Control of Main-Chain Stereostructure of Graft Polymers* *via* Stereospecific Anionic Copolymerization of Syndiotactic Poly(methyl methacrylate) Macromonomer Having Methacryloyl Function with Methacrylate Monomers

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ABSTRACT: Highly syndiotactic PMMA macromonomer having methacryloyl group as a polymerizable function was prepared from the corresponding living PMMA anion formed with $t\text{-C}_4\text{H}_9\text{Li}/(n\text{-C}_4\text{H}_9)_3\text{Al}$ (1/3) in toluene at -78°C . Anionic copolymerization of the macromonomer with methyl (MMA) or ethyl methacrylate was carried out with anionic initiators. Copolymerization with 1,1-diphenylhexyllithium in tetrahydrofuran at -78°C gave graft polymers* with syndiotactic main chain in high yields. Copolymerization with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -78°C afforded graft polymers with highly isotactic main chain in good yields, although the molecular weight distributions were broad. The graft polymer with main-chain MMA units obtained in the latter system exhibited melting endotherm due to stereocomplex formation between isotactic main chain and syndiotactic side chains.

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

Many investigations have been reported on the preparation and polymerization of macromonomer aiming at the structural control of graft polymer and comb-like polymer.^{1–11} It has been well recognized that stereoregularity of polymer is one of the most important characteristics which affect polymer properties. However, little attention has been paid on the stereoregularity of the macromonomer itself and the polymer or copolymer obtained therefrom. We have reported the preparation

of isotactic (*it*-) and syndiotactic (*st*-) poly(methyl methacrylate) (PMMA) macromonomers with styrene-type end group, which give graft polymers and comb-like polymers with stereoregular PMMA branches.^{6–10} Recently, we have also reported the stereospecific anionic polymerization of polyisobutylene macromonomer having methacryloyl function, which afforded comb-like polymers with stereoregular main chain.¹¹ In this case the methacryloyl group was selected as a polymerizable function,

* In the IUPAC's definitions [Basic Definitions of Terms Relating to Polymer (1974), *Pure Appl. Chem.*, **40**, 477 (1974)], graft polymer and graft copolymer are defined in the different categories, structure-based and source-based, respectively. In the structure-based definition, graft polymer is defined as a polymer whose molecules have one or more species of block connected to the main chain as side chains, these side chains having constitutional or configurational features different from the constitutional units comprising the main chain, exclusive of junction points. The polymers dealt in this article are mostly graft polymers in this definition except for the polymer comprised of *st*-PMMA main chain and *st*-PMMA side chains, which should be called branched polymer. For avoiding the confusion, "graft polymer" is used in this paper to describe the products from copolymerization of macromonomer and MMA.

because many papers have been published on the stereospecific polymerization of methacrylates with various anionic initiators and a wide variety of stereoregular polymethacrylates can be obtained by selecting proper initiator and polymerization conditions.^{12,13}

The next research objective in this line will be the synthesis of graft polymer or comb-like polymer comprising stereoregular branches with high stereoregularity of the main chain. For the first step toward the objective, we attempted the synthesis of *st*-PMMA macromonomer having methacryloyl function and its copolymerization with low molecular weight methacrylate by anionic initiators to obtain the stereoregular graft polymers with controlled stereoregularities of the main chain as well as side chains.

EXPERIMENTAL

Materials

Toluene, purified in the usual manner, was mixed with a small amount of *n*-C₄H₉Li and distilled under vacuum. Tetrahydrofuran (THF), purified by distillation from calcium dihydride (CaH₂), was distilled again over lithium aluminium hydride and vacuum-distilled just before use. Methyl (MMA) and ethyl (EMA) methacrylates, allyl iodide, and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were purified by distillation and then distilled over CaH₂ under vacuum just before use. 9-Borabicyclo[3.3.1]nonane (9-BBN) was purchased as a THF solution and used as received. Pyridine was purified by distillation and dried over molecular sieves 4A (MS-4A). Methacryloyl chloride was synthesized from methacrylic acid and phosphorus trichloride. The methacryloyl chloride, purified by distillation, was dried over MS-4A at 0°C for 2 h and vacuum-distilled. *t*-C₄H₉Li and (*n*-C₄H₉)₃Al were obtained commercially and used as heptane solutions. *t*-C₄H₉MgBr was prepared from *t*-C₄H₉Br and Mg in diethyl ether.¹⁴ Diphenylhexyllithium (DPHLi) was synthe-

sized from 1,1-diphenylethylene and *n*-C₄H₉Li in THF.¹⁵⁻¹⁷

Preparation of *st*-PMMA Macromonomer

The *st*-PMMA macromonomer having methacryloyl function was prepared by three-step reactions from *st*-PMMA anion as shown Scheme 1.

(1) *Preparation of st-PMMA with Allyl End Group (st-PMMA-CH₂-CH=CH₂)* *st*-PMMA anion was obtained by the polymerization of MMA initiated with *t*-C₄H₉Li/(*n*-C₄H₉)₃Al (1/3)¹⁸ at -78°C in toluene. The polymerization was carried out in a glass ampoule filled with dry nitrogen. *t*-C₄H₉Li was added to a solution of (*n*-C₄H₉)₃Al in toluene cooled to -78°C. MMA was added slowly to the initiator mixture to initiate the polymerization reaction. After the completion of the polymerization, 10 equivalents of allyl iodide to the living anions were added to the polymerization mixture at -78°C with vigorous stirring. After 1 h TMEDA in toluene was added to this mixture and the reaction was continued at -78°C for 24 h and then at 0°C for further 3 h. The reaction mixture was centrifuged to remove insoluble materials and the supernatant was poured into a large amount of hexane. The precipitated polymer was collected by filtration, washed successively with hexane, diluted aqueous HCl, water and hexane, and dried under vacuum at

Scheme 1

40°C. The polymer obtained was redissolved in benzene and recovered from the benzene solution by freeze-drying after removing undissolved materials by centrifugation.

(2) *Preparation of *st*-PMMA with Hydroxyl End Group* (*st*-PMMA-(CH₂)₃-OH) To a THF solution of *st*-PMMA-CH₂-CH=CH₂, 9-BBN in THF (0.5 M) was added at room temperature under dry nitrogen. After 5 h aqueous NaOH (3 N) and aqueous H₂O₂ (30%) were added successively. Aqueous H₂O₂ was added carefully to the solution so that the temperature of the reaction mixture was kept below 30°C in order to prevent decomposition of H₂O₂. The mixture was stirred for 4 h at room temperature. After the completion of the reaction, toluene and K₂CO₃ were added to the mixture and the organic layer was separated and concentrated under reduced pressure. The remaining solution was poured into a large amount of hexane and the precipitated polymer was collected by filtration, washed successively with hexane, diluted aqueous HCl, water, and hexane, and dried *in vacuo* at 40°C.

(3) *Preparation of *st*-PMMA Macromonomer with Methacryloyl End Group* *st*-PMMA-(CH₂)₃-OH was dissolved in toluene under dry nitrogen. Methacryloyl chloride was added to the solution in the presence of pyridine at 0°C, and the reaction mixture was stirred for 4 h at room temperature. Then, the mixture was poured into a large amount of hexane. The precipitated polymer was collected by filtration, washed successively with hexane, diluted aqueous HCl solution, water and hexane, and dried under vacuum at room temperature.

Preparation of Graft Polymer

The copolymerizations of the macromonomer with MMA or EMA were carried out under dry nitrogen in glass ampoules. The macromonomer was dissolved in benzene and the solution was dried over CaH₂. The CaH₂ was removed by filtration using membrane filter made of Teflon under dry nitrogen, and

the macromonomer was recovered by freeze-drying. The macromonomer was redissolved in the polymerization solvent, and MMA or EMA was added to the solution. The polymerization was initiated by adding an initiator to the mixture at -78°C. After a certain polymerization time the reaction was quenched by adding a small amount of methanol containing acetic acid. The reaction mixture obtained with *t*-C₄H₉MgBr in toluene was dissolved in benzene after removing the polymerization solvent under vacuum. The mixture was recovered from the benzene solution by freeze-drying after removing a small amount of insoluble materials by centrifugation. The mixture obtained with DPHLi in THF was poured into a large amount of hexane. The precipitated polymer was collected by filtration, washed and dried under vacuum at 40°C.

To separate the graft polymer from the unreacted *st*-PMMA macromonomer the mixtures were redissolved in toluene or chloroform and certain amounts of hexane were added slowly to the solutions. The graft polymers precipitated were isolated from the remaining *st*-PMMA macromonomer by repeated reprecipitation.

Measurements

¹H NMR spectra of the polymers were recorded on a JNM GSX270 NMR spectrometer (JEOL) at 270 MHz or a JNM GX500 NMR spectrometer (JEOL) at 500 MHz. ¹³C 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 TRI ROTAR-V chromatograph equipped with Shodex GPC columns KF-80M (30 cm × 0.80 cm) and KF-802.5 (30 cm × 0.80 cm) with maximum porosities of 2 × 10⁷ and 2 × 10⁴, respectively, using THF as an eluent or on a JASCO TRI ROTAR-II^P chromatograph equipped with Shodex GPC columns K-806L (30 cm ×

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

MMA	Init. ^b	Iodide ^c	TMEDA ^d	Yield	$\bar{M}_n$		$\bar{M}_w/\bar{M}_n^f$	Tacticity ^e			f^g
					NMR ^e	Calcd		<i>mm</i>	<i>mr</i>	<i>rr</i>	
mmol	mmol	mmol	mmol	%							%
192	8.0	75.7	41.2	95	3310	2380	1.07	1	10	89	99

^a Solvent, toluene 200 ml; temperature, -78°C ; time, 24 h.^b Initiator: *t*-C₄H₉Li/(*n*-C₄H₉)₃Al = 1/3, *t*-C₄H₉Li 8.0 mmol.^c Allyl iodide.^d *N,N,N',N'*-Tetramethylethylenediamine was added as a toluene solution (4.02 mmol g⁻¹).^e Determined by ¹H NMR spectroscopy.^f Determined by GPC.^g Functionality of allyl group determined by ¹H NMR spectroscopy.

0.80 cm) $\times$ 2 with maximum porosity of 2×10^7 using chloroform as an eluent. The chromatograms were calibrated against standard polystyrene samples. Molecular weight of graft polymers determined based on the calibration with the linear polymer standards were used without taking the branching factor into account as the first approximation.

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

RESULTS AND DISCUSSION

Preparation of *st*-PMMA Macromonomer

st-PMMA macromonomer was prepared from *st*-PMMA living anion formed with *t*-C₄H₉Li/(*n*-C₄H₉)₃Al¹⁸ by three step reactions. The results of each reaction are summarized in Tables I—III.

(1) *Preparation of st-PMMA-CH₂-CH=CH₂* PMMA having allyl end group has been prepared by the reaction of allyl bromide and PMMA living anion formed in THF with DPHLi.¹⁵ Tacticity of the PMMA was predominantly syndiotactic but not so high. To obtain highly syndiotactic PMMA macromonomer, we utilized the living polymerization of MMA with *t*-C₄H₉Li/(*n*-C₄H₉)₃Al (1/3),¹⁸ which has been successfully applied to the preparation of styrene-type, highly syndiotactic PMMA macromonomer.⁸ Since the living *st*-PMMA anion is less reactive than that

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

THF	160 ml
<i>st</i> -PMMA-CH ₂ -CH=CH ₂	16.6 g
Allyl end group	5.0 mmol
9-BBN ^a	53 mmol
NaOH ^b	53 mmol
H ₂ O ₂ ^c	160 mmol
Yield	100%
Functionality of -OH ^d	96%

^a 0.5 M THF solution of 9-borabicyclo[3.3.1]nonane.^b 3 N aqueous solution.^c 30% aqueous solution.^d Determined by ¹H NMR spectroscopy.**Table III.** Preparation of *st*-PMMA macromonomer

Toluene	20 ml
<i>st</i> -PMMA-(CH ₂) ₃ -OH	2.00 g
Hydroxyl end group	0.58 mmol
Pyridine	6.2 mmol
Methacryloyl chloride	1.9 mmol
Yield	95%
Functionality of methacryloyl end group ^a	89%

^a Determined by ¹H NMR spectroscopy.

formed in THF with DPHLi, allyl iodide instead of allyl bromide was used as a source of the allyl end group. From the experience in the synthesis of the styrene-type PMMA macromonomer, TMEDA was also used to facilitate the coupling reaction between the living PMMA and allyl iodide. The details of

Figure 1. 270 MHz ^1H NMR spectra of *st*-PMMA- $\text{CH}_2\text{-CH=CH}_2$ (a and b), *st*-PMMA- $(\text{CH}_2)_3\text{-OH}$ (c), *st*-PMMA- $(\text{CH}_2)_3\text{-O-CONH-CO-CCl}_3$ (d), and *st*-PMMA macromonomer (e) measured in nitrobenzene- d_5 at 110°C . * ^{13}C satellite signal of OCH_3 signal.

* Signal due to the reaction product of trichloroacetyl isocyanate and 1,5-cyclooctanediol derived from 9-BBN.

the coupling reaction are described in the Experimental section. The results and the ^1H NMR spectra of *st*-PMMA- $\text{CH}_2\text{-CH=CH}_2$ are shown in Table I and Figures 1a and 1b, respectively. Number average molecular weight ($\bar{M}_n$) was determined from the intensity ratio of the signals due to the protons of *t*- C_4H_9 (0.82 ppm) and OCH_3 (3.61 ppm) (Figure 1a). The functionality of allyl end group was determined to be very close to unity from the intensity ratio of the signals due to *t*- C_4H_9 and olefinic protons in $-\text{CH}_2\text{-CH=CH}_2$ group ($-\text{CH=}$: 5.54–5.67 ppm, $=\text{CH}_2$: 4.92–4.98 ppm) (Figure 1b).

(2) Preparation of *st*-PMMA- $(\text{CH}_2)_3\text{-OH}$

st-PMMA- $(\text{CH}_2)_3\text{-OH}$ was prepared from *st*-PMMA- $\text{CH}_2\text{-CH=CH}_2$ through hydroboration with 9-BBN, and the results are summarized in Table II. Though the olefinic proton signals of $-\text{CH}_2\text{-CH=CH}_2$ disappeared completely in the ^1H NMR spectrum of the product as shown in Figure 1c, the functionality of hydroxyl end group could not be estimated from the spectrum. In order to determine the hydroxyl functionality, an excess amount of trichloroacetyl isocyanate was added to a nitrobenzene- d_5 solution of *st*-PMMA- $(\text{CH}_2)_3\text{-OH}$ in an NMR sample tube, which reacted with the hydroxyl group to form *st*-PMMA- $(\text{CH}_2)_3\text{-O-CONH-CO-CCl}_3$ immediately. The same method has been successfully utilized in the analysis of hydroxyl end groups of poly(ethylene oxide)¹⁹ and poly(propylene oxide)²⁰. In the ^1H NMR spectrum of *st*-PMMA- $(\text{CH}_2)_3\text{-O-CONH-CO-CCl}_3$ shown in Figure 1d, a new signal ascribable to the methylene protons of $-\text{CH}_2\text{-O-CONH-CO-CCl}_3$ was observed at 4.17 ppm. Another new signal appeared at 4.91 ppm was assigned to the reaction product of trichloroacetyl isocyanate and 1,5-cyclooctanediol derived from 9-BBN. The functionality of hydroxyl end group was determined to be 0.96 from the intensity ratio of the signals due to protons of *t*- C_4H_9 and $-\text{CH}_2\text{-O-CONH-CO-CCl}_3$ (Figure 1d).

(3) *Preparation of st-PMMA Macromonomer*
st-PMMA macromonomer was prepared from *st*-PMMA- $(\text{CH}_2)_3\text{-OH}$ and the results are shown in Table III. In the ^1H NMR spectrum of *st*-PMMA macromonomer, new signals ascribable to vinylidene protons of methacryloyl end group were observed at 5.40 ppm and 5.99 ppm (Figure 1e). The functionality of methacryloyl end group of the macromonomer was determined as 0.89 from the intensity ratio of the signals due to protons of *t*- C_4H_9 and the vinylidene group.

^{13}C NMR spectrum of the macromonomer showed the signals of the methacryloyl group as follows: $\text{CH}_2=$ 125.35, $=\text{C}$ 136.40, C=O

Table IV. Copolymerization of *st*-PMMA macromonomer (Mac) and methacrylate monomer (RMA) with DPHLi in THF at -78°C^a

Mac ^b	Comonomer	RMA	Init. ^c	Time	Conversion ^d		Yield ^e /%	
mmol	RMA (mmol)	Mac ^b	mmol	day	Mac ^b	RMA	Total	Graft polymer
0.13	MMA (1.60)	12.3	0.060	15.9	100	—	100	92
0.13	EMA (0.61)	5.1	0.058	11.8	100	100	100	71
0.13	EMA (1.40)	10.8	0.058	15.9	100	96	98	78

^a THF 4.0 ml.^b *st*-PMMA macromonomer: $\overline{\text{DP}} = 32.1$; $mm:mr:rr = 1:10:89$; $f = 0.89$.^c Initiator.^d Determined by ^1H NMR spectroscopy.^e Total, total yield of polymerization mixture; graft polymer, yield of fractionated graft polymer.

167.32 ppm. These values are close to the corresponding ones of MMA and EMA observed under the same conditions (CDCl_3 , 35°C), MMA; $\text{CH}_2 = 125.29$, $=\text{C}$ 136.28, $\text{C}=\text{O}$ 167.88 ppm, EMA; $\text{CH}_2 = 124.99$, $=\text{C}$ 136.60, $\text{C}=\text{O}$ 167.44 ppm.

Copolymerization of *st*-PMMA Macromonomer

Anionic copolymerization of *st*-PMMA macromonomer with MMA or EMA was carried out in THF with DPHLi at -78°C . The results are shown in Table IV. The reaction products were recovered by precipitation into hexane and thus might contain unreacted macromonomer. However, the ^1H NMR spectra of all the products did not show any peaks due to vinylidene protons of the macromonomer. The results mean that the conversions of the macromonomer are 100% in all the cases. The GPC chromatogram for the product from the copolymerization with EMA is shown in Figure 2a as an example. The chromatogram indicated the presence of low molecular weight fraction, which should not be the starting macromonomer itself but PMMA without methacryloyl function contained in the starting material and the product from the macromonomer reacted but failed to

Figure 2. GPC chromatograms of the reaction mixture of the copolymerization of *st*-PMMA macromonomer with EMA by DPHLi in THF at -78°C (a) and the graft polymer fractionated therefrom (b).

propagate further. The graft polymer was fractionated from the product by repeated precipitation in toluene–hexane mixtures. The GPC curve of the graft polymer shown in Figure 2b corresponds to that of the higher molecular weight fraction of the product mixture (Figure 2a).

The characteristics of the graft polymers are shown in Table V. The triad tacticities** of

** 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.

Table V. Characteristics of graft polymer of *st*-PMMA macromonomer (Mac) and methacrylate monomer (RMA) prepared with DPHLi in THF at -78°C

RMA	RMA/Mac ^a	$\bar{M}_n$		$\bar{M}_w/\bar{M}_n^b$	Tacticity ^c /%			Number of branch ^d
		GPC	NMR		<i>mm</i>	<i>mr</i>	<i>rr</i>	
MMA	14.7	26500	32500	1.35	0	22	78	6.62
EMA	2.8	21300	21900	1.34	0	14	86	5.82
EMA	8.9	27300	35100	1.39	0	12	88	7.89

^a Monomeric unit ratio of RMA and *st*-PMMA macromonomer in the graft polymer.^b Determined by GPC based on the calibration against linear polystyrene samples.^c Tacticity of the main chain determined by ^{13}C NMR spectroscopy.^d Determined by ^1H NMR spectroscopy. **Figure 3.** 500 MHz ^1H NMR spectra of the graft polymers of *st*-PMMA macromonomer with MMA (a) and with EMA (b) prepared by DPHLi in THF at -78°C measured in nitrobenzene- d_5 at 110°C .* Signals due to the remaining protons in nitrobenzene- d_5 .# ^{13}C satellite signal of OCH_3 signal.

the main chain were determined by ^{13}C NMR spectroscopy as described later. The composition of the graft polymer with EMA main chain could be determined from ^1H NMR spectrum (Figure 3b) from the comparison of peak intensities of OCH_2 (EMA) at 4.12 ppm and OCH_3 (macromonomer) at 3.61 ppm by assuming that the $\bar{M}_n$ of the PMMA branches in the graft polymer was the same as that of the starting macromonomer. It should be noted that OCH_2 protons of the macro-

monomer unit resonated at 4.04 ppm as observed in the ^1H NMR spectrum of the graft polymer with MMA main chain (Figure 3a) and thus partly overlapped with the OCH_2 protons of EMA unit. Therefore, the contribution of the methylene proton signals due to the macromonomer unit in the signals around 4.04 ppm was subtracted by taking the $\bar{DP}$ of the macromonomer into account.

In the case of the graft polymer prepared from the macromonomer and MMA, a similar analysis for the composition is difficult because MMA units in the main chain and those in the side chains are indistinguishable by ^1H NMR spectroscopy; OCH_3 signal observed is the superpose of the signals from both MMA units. However, as mentioned above, OCH_2 signal due to the macromonomer units could be observed separately from OCH_3 signal of MMA units, and the contribution of the side-chain MMA unit could be subtracted by assuming the $\bar{DP}$ of the *st*-PMMA branches to be equal to that of the starting macromonomer.

DPHLi is an efficient initiator for the living polymerization of methacrylate monomers in THF at low temperature.¹⁵⁻¹⁷ Thus the polymer formed with this initiator should contain one 1,1-diphenylhexyl group at its initiating chain end:

Thus the number of PMMA branches could be determined directly from the relative peak intensities of the phenyl protons (6.95–7.25 ppm) and *t*-C₄H₉ protons. The $\bar{M}_n$ of the graft polymer could be determined from the number of branch (N) and the composition ($C = [\text{RMA}]/[\text{macromonomer}]$);

$$\begin{aligned} \bar{M}_n = & N \times (\bar{M}_n \text{ of macromonomer}) \\ & + C \times N \times (\text{molecular weight of} \\ & \text{comonomer unit}) \\ & + (\text{molecular weight of initiator} \\ & \text{fragment}) + 1 \end{aligned}$$

The values shown in Table V are fairly consistent with $\bar{M}_n$ estimated by GPC, confirming the NMR analysis. The slightly smaller $\bar{M}_n$ values obtained from GPC analyses may be due to the smaller hydrodynamic volume of graft polymer as compared with the corresponding linear polymer.

Main-chain methylene proton regions in the

¹H NMR spectra of the graft polymers did not show *meso* methylene signals due to MMA or EMA units in the main chain, suggesting that the main-chain tacticity is predominantly syndiotactic. The quantitative data were obtained by ¹³C NMR spectroscopy as described later.

Anionic copolymerization of the macromonomer with MMA or EMA was carried out in toluene at –78°C using *t*-C₄H₉MgBr as an initiator (Table VI). Polymerization of MMA alone under the same conditions proceeds in a living manner to give highly isotactic PMMA.¹⁴ The conversions of the macromonomer were lower than those in the copolymerizations with DPHLi (Table IV), indicating that the rate of polymerization with respect to the macromonomer was smaller for the copolymerization with *t*-C₄H₉MgBr in toluene than for that with DPHLi in THF, as observed for the polymerizations of low molecular weight methacrylates such as MMA and EMA. The conversions of EMA were close to 100% in all the experiments, and it is not possible to discuss the reactivities of EMA in these copolymerizations. Molecular weight distributions (MWD's) of the graft polymers were bimodal and broader than those for the graft polymers prepared with DPHLi. The GPC curve of the reaction product from the

Table VI. Copolymerization of *st*-PMMA macromonomer (Mac) and methacrylate monomer (RMA) with *t*-C₄H₉MgBr in toluene at –78°C^a

Mac ^b	Comonomer	RMA	Init. ^c	Time	Conversion ^d /%		Yield ^e /%	
mmol	RMA (mmol)	Mac ^b	mmol	day	Mac ^b	RMA	Total	Graft polymer
0.13	MMA (1.40)	10.8	0.060	15.9	65	—	100	36 ^f , 26 ^g
0.13	EMA (0.70)	5.8	0.063	11.8	78	91	95	49
0.13	EMA (1.32)	10.0	0.058	15.9	83	98	100	67

^a Toluene 4.0 ml.

^b *st*-PMMA macromonomer: $\overline{\text{DP}} = 32.1$; *mm*:*mr*:*rr* = 1:10:89; *f* = 0.89.

^c Initiator.

^d Determined by ¹H NMR spectroscopy.

^e Total, total yield of polymerization mixture; graft polymer, yield of fractionated graft polymer.

^f The higher molecular weight fraction of the graft polymer (see Figure 4c).

^g The lower molecular weight fraction of the graft polymer (see Figure 4b).

copolymerization of the macromonomer with MMA is shown in Figure 4a as an example.

The reaction product of the macromonomer and MMA was soluble in chloroform but partly insoluble in toluene, in which stereo-complex formation between *it*- and *st*-PMMA takes place.²¹ The graft polymer was separated

Figure 4. GPC chromatograms of the reaction mixture of the copolymerization of *st*-PMMA macromonomer with MMA by *t*-C₄H₉MgBr in toluene at -78°C (a) and the lower (b) and the higher molecular weight fractions (c) of the graft polymer obtained therefrom.

from the product by repeated precipitation in chloroform-hexane mixtures, and was further fractionated into higher and lower molecular weight fractions as shown in Figures 4b and 4c. The compositions of these graft polymers were determined from their ¹H NMR spectra in a similar manner to those of the graft polymers formed with DPHLi. The compositions of the higher and lower molecular weight fractions were fairly close to each other as shown in Table VII.

The ¹H NMR spectrum of the fractionated graft polymer is shown in Figure 5a. The main-chain methylene proton region showed *meso* methylene signals along with *racemo* ones due to the macromonomer units, indicating that the tacticity of the main-chain MMA sequence was isotactic and the quantitative data for the tacticity were determined by ¹³C NMR spectroscopy to be highly isotactic as described later. The results suggest that there exist at least two types of active species which are different in reactivity but both highly isotactic-specific. A similar phenomenon has been observed for the copolymerization of MMA and EMA with *t*-C₄H₉MgBr in toluene at low temperature.²²

Since the *t*-C₄H₉ groups at the initiating

Table VII. Characteristics of graft polymer of *st*-PMMA macromonomer (Mac) and methacrylate monomer (RMA) prepared with *t*-C₄H₉MgBr in toluene

RMA	RMA/Mac ^a	$\bar{M}_n$		$\bar{M}_w/\bar{M}_n^b$	Tacticity ^c /%			Number of branch
		GPC	NMR		<i>mm</i>	<i>mr</i>	<i>rr</i>	
MMA ^d	22.2	77300 ^f	101800	2.63	99	1	0	18.1 ^h
MMA ^e	23.9	15300 ^f	14200	1.27	96	4	0	2.45 ^h
EMA	4.5	22000 ^g	—	2.10	84	11	5	5.74 ⁱ
EMA	9.1	41400 ^g	—	3.38	85	7	8	9.51 ⁱ

^a Monomeric unit ratio of RMA and *st*-PMMA macromonomer in the graft polymer.

^b Determined by GPC based on the calibration against linear polystyrene samples.

^c Tacticity of the main chain determined by ¹³C NMR spectroscopy.

^d The higher molecular weight fraction of the graft polymer (see Figure 4c).

^e The lower molecular weight fraction of the graft polymer (see Figure 4b).

^f Measured in chloroform.

^g Measured in THF.

^h Determined by ¹H NMR spectroscopy.

ⁱ Estimated from $\bar{M}_n$ determined by GPC and composition.

Figure 5. 270 MHz ^1H NMR spectra of the graft polymers of *st*-PMMA macromonomer with MMA (a) and with EMA (b) prepared by $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -78°C measured in nitrobenzene- d_5 at 110°C . (a) The lower molecular weight fraction of the graft polymer (see Figure 4b).

* ^{13}C satellite signal of OCH_3 signal.

* Signal due to incidentally introduced water.

chain end and the terminal of the branches did not show different ^1H NMR chemical shift, direct determination of number of branch in the graft polymer from end group analysis by NMR was difficult. However, the peak intensity for the $t\text{-C}_4\text{H}_9$ at the initiating chain end could be determined by subtracting the contribution from the $t\text{-C}_4\text{H}_9$ group at the branch ends, which was estimated from the peak intensity of OCH_2 protons of the macromonomer unit.

The obtained $\bar{M}_n$ values are shown in Table VII, which agree well with those estimated by GPC.

The graft polymer obtained from the copolymerization of *st*-PMMA macromonomer

with EMA by $t\text{-C}_4\text{H}_9\text{MgBr}$ was also separated from the reaction product by repeated precipitation from toluene–hexane mixtures. MWD's of the graft polymers were bimodal and much broader than those for the graft polymers prepared with DPHLi. The compositions were determined in the same way as the case of graft polymers prepared with DPHLi. For the determination of the number of branch, the ratio of $t\text{-C}_4\text{H}_9$ group at the initiation chain end to that of the macromonomer unit (branch end) should be estimated. However, since the OCH_2 signals due to the macromonomer unit overlapped with those of EMA unit as shown in Figure 5b, the peak intensity of the latter $t\text{-C}_4\text{H}_9$ group could not be determined from the intensity of the OCH_2 protons and should be estimated from the intensity of OCH_3 and the DP of the macromonomer. Even a small error in the estimation of the peak intensity of the branch-end $t\text{-C}_4\text{H}_9$ group results in a large error in the determination of the ratio of the two $t\text{-C}_4\text{H}_9$ groups. As the first approximation, therefore, the number of branch of the graft polymer was estimated based on the $\bar{M}_n$ determined by GPC and the composition (Table VII).

Stereoregularity of the Main Chain

From the methylene proton signals in the ^1H NMR spectra, main-chain stereoregularity of the graft polymers prepared with DPHLi and $t\text{-C}_4\text{H}_9\text{MgBr}$ were found to be syndiotactic and isotactic, respectively. For the quantitative determination of the tacticity, ^{13}C NMR spectra of the graft polymers were measured in chloroform- d at 55°C .

Figure 6 illustrates the carbonyl carbon spectra of the graft polymers prepared from *st*-PMMA macromonomer and MMA or EMA with DPHLi, along with those of the macromonomer and poly(EMA) prepared with DPHLi in THF at -78°C . Commonly observed signals in these spectra are mostly due to MMA units in the macromonomer chains. The spectrum of the graft polymer

Figure 6. 67.8 MHz ^{13}C NMR spectra of carbonyl carbons of *st*-PMMA macromonomer (a), the graft polymers with MMA (b) and with EMA (c) prepared with DPHLi in THF at -78°C , and poly(EMA) (d) prepared under the same conditions. The spectra were measured in chloroform-*d* at 55°C .

* The signal was not observed in the spectrum of *st*-PMMA²³ and is probably due to the ω end unit,

with EMA main chain (Figure 6c) showed new peaks ascribable to heterotactic (176.7 ppm) and syndiotactic (177.4 ppm) sequences of EMA units. Comparing the spectrum of the graft polymer (Figure 6c) with that of poly(EMA) (Figure 6d), the signals due to EMA-centered syndiotactic and heterotactic sequences are expected to be observed in the shift ranges shown in Figure 6c. The signals due to isotactic sequence were not observed in the spectrum because of the lower content of isotactic sequence, but are expected to be

Figure 7. 67.8 MHz ^{13}C NMR spectra of carbonyl carbons of *st*-PMMA macromonomer (a), and the graft polymers with MMA (b) and with EMA (c) prepared with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -78°C measured in chloroform-*d* at 55°C . (b) The lower molecular weight fraction (see Figure 4b).

* The signal was not observed in the spectrum of *st*-PMMA²³ and is probably due to the ω end unit,

observed at 175.9–176.5 ppm (see Figure 7c). The signals due to the carbonyl carbons of the methacrylate units derived from the methacryloyl function at the end of the macromonomer are also expected to exhibit similar tactic splitting to those of MMA and EMA units, although they were not distinguishable in the spectrum. Anyway, the signals of carbonyl carbons consisted of those from three types of monomer units, that is, MMA units in the side chains, EMA units and the methacryloyl units of the macromonomer in the main chain. Macromonomer units in the graft polymer are mostly flanked by EMA units on both sides. Since the chemical shift difference in tactic triads is usually larger than that in triad monomer sequences,¹⁸ it is assumed that carbonyl carbon signals due to the main-chain methacrylate units of the

macromonomer are observed in the same chemical shift ranges as those of MMA and EMA units. In the determination of the main-chain tacticity, the chemical shift ranges for *mm*, *mr*, and *rr* triads for all the three types of monomer units are assumed to be 175.85–176.50 ppm, 176.50–177.20 ppm, and 177.20–178.10 ppm, respectively (Figure 6c). The chemical shift ranges for *mr* triad (*mr*(EMA) + *mr*(MMA)) partly overlaps with that for *mm* triad of MMA units (*mm*(MMA)) (Figure 7b). Since the signal due to *mm* triad of MMA units was not observed in the spectrum of the macromonomer (Figure 6a), the estimation of signal intensity of *mr* triad was not interfered by the overlapping. An average tacticity of the main chain was determined by subtraction of the signals due to MMA units in the macromonomer chains as follows. The sharp resonance at 178.2 ppm observed in the spectrum of the macromonomer (Figure 6a) can be assigned to the carbonyl carbons in the first and second MMA units at the initiating chain end (α_1 and α_2 units).²³ The same signal observed in the spectra of the graft polymers was used as an intensity standard for the estimation of the contributions of the macromonomer unit signals. The quantitative condition was fulfilled, since the $\overline{DP}$ (32.2) of the macromonomer estimated from signal intensities of the α_1 and α_2 carbonyl carbons relative to those of all the carbonyl carbons agreed well with that determined from the ^1H NMR spectrum (32.1). The possibility that the signal due to EMA units overlaps with the α_1 and α_2 signal was ruled out by the fact that no peak was observed at 178.2 ppm in the spectrum of carbonyl carbons of poly(EMA) prepared with DPHLi in THF (Figure 6d). Thus, the signal at 178.2 ppm was assumed to be derived from only the α_1 and α_2 carbonyl carbons of the macromonomer chains. The same procedure was made in the estimation for the main-chain tacticities of the other graft polymers described later. Tacticities thus determined are

shown in Table V.

In the spectrum of the graft polymer with main-chain MMA units, signals from the main-chain MMA units should overlap with those from MMA units of the macromonomer chains. The main-chain tacticity was determined by the same method as mentioned above, based on the assumption that the chemical shift ranges for *mm*, *mr*, and *rr* triads are 176.10–176.65 ppm, 176.65–177.25 ppm, and 177.40–178.10 ppm, respectively. Tacticity thus determined is shown in Table V.

The main-chain tacticities of all the graft polymers were predominantly syndiotactic. Tacticities of PMMA and poly(EMA) formed under the same conditions were as follows; PMMA, *mm*:*mr*:*rr* = 2:19:79, and poly(EMA), *mm*:*mr*:*rr* = 1:23:76. The syndiotacticities of the graft polymers with EMA main-chain units were higher than that of poly(EMA). The higher syndiotacticities for the graft polymers might be caused by the steric effect of the macromonomer chain. However, the considerable overlap between the signals from main-chain units should make it difficult to discuss the differences in tacticity due to the low precision of the values of tacticities.

In the ^{13}C NMR spectra of the graft polymers formed with *t*-C₄H₉MgBr in toluene (Figure 7), the new peaks ascribable to MMA or EMA units in isotactic main chain were observed (Figures 7b and 7c). The tacticities were estimated by the same method as described previously and found to be highly isotactic as shown in Table VII. In the determination of the main-chain tacticities of the graft polymers, the chemical shift ranges for *mm*, *mr*, and *rr* triads for all the monomer units are assumed to be the same ranges as those for the graft polymers formed with DPHLi (the graft polymer with EMA main chain, *mm*: 175.85–176.50 ppm, *mr*: 176.50–177.20 ppm, *rr*: 177.20–178.10 ppm; the graft polymer with MMA main chain, *mm*: 176.10–176.65 ppm, *mr*: 176.65–177.25 ppm, *rr*:

Table VIII. Intrinsic viscosity and Huggins' coefficient (k_H) of the graft polymers of MMA and PMMA measured in chloroform or acetone at 35°C

Polymer	Number of branch	$\overline{DP}$ of main chain	Chloroform		Acetone	
			$[\eta]/\text{dl} \cdot \text{g}^{-1}$	k_H	$[\eta]/\text{dl} \cdot \text{g}^{-1}$	k_H
<i>st</i> -Graft polymer ^a	6.62	103.9	0.139	0.86	0.086	1.57
<i>it</i> -Graft polymer ^b	2.45	61.0	0.111	1.23	0.072	4.99
<i>st</i> -PMMA ^c		226.1	0.220	0.88	0.118	1.35
<i>it</i> -PMMA ^d + <i>st</i> -Macromonomer ^e (42:58)			0.070	1.23	0.057	1.82
<i>st</i> -Macromonomer ^e		32.1	0.055	1.25	0.040	1.48

^a The graft polymer prepared with DPHLi in THF (see Table V).

^b The lower molecular weight fraction of the graft polymer prepared with *t*-C₄H₉MgBr in toluene (see Table VII and Figure 4b).

^c *st*-PMMA ($\overline{M}_n = 22700$; $\overline{M}_w/\overline{M}_n = 1.26$; *mm:mr:rr* = 0:11:89).

^d *it*-PMMA ($\overline{M}_n = 5370$; $\overline{M}_w/\overline{M}_n = 1.10$; *mm:mr:rr* = 97:2:1).

^e *st*-PMMA macromonomer ($\overline{M}_n = 3400$; $\overline{M}_w/\overline{M}_n = 1.07$; *mm:mr:rr* = 1:10:89).

177.40—178.10 ppm).

The main-chain tacticities of the graft polymer with main-chain MMA units were close to those of PMMA obtained under the same conditions (*mm:mr:rr* = 96:4:0).¹⁴ The tacticities for the graft polymer with main-chain EMA units were a little different from those of poly(EMA) formed under the same conditions (*mm:mr:rr* = 97:3:0).²² This is partly due to the higher content of macromonomer unit in the chain, which may decrease isotacticity of the EMA sequence. Thus the anionic copolymerization of *st*-PMMA macromonomer and methacrylate monomers could give the graft polymers with controlled main-chain stereoregularities with highly stereoregular side chains.

It should be noted that the graft polymer obtained from the macromonomer and MMA with *t*-C₄H₉MgBr comprises of the main chain and the side chains with opposite stereoregularities, namely, isotactic main chain with syndiotactic side chains. As described previously, the higher molecular weight fraction of the graft polymer was insoluble in toluene at room temperature, suggesting that the polymer formed the stereocomplex. The solid polymer showed endothermic peak in DSC thermogram due to the melting of the stereo-

complex (141.5°C), melting point of which was lower than that of stereocomplex formed between linear *it*- and *st*-PMMA with similar $\overline{M}_n$'s. The lower molecular weight fraction, however, was soluble in toluene and in acetone, which is also known as a complex forming solvent, probably due to short isotactic sequence in the main chain.

Characteristics of Stereoregular Graft Polymers

Some of the solution properties of the stereoregular graft polymers of MMA were examined. Table VIII summarizes the intrinsic viscosities $[\eta]$'s and the Huggins' coefficients k_H 's of the graft polymers in chloroform and in acetone. Graft polymer with syndiotactic main chain (*st*-graft polymer) showed lower viscosity than linear *st*-PMMA of a similar $\overline{M}_n$ as commonly observed for branched polymers.²⁴ The k_H 's for these *st*-polymers did not differ significantly. We reported that homopolymers of *it*- and *st*-PMMA macromonomers exhibited larger k_H values than the corresponding linear PMMA's.⁸ The smaller difference of k_H values in the present case may be due to the smaller branching density than the polymacromonomers.

While the different numbers of branch per chain and the different $\overline{M}_n$'s do not allow

direct comparison of $[\eta]$'s between graft polymer with isotactic main chain (*it*-graft polymer) and the *st*-graft polymer, k_H values for these graft polymers are apparently different, especially in acetone. The large k_H of the *it*-graft polymer (4.99), or strong dependence of reduced viscosity on concentration (the range of the concentration; 0.25—1.00 g dl⁻¹), suggests the possibility of association of the polymer in acetone. Absolute peak intensities in the ¹H NMR spectrum of the graft polymer in acetone-*d*₆ (1 w/v%) at 35°C was 61% of the expected value and thus indicated that 39% of the polymer did not show the signals due to association, that is, stereocomplex formation. Viscosity and ¹H NMR measurements of a mixture of *it*-PMMA of $\overline{DP}$ = 53.1 and the *st*-PMMA macromonomer as a reference sample for the *it*-graft polymer were carried out under the same conditions. The mixture also exhibited large k_H (1.82) and diminished ¹H NMR signal intensity in acetone-*d*₆ (68% of the theoretical value). The degree of association in acetone at 35°C as observed from ¹H NMR intensity was not so different between the mixture and the *it*-graft polymer. However, the k_H value for the latter was almost three times as large as that for the former, though the k_H values exceeded the range usually observed. The *it*-graft polymer may undergo, at least in part, intramolecular association between isotactic main chain and *st*-PMMA branch, and thus exist as shrunken particles. This might be one of the reasons for the large k_H value, since spherical particles in solution usually exhibit large k_H values, that is, strong concentration dependence of reduced viscosity (η_{sp}/c).²⁴ Intermolecular association due to the complex formation should become significant as the concentration increases. The intermolecular association in the *it*-graft polymer may be weakened by the occurrence of the intramolecular association. Such a weak association is expected to be sensitive to concentration and thus cause further enhancement of concentration dependence of η_{sp}/c , *i.e.*, larger k_H .

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