signals due to the remaining protons in nitrobenzene- d_5 .

the macromonomer units, and the signal of CH_3 protons of the ester group of EMA overlaps with the $\alpha\text{-CH}_3$ signals. However, the CH_2 proton region is almost devoid of signals due to *racemo* (*r*) sequence (*cf.*, Figure 3c), and the CH_2 signals due to EMA units are ascribable to isotactic sequence in the main chain. Thus, both the graft polymers prepared by $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene have isotactic main chains. These results are quite similar to those for the copolymerization of *st*-PMMA macromonomer by $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene.^{12,13}

Figure 3 shows ^1H NMR spectra of the graft polymers prepared with DPHLi in THF. The region of CH_2 protons in these spectra showed *racemo* methylene (CH_2 [*r*]) proton signals along with *meso* methylene (CH_2 [*m*]) proton signals due to the *it*-PMMA macromonomer units, indicating that the main-chain stereoregularities of the graft polymers prepared with DPHLi in THF are syndiotactic.

Quantitative determination of triad tacticity

ties*² of the graft polymers was made from quaternary carbon signals of their ^{13}C NMR spectra. The detailed procedure for the determination of main-chain tacticity will be described later.

Determination of Composition The compositions of the graft polymers with MMA main chain prepared with $t\text{-C}_4\text{H}_9\text{MgBr}$ and with DPHLi could be determined as 13.1 and 9.41, respectively, from the ^1H NMR (Figures 2b and 3a) signal intensities of OCH_2 (macromonomer), $[\text{OCH}_2]$, and OCH_3 (MMA and macromonomer), $[\text{OCH}_3]$, according to eq 1,

$$\text{MMA/macromonomer} = \frac{\{[\text{OCH}_3] - (1.5[\text{OCH}_2] \times \text{DP})\}}{1.5[\text{OCH}_2]} \quad (1)$$

where DP (degree of polymerization) is that of the *it*-PMMA branches which is assumed to be the same as that of the starting macromonomer. The term $(1.5[\text{OCH}_2] \times \text{DP})$ in the numerator corresponds to the contribution of the side-chain MMA units.

The compositions of the graft polymers with EMA main chain prepared with $t\text{-C}_4\text{H}_9\text{MgBr}$ and with DPHLi were determined as 8.90 and 7.70, respectively, from the ^1H NMR spectra (Figures 2c and 3b) by comparing signal intensities of OCH_2 (EMA and macromonomer) and OCH_3 (macromonomer) according to eq 2. It should be noted that OCH_2 proton resonances at 4.04 ppm are the overlap signals of the macromonomer unit (*cf.*, Figures 2b or 3a) and of EMA units. The contribution of the OCH_2 protons of EMA units could be estimated by subtracting the contribution of the macromonomer units ($[\text{OCH}_3]/\text{DP}$).

$$\text{EMA/macromonomer} = \frac{\{1.5[\text{OCH}_2] - ([\text{OCH}_3]/\text{DP})\}}{([\text{OCH}_3]/\text{DP})} \quad (2)$$

Determination of Number of Branches In

*² The main-chain tacticities of the graft polymers are cotacticities in a strict sense. However, the term, tacticity, is used in this paper for the simplicity.

order to determine the number of branches per molecule (N_{br}), the same procedures as in the case of the graft polymer of *st*-PMMA macromonomer^{12,13} were applied. The graft polymers formed with DPHLi should contain one 1,1-diphenylhexyl group at its initiating chain end as depicted in the following structural formula (3), since DPHLi is an efficient initiator for the living polymerization of methacrylate monomers in THF at low temperature.²⁰⁻²²

Thus, the N_{br} 's of the graft polymers formed with MMA and EMA could be determined as 2.89 and 3.57, respectively, directly from the peak intensities of the phenyl protons (6.95–7.25 ppm), [Phenyl], and *t*-C₄H₉ protons (0.82 ppm), [*t*-C₄H₉], (Figure 3), according to eq 4.

$$N_{br} = ([t\text{-C}_4\text{H}_9]/9)/([Phenyl]/10) \quad (4)$$

The same procedure could not be applied to the analysis of the graft polymers prepared with *t*-C₄H₉MgBr, since the initiating chain end of the main chain and the terminal of the side chain were both *t*-C₄H₉ group as shown below (5), which were indistinguishable in the ¹H NMR spectra (Figures 2b and 2c).

When the main chain comprises MMA units, however, the peak intensity of *t*-C₄H₉ at the side-chain end could be estimated from the peak intensity of OCH₂ protons of the macromonomer unit (*cf.*, Figure 2b). Thus, the intensity of *t*-C₄H₉ protons at the initiating chain end of the main chain could be estimated

by subtracting the contribution of the side-chain *t*-C₄H₉ group from the total *t*-C₄H₉ signals. The N_{br} was determined as 5.47 from the signal intensities of the *t*-C₄H₉, [*t*-C₄H₉], and OCH₂, [OCH₂], according to eq 6.

$$N_{br} = 4.5[OCH_2]/([t\text{-C}_4\text{H}_9] - 4.5[OCH_2]) \quad (6)$$

In the case of the graft polymer with EMA main chain, the OCH₂ signal of the macromonomer unit overlapped with OCH₂ signal of EMA unit (Figure 2c), and thus could not be used to estimate the contribution of *t*-C₄H₉ group at the side-chain end. Although the contribution of *t*-C₄H₉ group at the side-chain end could be estimated from the intensity of OCH₃ signal and the DP of the macromonomer according to eq 7, the N_{br} value estimated was affected strongly by even a small error in the estimation of the number of *t*-C₄H₉ groups of side-chain end.

$$[t\text{-C}_4\text{H}_9 \text{ (side chain)}] = 3[OCH_3]/(\text{DP of macromonomer}) \quad (7)$$

Therefore, the N_{br} of the graft polymer was estimated from the $\bar{M}_n$ determined by GPC and the composition as 8.13.

Determination of $\bar{M}_n$ From the values of the composition (C) and N_{br} of the graft polymers thus determined, $\bar{M}_n$'s of the graft polymers could be determined according to eq 8, except for the case of the graft polymer prepared with EMA by *t*-C₄H₉MgBr.

$$\begin{aligned} \bar{M}_n &= N_{br} \times (\bar{M}_n \text{ of macromonomer}) \\ &+ C \times N_{br} \times (MW \text{ of comonomer}) \\ &+ (MW \text{ of initiator fragment}) + 1 \end{aligned} \quad (8)$$

The $\bar{M}_n$ values estimated by GPC were slightly smaller than those determined by NMR according to eq 8. This result may be due to the smaller hydrodynamic volume of graft polymer as compared with the corresponding linear polymer.

Quantitative Determination of Main-Chain Tacticity The CH₂ proton signals in the ¹H NMR spectra shown in Figures 2 and 3 suggest

qualitatively that main-chain tacticity of the graft polymer prepared with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene was isotactic and that prepared with DPHLi in THF was predominantly syndiotactic.

For the quantitative determination of the tacticity, ^{13}C NMR spectra of the graft polymers were measured. Figure 4 shows ^{13}C NMR spectra of quaternary carbon of graft polymers prepared from the *it*-PMMA macromonomer with MMA, together with that of the *it*-PMMA macromonomer. Figure 4 clearly indicates that the main-chain tacticity of the graft polymer prepared with DPHLi in THF (Figure 4c) differs from that of the graft polymer prepared with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene (Figure 4b). The triad tacticities of the whole polymer could be determined from the quaternary carbon signals as shown in Figures 4b and 4c, and should be expressed as a sum of those of the main chain and side chain.

Figure 4. 67.8 MHz ^{13}C NMR spectra measured in chloroform- d at 55°C of quaternary carbons of *it*-PMMA macromonomer (a), and graft polymers of the *it*-PMMA macromonomer with MMA prepared by $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene (b) and by DPHLi in THF (c). * Signals due to quaternary carbons near the chain-ends.

$$mm = x_M mm_M + x_S mm_S \quad (9)$$

$$mr = x_M mr_M + x_S mr_S \quad (10)$$

$$rr = x_M rr_M + x_S rr_S \quad (11)$$

mm , mr , rr ; fractions of triad tacticity obtained from the quaternary carbon.

mm_M , mr_M , rr_M ; triad tacticities in the main chain.

mm_S , mr_S , rr_S ; triad tacticities in the side chains.

x_M , x_S ; mole fractions of methacrylate units in the main chain and in the side chains, respectively ($x_M + x_S = 1$).

The values of mm_S , mr_S , and rr_S should correspond to those of the starting macromonomer, and x_M and x_S can be derived from the composition of a given graft polymer and the DP of the macromonomer. The chemical shift ranges for mm , mr , and rr triad signals were assumed to be 45.55–45.90 ppm, 45.05–45.40 ppm, and 44.60–45.05 ppm, respectively. Four small peaks (44.97, 45.10, 45.19, and 46.00 ppm) commonly observed in the three spectra are ascribable to quaternary carbons near the chain ends of the macromonomer units. From the comparison with the spectrum of *it*-PMMA prepared with $t\text{-C}_4\text{H}_9\text{MgBr}$, the signal at 46.00 ppm is assigned to the quaternary carbon in the first MMA unit at the initiating chain end (α_1 unit).²³ Three other signals, which were observed in the signal regions for mr and rr triads overlapping with the signals of the graft polymer, were subtracted using the α_1 carbon signal as an intensity standard. Based on these data, the tacticity of the main chain can be calculated using eq 9, 10, and 11.

In the previous paper,^{12,13} the determination of graft polymers derived from *st*-PMMA macromonomer was carried out by using carbonyl carbons in the first and second MMA units from $t\text{-C}_4\text{H}_9$ chain end (α_1 and α_2 units)²³ of the starting *st*-PMMA macromonomer as an intensity standard. The corresponding signals of the *it*-PMMA macromonomer, however, were observed in mm and mr triad

regions with complicated splitting owing to lower stereoregularity at the initiating chain end than that at in-chain unit,²⁴ and thus not useful as an intensity standard. Therefore, the procedure using quaternary carbon signals mentioned above applied to the graft polymer derived from *it*-PMMA macromonomer.

The main-chain tacticities of the graft polymers with EMA main chain were also determined by the same procedure and summarized in Table V, where some of important structural characteristics of the graft polymers are also included. The main-chain tacticities of the graft polymers prepared with *t*-C₄H₉MgBr in toluene and with DPHLi in THF were isotactic and syndiotactic, respectively. Stereoregularities in the MMA and EMA sequences in the main chain were close to those for PMMA and poly(EMA), respectively, formed under the same conditions; PMMA¹⁴ *mm:mr:rr* = 96:4:0, poly(EMA)²⁵ *mm:mr:rr* = 97:3:0 [*t*-C₄H₉MgBr, toluene], PMMA¹² *mm:mr:rr* = 2:19:79, poly(EMA)¹² *mm:mr:rr* = 1:23:76 [DPHLi, THF]. In addition to the previous results,^{12,13} the present results confirm that stereospecific copolymerizations of PMMA macromonomers having methacryloyl function with methacrylate monomer are useful for the control of the main-chain stereoregularity of graft polymer.

The values of $\bar{M}_n$ and N_{br} of the graft polymers were larger than those expected from the feed ratios of the initiator and the total of the macromonomer and comonomer. These results mean that the initiator efficiencies are not 100%, probably due to the difficulty of complete removal of impurities in the starting macromonomer. The present results, however, display that the anionic synthesis of the graft polymer provides us a superior way to attain structural control of the graft polymer such as tacticity and end group. Since the chain-end structures of the graft polymers are well predictable, the end-group analysis by ¹H NMR spectroscopy provides the detailed information on the structure of the graft

polymers. For example, N_{br} value of the graft polymer prepared with DPHLi could be determined directly, which is more reliable than N_{br} value obtained by viscometry. Moreover, $\bar{M}_n$ of the graft polymer could also be determined from the N_{br} value and the composition.

From the present and previous^{12,13} studies, stereoregular graft polymers with well-defined structure are now obtainable in four kinds of combination of stereoregularity in the main chain/side chains; *it*-/ *it*-, *it*-/ *st*-, *st*-/ *it*-, and *st*-/ *st*-. These stereoregular branched polymers are useful for the investigation of the relationship between properties and stereoregularities of graft polymers.

Solution Property of the Stereoregular Graft Polymer

Solution properties of branched polymer are interesting subject by themselves. Moreover, PMMA segments of opposite stereoregularities are known to interact stereospecifically to form a stereocomplex,¹⁹ and thus solution properties of stereoregular graft PMMA are particularly interesting. Table VI summarizes the intrinsic viscosities ($[\eta]$) and Huggins' coefficients (k_H) of the stereoregular graft polymers of MMA, which were obtained in the previous^{12,13} and present works, measured in acetone (a complex-forming solvent) and in chloroform (a non-complexing solvent) at 35°C. The table also includes the values for linear *it*- and *st*-PMMA whose $\bar{M}_n$'s are close to those of the graft polymers with *it*-main chain and *it*-side chains (*it*-/ *it*-graft polymer) and with *st*-main chain and *st*-side chains (*st*-/ *st*-graft polymer), respectively, and the values for *it*-PMMA macromonomer and a mixture of *it*- and *st*-PMMA as references.

Branched polymer generally shows lower $[\eta]$ value than linear polymer of a similar molecular weight.²⁶ In the present case, however, the *it*-/ *it*-graft polymer showed $[\eta]$ values larger than those of the linear *it*-PMMA both in chloroform and in acetone. This is due

to the larger weight-average molecular weight ($\bar{M}_w$) of the graft polymer compared to that of the linear *it*-PMMA. The $\bar{M}_w$ values were determined by GPC-LALLS; 75400 for the graft polymer and 36900 for the linear *it*-PMMA. The values were used tentatively for the calculation of $[\eta]$ values based on a Mark-Houwink-Sakurada's equation for *it*-PMMA in acetone at 30°C, $[\eta] = K \cdot M_w^a$ [$K = 2.3 \times 10^{-4} (\text{dl g}^{-1})$, $a = 0.63$],²⁷ though the temperature of measurement is slightly different from the present case. The $[\eta]$ value estimated for the graft polymer is 0.272 and the observed value is 0.238. In the case of the linear *it*-PMMA, the $[\eta]$ value estimated from the equation is 0.173 and the observed value is 0.167. In spite of rough estimation, the agreement between the estimated and observed $[\eta]$ values for the linear *it*-PMMA suggests that the slightly negative deviation of the observed $[\eta]$ value for the graft polymer from the estimated value is meaningful. This may be ascribed to the branching effect.

The same estimation of $[\eta]$ values was made for the *st/st*-graft polymer and the linear *st*-PMMA. $\bar{M}_w$ values determined by GPC-LALLS are 41600 for the *st/st*-graft polymer and 30500 for the linear *st*-PMMA. A Mark-Houwink-Sakurada's equation for atactic PMMA in acetone at 30°C was used for the estimation; $[K = 0.77 \times 10^{-4} (\text{dl g}^{-1})$, $a = 0.70]$.²⁷ The results are as follows; for the *st/st*-graft polymer, the estimated $[\eta]$ value is 0.132 while the observed $[\eta]$ value was 0.086,^{12,13} and for the linear *st*-PMMA, the estimated $[\eta]$ value is 0.106 while the observed $[\eta]$ value is 0.118.^{12,13} Again the agreement for the linear *st*-PMMA between the estimated and observed $[\eta]$ values is good. The observed $[\eta]$ value for the *st/st*-graft polymer deviates negatively from the estimated $[\eta]$ value in a larger extent compared with the *it/it*-graft polymer. One of the possible reasons for the result is as follows. It has been reported that *st*-PMMA undergoes self-aggregation in certain solvents such as toluene.²⁸ If such an

aggregation of *st*-PMMA chains occurs in acetone, *st*-PMMA in acetone may exhibit a large k_H value exceeding the range usually observed.²⁶ In fact, both the *st/st*-graft polymer and the linear *st*-PMMA showed k_H values exceeding unity (1.57 and 1.35, respectively), suggesting the possibility of the self-aggregation in acetone. In the case of the *st/st*-graft polymer, the self-aggregation takes place not only intermolecularly but also intramolecularly. Such an intramolecular aggregation is possible even at infinite dilution, and should make the graft polymer molecules compact, thus leading to the decrease of $[\eta]$ value.

In the present results, the k_H values of the *it/it*- and *st/st*-graft polymers are almost the same as those of the linear *it*- and *st*-PMMA, respectively, both in chloroform and in acetone, while k_H values of comblike polymers (polymacromonomers) with *it*- and *st*-PMMA side chains have been reported to be larger than those of linear *it*- and *st*-PMMA, respectively.^{8,13} For further discussion on the influence of branching effect on k_H values in the case of the stereoregular graft polymers, graft polymers with a wider range degree of branching should be needed and now are being prepared.

In the previous paper,^{12,13} we reported that a graft polymer of MMA with *it*-main chain and *st*-side chains (*it/st*-graft polymer) formed a stereocomplex in solution and in the solid state through intermolecular and intramolecular interactions between its *it*- and *st*-PMMA chain segments.¹⁹ The intramolecular association in acetone may decrease the fraction of the chain segments available for the intermolecular association, enhancing the concentration dependence of the viscosity. In fact, the reduced viscosity of the graft polymer in acetone increased more remarkably than that of a mixture of *st*-PMMA macromonomer and *it*-PMMA and that of the *st/st*-graft polymer, as concentration increased, resulting in a large k_H value (4.99).^{12,13}

Table VI. Intrinsic viscosity $[\eta]$ and Huggins' coefficient (k_H) of the stereoregular graft polymers of MMA and PMMA measured in chloroform and in acetone at 35°C

Main chain (DP)	Side chain (DP)	N_{br}	$\bar{M}_n^a$	$\bar{M}_w$	Chloroform		Acetone	
				$\bar{M}_n$	$[\eta]$	k_H	$[\eta]$	k_H
<i>it</i> - (77.1)	<i>it</i> - (28.1)	5.47	23600	1.69	0.404	0.54	0.238	0.61
<i>st</i> - (30.1)	<i>it</i> - (29.5)	2.89	12000	1.30	0.108	0.83	0.075	1.36
<i>st</i> - ^b (198.6)	<i>it</i> - ^b (30.4)	4.02	32700	1.45	0.246	0.67	0.172	2.15
<i>st</i> - ^c (103.9)	<i>st</i> - ^c (32.1)	6.62	32500	1.35	0.139	0.86	0.086	1.57
<i>it</i> - ^c (61.0)	<i>st</i> - ^c (32.1)	2.45	14200	1.27	0.111	1.23	0.072	4.99
<i>it</i> -PMMA ^d			24270	1.18	0.252	0.61	0.167	0.78
<i>st</i> -PMMA ^{e,e}			22700	1.26	0.220	0.88	0.118	1.35
<i>it</i> -PMMA macromonomer ^f			3140	1.11	0.062	0.75	0.049	0.84
<i>st</i> -PMMA ^e + <i>it</i> -PMMA macromonomer ^f					0.158	0.58	0.079	1.38

^a Determined by ¹H NMR spectroscopy. ^b Synthesized by the copolymerization of *it*-PMMA macromonomer and MMA by DPHLi in THF ($[MMA]_0/[Mac]_0 = 30$). ^c See ref 12. ^d *mm*:*mr*:*rr* = 97:2:1. ^e $\bar{M}_n = 22700$; $\bar{M}_w/\bar{M}_n = 1.26$; *mm*:*mr*:*rr* = 0:11:89. ^f *mm*:*mr*:*rr* = 94:3:3.

A similar phenomenon is expected for the graft polymer with *st*-main chain and *it*-side chains (*st*-/*it*-graft polymer) obtained in this work. However, the *st*-/*it*-graft polymer whose DP of the main chain was 30.1 showed smaller k_H values not only in chloroform (0.83) but also in acetone (1.36) (Table VI). The results suggest the weaker interaction between *it*- and *st*-PMMA segments in this graft polymer in acetone compared with the case of the *it*-/*st*-graft polymer. In fact, a solid sample of this *st*-/*it*-graft polymer recovered from acetone solution did not show an endothermic peak due to the melting of stereocomplex in DSC measurement. These results indicate that this graft polymer could not form a stereocomplex.

On the other hand, an *st*-/*it*-graft polymer with a larger DP (198.6) formed a stereocomplex, which was confirmed by an endotherm at 154.7°C ($\Delta H = 7.37 \text{ cal g}^{-1}$) observed in the DSC measurement of the sample recovered from acetone solution. The k_H value of this *st*-/*it*-graft polymer in acetone (2.15) is

significantly larger than that in chloroform (0.67). The k_H value in acetone (2.15) is larger than that for the mixture of *it*-macromonomer and *st*-PMMA (1.38), in which a stereocomplex formation may take place only intermolecularly (Table VI). These results suggest that the intramolecular complex formation results in larger k_H value, since only a part of PMMA segments can be involved in intermolecular complexation, enhancing the concentration dependence of viscosity.

The k_H value of the *st*-/*it*-graft polymer in acetone (2.15) is smaller than that of the *it*-/*st*-graft polymer (4.99). The fact suggests the smaller degree of intramolecular stereocomplex formation in the *st*-/*it*-graft polymer. The phenomenon can be explained in the following manner. Challa and his coworkers proposed a double-stranded helix structure for PMMA stereocomplex, in which *it*-PMMA helical chain is surrounded by *st*-PMMA helix with a larger radius with the ester functions pointing outward from the double helix.²⁹ The mod-

el is consistent with our recent findings that a large variety of *st*-polymethacrylates form stereocomplexes with *it*-PMMA and that no *it*-polymethacrylates except *it*-PMMA form stereocomplex with *st*-PMMA.³⁰⁻³² If the double-stranded helix model is adopted for the intramolecular complex formation in the *st*-/*it*-graft polymer, the main-chain *st*-PMMA segment should surround *it*-PMMA side chains. Since the main-chain mobility is restricted more than the side chain mobility, the process of such an intramolecular complex formation should be much hindered than that of the corresponding intramolecular process for the *it*-/*st*-graft polymer. When the *st*-main-chain segment is short, particularly, the complex formation becomes almost impossible as described above. The present results indicate that geometrical arrangement of *it*- and *st*-PMMA segments in the graft polymers is an important factor for the intramolecular stereocomplex formation in stereoregular graft polymers.

The *it*-/*st*-graft polymer whose k_H value in acetone was the largest, showed a k_H value of 1.23 in chloroform, while k_H values of the other polymers were less than unity. Therefore, the *it*- and *st*-PMMA segments in the *it*-/*st*-graft polymer may interact stereospecifically even in chloroform. This indicates that a proper geometrical arrangement of *it*- and *st*-PMMA chains in graft polymer makes stereocomplex formation possible even in the solvent formally regarded as a non-complex forming solvent.

Stereospecific interactions of stereoregular chain segments arranged in stereoregular chain architecture such as graft polymers and comb-like polymers will be investigated in detail.

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