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PREPARATION OF STAR-SHAPED POLYMER WITH STEREOREGULAR POLY(METHYL METHACRYLATE) ARMS

Koichi Hatada^{ab}; Tatsuki Kitayama^b; Nobutaka Fujimoto^b; Tetsuya Fukuoka^b; Osamu Nakagawa^b; Takafumi Nishiura^b

^a Fukui University of Technology, Fukui-shi, Fukui, Japan ^b Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

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Koichi Hatada,* Tatsuki Kitayama, Nobutaka Fujimoto,
Tetsuya Fukuoka, Osamu Nakagawa, and Takafumi Nishiura

Department of Chemistry, Graduate School of Engineering
Science, Osaka University, Toyonaka,
Osaka 560-8531, Japan

ABSTRACT

Isotactic (*it*-) PMMA anions prepared with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene were reacted with ethylene glycol dimethacrylate (EGDMA) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to obtain a star shaped polymer. ^1H NMR, SEC-LALLS and SEC-differential viscometric analyses of the polymer clearly indicated that the polymer is a highly branched star polymer with crosslinked dimethacrylate core; the number of arms was estimated to be 20–30. A similar reaction of syndiotactic (*st*-) PMMA anions formed with $t\text{-C}_4\text{H}_9\text{Li}-(n\text{-C}_4\text{H}_9)_3\text{Al}$ in toluene with EGDMA was unsuccessful. However, the use of butane-1,4-diol dimethacrylate instead of EGDMA resulted in the effective formation of star polymers having *st*-PMMA arms; the number of arms was estimated to be 139. As a result, two types of star-shaped polymethacrylates with *it*- and *st*-PMMA arms were obtained.

Key Words: Star-shaped polymer; Stereoregular polymer; Anionic polymerization; Dimethacrylate; Methacrylate; NMR; SEC

*Corresponding author. Current address: Fukui University of Technology, 3-6-1 Gakuen Fukui-shi, Fukui, Japan.

INTRODUCTION

Star polymers are of interest partly because of their unique solution properties, such as lower solution viscosity than the corresponding linear polymers,^[1] and partly because of material applications, such as reinforcement materials for urethane elastomers^[2] or crosslinking agents for thermoplastic elastomer.^[3] Among various methods applicable to the preparation of star polymers,^[4,5] reactions of living polymers with divinyl monomers such as divinylbenzene and ethylene glycol dimethacrylate (EGDMA) are particularly important to afford star polymers having large number of arms as compared with coupling reaction of living polymers with multifunctional terminators such as chlorosilanes. The former method gives star-shaped polymers with linear arms radiating out from a highly crosslinked core formed by the crosslinking reaction involving a divinyl compound. Although the number of arms is not controllable with certainty, the length of the arms can be controlled through the living polymerization processes that produce the arm precursors. Recently, a number of works in this line have been reported, in which group transfer, anionic and radical polymerizations are used to produce living polymers for arm precursors, and dimethacrylates are used as the core-forming monomers.^[6–16]

Properties of polymethacrylates depend strongly on their tacticity and thus, it is important to control the stereoregularity of arms in methacrylate star polymers. We have reported two systems of highly stereospecific living polymerizations of methyl methacrylate (MMA); one with *t*-C₄H₉MgBr in toluene at low temperatures giving highly isotactic (*it*-) poly(methyl methacrylate) (PMMA)^[17] and the other with *t*-C₄H₉Li-R₃Al (R; C₂H₅, *n*-C₄H₉, *n*-C₈H₁₇) in toluene at low temperatures giving highly syndiotactic (*st*-) PMMA.^[18]

This report describes the first successful synthesis of star polymers with stereoregular PMMA arms by using the *it*- and *st*-PMMA living anions as the precursor polymers for star arms and ethylene glycol dimethacrylate (EGDMA) or butane-1,4-diol dimethacrylate (BDDMA) as a core-forming monomer. Some of the properties of the stereoregular star polymers are also described.

EXPERIMENTAL

Materials

Monomers and solvents were of commercial source and purified as described in the previous publications.^[17,18] *t*-C₄H₉Li (Aldrich) was obtained commercially as a hexane solution and used as a heptane solution through solvent exchange under vacuum. (*n*-C₄H₉)₃Al (Nippon Alkyl Aluminum Co.)

was used as a heptane solution. $t\text{-C}_4\text{H}_9\text{MgBr}$ in diethyl ether was prepared as described in the previous report.^[17] 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (Aldrich) was dried over CaH_2 , distilled under vacuum, and used as a toluene solution.

Polymerization

Polymerization were carried out in glass ampoules filled with dried nitrogen. Procedures for the synthesis of star polymers with stereoregular PMMA arms are as follows. In the first stage, *it*- and *st*-PMMA living anions were prepared in toluene with $t\text{-C}_4\text{H}_9\text{MgBr}$ at -60°C and with $t\text{-C}_4\text{H}_9\text{Li}-(n\text{-C}_4\text{H}_9)_3\text{Al}$ ($\text{Li}/\text{Al} = 1/3$ mol/mol) at -78°C , respectively. After the completion of the first-stage polymerization, EGDMA or BDDMA, and, in some cases, polar additives, such as DBU and 1,4-dioxane, were added successively to the PMMA living anions at -78°C . The reaction was terminated by adding methanol containing HCl at -78°C . The reaction mixture was poured into a large amount of hexane to precipitate the polymeric product. The precipitate was collected by filtration, washed successively with hexane, dilute HCl and water, and dried under vacuum at 30°C .

Measurement

^1H NMR spectra of the polymers were taken in CDCl_3 at 55°C and in nitrobenzene- d_5 at 110°C on a JNM-GSX270 NMR spectrometer at 270 MHz.

Molecular weights were determined on a JASCO 880-PU chromatograph equipped with Shodex SEC columns of KF-80M and KF-802.5 ($30\text{ cm} \times 0.80\text{ cm}$ i.d.) with maximum porosities of 2×10^7 and 2×10^4 , respectively, using tetrahydrofuran (THF) as an eluent. The chromatograms were calibrated against standard polystyrene samples.

Using Tosoh LS-8000 low angle laser light scattering (LALLS) detector together with a refractive index (RI) detector, weight average molecular weights (\bar{M}_w) of star-polymers were determined by SEC-LALLS method, according to the following equation:

$$S(\text{LALLS})/S(\text{RI}) = A \times K \times \bar{M}_w \quad (1)$$

where $S(\text{LALLS})$ and $S(\text{RI})$ were areas of chromatograms detected by LALLS and RI detectors, respectively, K the detector response constant, which was determined by using a standard polystyrene sample ($\bar{M}_n = 110,000$, $\bar{M}_w/\bar{M}_n = 1.06$), A the correction coefficient, which is the

ratio of refractive index increments (dn/dc) of the star polymer to that of the standard polystyrene sample ($A = 0.477$, $dn/dc(\text{polystyrene}) = 0.181 \text{ mL/g}$, $dn/dc(\text{PMMA star polymer}) = 0.086 \text{ mL/g}$). The dn/dc value of for the star polymer was obtained by extrapolating the values of the dn/dc measured at 436 and 546 nm by differential refractometer to that at 633 nm.

Number average molecular weights (\bar{M}_n 's) of star polymers were obtained from SEC-LALLS data using the equations shown below:

$$\bar{M}_n = 1/\Sigma(W_i/M_i) \quad (2)$$

$$W_i = h_i(\text{RI})/\Sigma h_i(\text{RI}) \quad (3)$$

$$M_i = [h_i(\text{LALLS})/h_i(\text{RI})]/(A \times K) \quad (4)$$

where h_i represents the height of the chromatogram at elution time i .

Differential scanning calorimetry (DSC) analysis was performed on a Rigaku DSC 8230 calorimeter under nitrogen flow (100 mL/min) with a heating rate of 10°C/min. The weight of the sample was about 10 mg.

Intrinsic viscosity $[\eta]$ was measured in THF at 40°C, using an Ubbelohde viscometer. A VISCOTEK differential viscometer model 110-02 was used as an SEC detector in some cases.

RESULTS AND DISCUSSION

Star Polymer with Isotactic PMMA Arms

Synthesis of star polymer with *it*-PMMA arms was attempted by using *it*-PMMA living anion and EGDMA as a crosslinking and core-forming monomer. Isotactic PMMA living anion with an approximate degree of polymerization (DP) of 50 was prepared by the polymerization of MMA with *t*-C₄H₉MgBr in toluene at -60°C.^[17] To the living polymer solution was added EGDMA in various amounts ($[\text{EGDMA}]/[t\text{-C}_4\text{H}_9\text{MgBr}] = 0\text{--}10 \text{ mol/mol}$) and the reaction was continued at -78°C for a further 168 h. (Table 1). All the products were soluble in good solvents for PMMA such as toluene and chloroform. Conversions of EGDMA were estimated from the total yield by assuming that the conversion of MMA in the first stage of polymerization was quantitative. SEC curves of the products were always bimodal and the \bar{M}_n of the higher molecular weight fraction increased with an increase of the amount of EGDMA added, indicating that crosslinking of *it*-PMMA chains through the reaction with EGDMA occurred to some extent. However, even with 10 equivalents of EGDMA to the initiator, molecular weight of the high molecular weight fraction of the product was not high enough for the corresponding SEC peak to be observed separately from

Table 1. Synthesis of Star Polymer from *it*-PMMA Living Anion^a and Ethylene Glycol Dimethacrylate (EGDMA) in the Absence or Presence of Polar Additives in Toluene at -78°C for 168 h^b

EGDMA (mmol)		Conversion of EGDMA (%) ^c	\bar{M}^d	\bar{M}_w/\bar{M}_n^d
0	–	–	5,880	1.12
0.2	–	100	15,600	1.81
0.7	–	44	15,900	1.78
1.0	–	40	23,800	1.71
1.4	–	95	26,100	1.55
2.0	–	56	26,100	1.55
1.4	DBU	82	35,860	4.45
1.4	THF	68	34,170	2.62
1.4	Dioxane	59	41,650	5.27

^aPrepared by polymerizing MMA (10 mmol) with *t*-C₄H₉MgBr (0.20 mmol, [Mg]/[*t*-C₄H₉]=1.50) in toluene at -60°C for 24 h. Tacticity of the PMMA; *mm:mr:rr* = 96:3:1.

^b[EGDMA] 2.0 mmol, [additive]/[Mg] = 3 mol/mol.

^cConversion of EGDMA was calculated from the total yield by assuming the yield of PMMA in the first-stage of polymerization to be 100%.

that of the starting *it*-PMMA (Figs. 1A and 1B). This may be due to the lower reactivity of the propagating anions of PMMA or EGDMA against pendant methacrylate groups of the EGDMA unit in the chain.

Homopolymerization of EGDMA with *t*-C₄H₉MgBr in toluene at -78°C proceeded rather slowly (15% yield for the polymerization at $[M]_0/[I]_0 = 50$ for 48 h) to give soluble poly(EGDMA) which retained most of the pendant methacrylate units unreacted.^[19] These results indicate that the insufficient crosslinking in the reaction of *it*-PMMA anion and EGDMA is due to the low reactivity of the EGDMA anion, and that the higher molecular weight product forms by the reaction of the PMMA anion to the pendant methacrylate groups of the EGDMA units. Thus once all the PMMA anions were transformed to EGDMA anions, further crosslinking reaction may scarcely occur.

Therefore, activation of the living polymer anions is necessary for the formation of high molecular weight star polymers. Reaction of EGDMA with *it*-PMMA living anions was attempted in the presence of several polar additives (Table 1). All of the SEC curves of the reaction products consisted of high and low molecular weight peaks (Figs. 1C–1E). The low molecular weight fraction kept its elution time the same as that of the *it*-PMMA obtained in the control experiment (see Fig. 1A). Among the additives examined, DBU was the most effective one for the formation of high molecular weight star polymer, whose SEC peak was observed well-separated from that of the low molecular weight peak (Fig. 1E). The amount of the

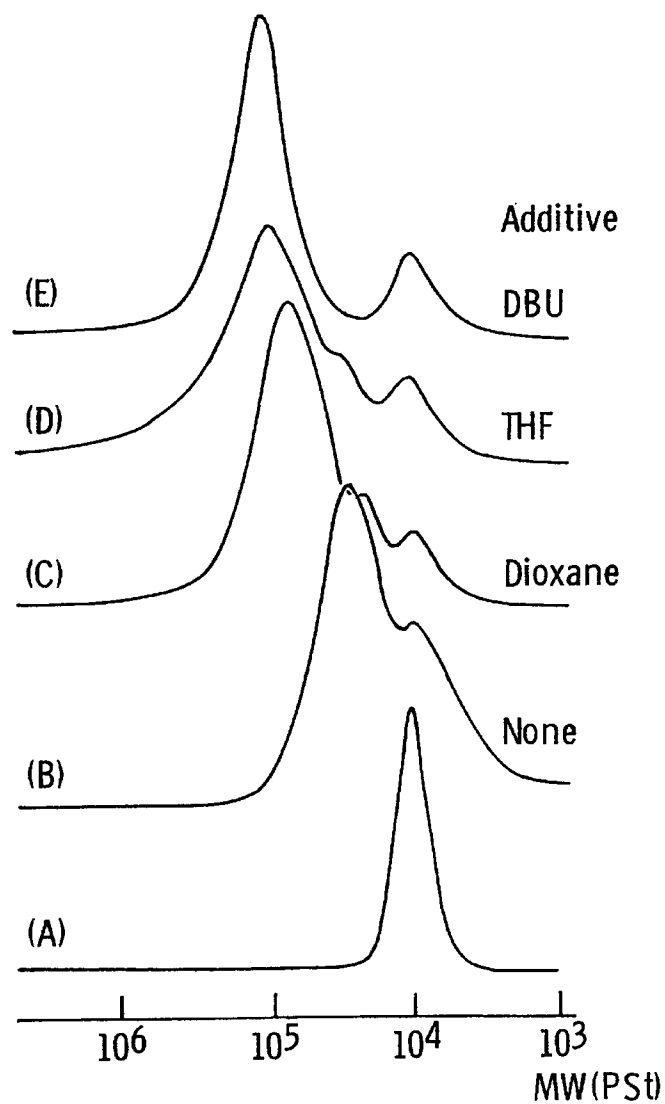


Figure 1. SEC curves of *it*-PMMA (A) and the reaction products of EGDMA and *it*-PMMA anion formed with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -78°C in the absence (B) and the presence of polar additives (C, D and E) (MMA 10 mmol, $t\text{-C}_4\text{H}_9\text{MgBr}$ 0.2 mmol, EGDMA 1.4 mmol).

high molecular weight fraction and its molecular weight increased as the molar ratio of EGDMA to $t\text{-C}_4\text{H}_9\text{MgBr}$ increased at least in the range of 1 to 10 (Fig. 2).

A reaction product formed at the $[\text{EGDMA}]/[t\text{-C}_4\text{H}_9\text{MgBr}]/[\text{MMA}]$ ratio of 2/0.2/10 was fractionated into high and low molecular weight fractions, whose ^1H NMR spectra are shown in Fig. 3. The high molecular weight fraction showed the small broad signals due to the vinylidene and

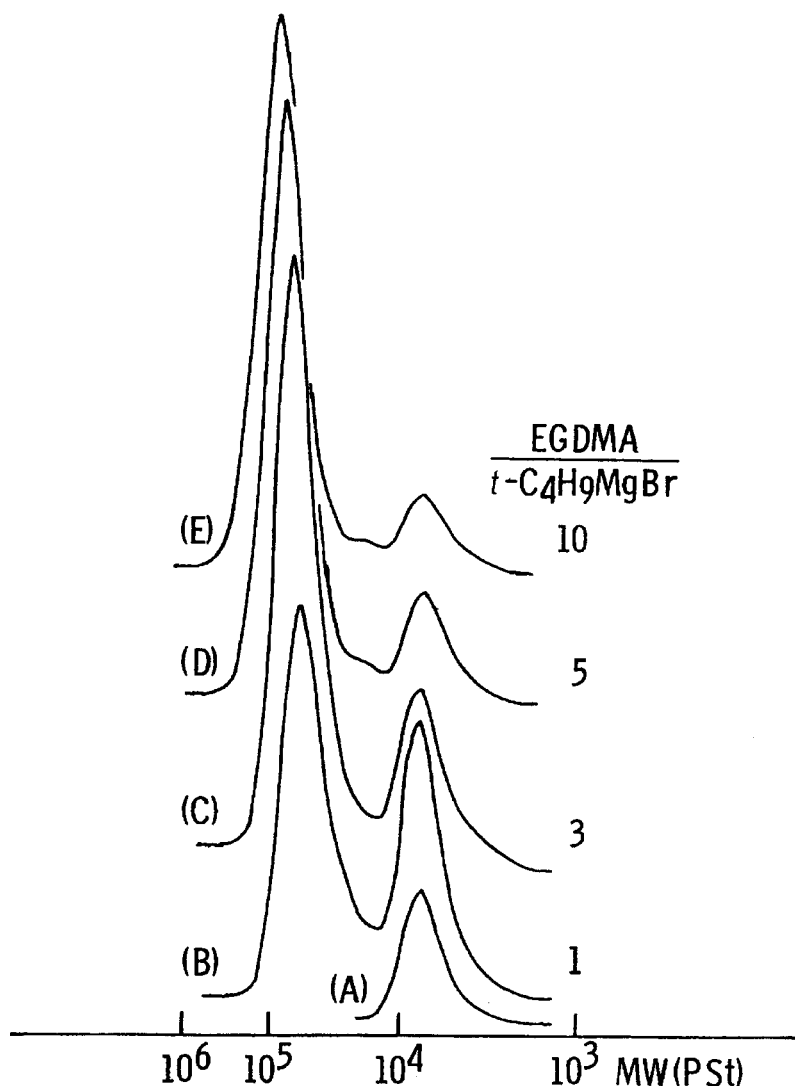


Figure 2. SEC curves of *it*-PMMA (A) and the reaction products of EGDMA and *it*-PMMA anion formed with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -78°C in the presence of DBU (B, C, D, and E) (MMA 10 mmol. $t\text{-C}_4\text{H}_9\text{MgBr}$ 0.2 mmol).

oxymethylene protons in the pendant methacrylate units, while the low molecular weight fraction did not. The results clearly indicate that the star polymer prepared by this method contained unreacted methacrylate units in the core, and that the low molecular weight fraction consisted of *it*-PMMA exclusively. The lower fraction should be deactivated through end cyclization of *it*-PMMA anion, since the fraction showed a singlet signal at 0.96 ppm assignable to $\alpha\text{-CH}_3$ group in the cyclic terminal group (* in the caption

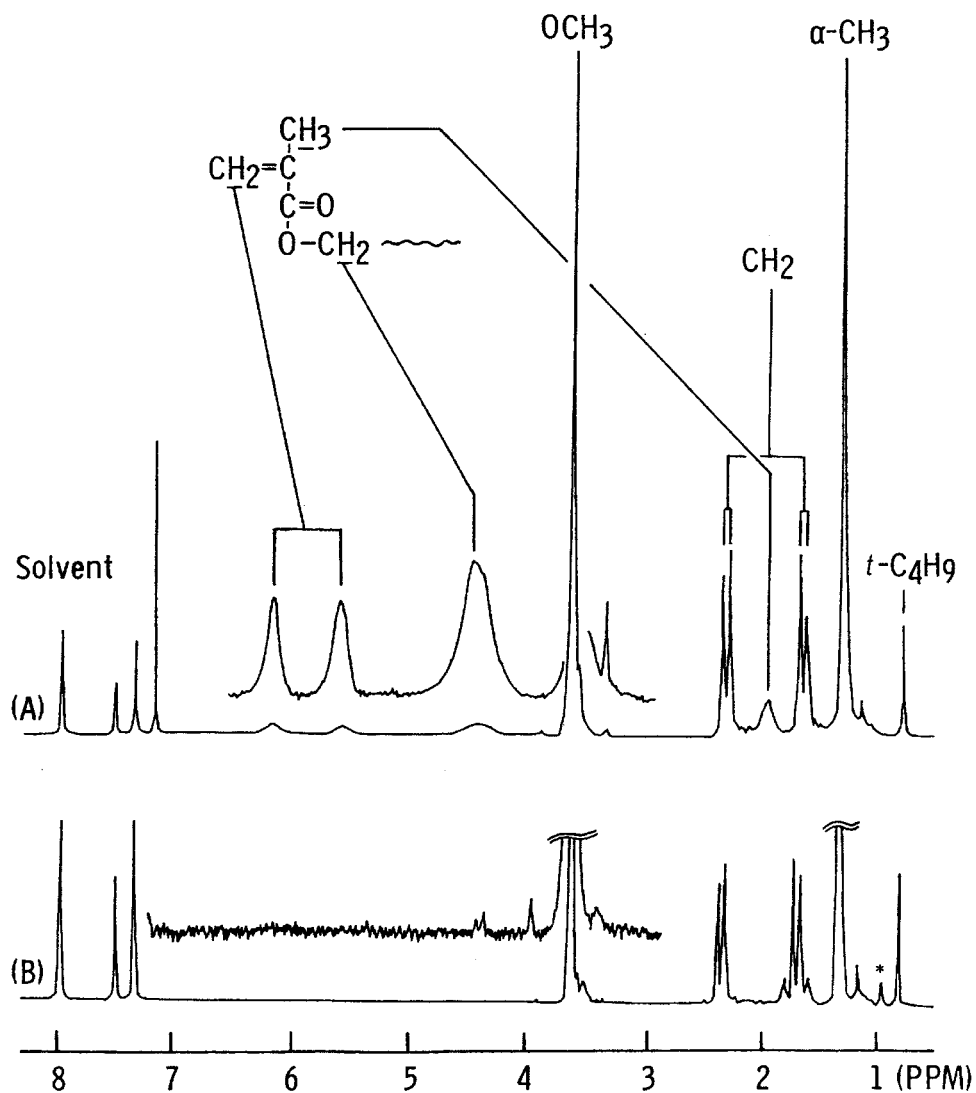
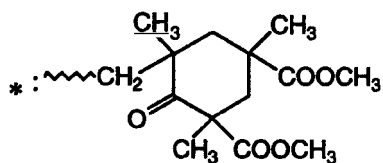


Figure 3. 270 MHz ^1H NMR spectra of high (A) and low (B) molecular weight fractions of the reaction product of EGDMA and *it*-PMMA anion formed with $t\text{-C}_4\text{H}_9\text{MgBr}$ in toluene at -78°C in the presence of DBU (MMA 10 mmol, $t\text{-C}_4\text{H}_9\text{MgBr}$ 0.2 mmol, EGDMA 1.4 mmol, DBU 0.6 mmol).



of Fig. 3).^[19,20] In the present method, DBU was added to the reaction mixture of EGDMA and *it*-PMMA anion. When DBU was added to the *it*-PMMA anion prior to the addition of EGDMA, the amount of the high molecular weight fraction decreased greatly to 10% of the total product. This is due to the deactivation of *it*-PMMA anion through the end cyclization.^[20] Thus, the activation of the polymer anion by the addition of DBU should follow the prior addition of EGDMA.

Star Polymer with Syndiotactic PMMA Arms

For the preparation of star polymers with *st*-PMMA arms, a similar approach to that for the *it*-PMMA star polymer described above was repeated several times using *st*-PMMA living anion formed with $t\text{-C}_4\text{H}_9\text{Li}-(n\text{-C}_4\text{H}_9)_3\text{Al}$ in toluene at -78°C . The addition of various additives including DBU was not effective for the formation of star polymer. Instead of EGDMA, BDDMA was employed as a core forming monomer**. Figure 4 shows the SEC curves of the products from the reaction of *st*-PMMA anion and BDDMA at -78°C without additives. The fraction of the high molecular weight peak as well as the molecular weight increased with an increase of the amount of BDDMA added in the range of $[\text{BDDMA}]/[t\text{-C}_4\text{H}_9\text{Li}]$ ratio of 1 to 5 (mol/mol). The product formed at the $[\text{BDDMA}]/[t\text{-C}_4\text{H}_9\text{Li}]$ ratio of 10 contained an insoluble gel. BDDMA was found to be much more reactive than EGDMA in the homopolymerization with $t\text{-C}_4\text{H}_9\text{Li}-(n\text{-C}_4\text{H}_9)_3\text{Al}$ in toluene at -78°C , giving an insoluble gel, while EGDMA afforded a soluble polymer. BDDMA is also more reactive than EGDMA with $t\text{-C}_4\text{H}_9\text{MgBr}$ and thus can be used as a core-forming monomer for the preparation of star polymers with *it*-PMMA arms without additives.^[21]

Characterization of Star Polymer

The reaction product consisted of high and low molecular weight fractions, which correspond to the star polymer and the unreacted PMMA, respectively, was analyzed by SEC-LALLS method to obtain \bar{M}_w and \bar{M}_n of the high molecular weight fraction as described in the Experimental section. The \bar{M}_n of the low molecular weight fraction can be regarded to be the same as that of the arms in the star polymer. The number of arms was determined in the following manner (Table 2). The yield of the star polymer was determined from the total yield and the relative peak areas in RI-detected SEC

**Haddleton and his coworkers succeeded to obtain star PMMA with narrow molecular weight distribution by the reaction between PMMA living anion obtained by $t\text{-C}_4\text{H}_9\text{Li}-(i\text{-C}_4\text{H}_9)_3\text{Al}$ and EGDMA in toluene at higher temperature (-10°C), but they did not mention about the stereoregularity.^[14]

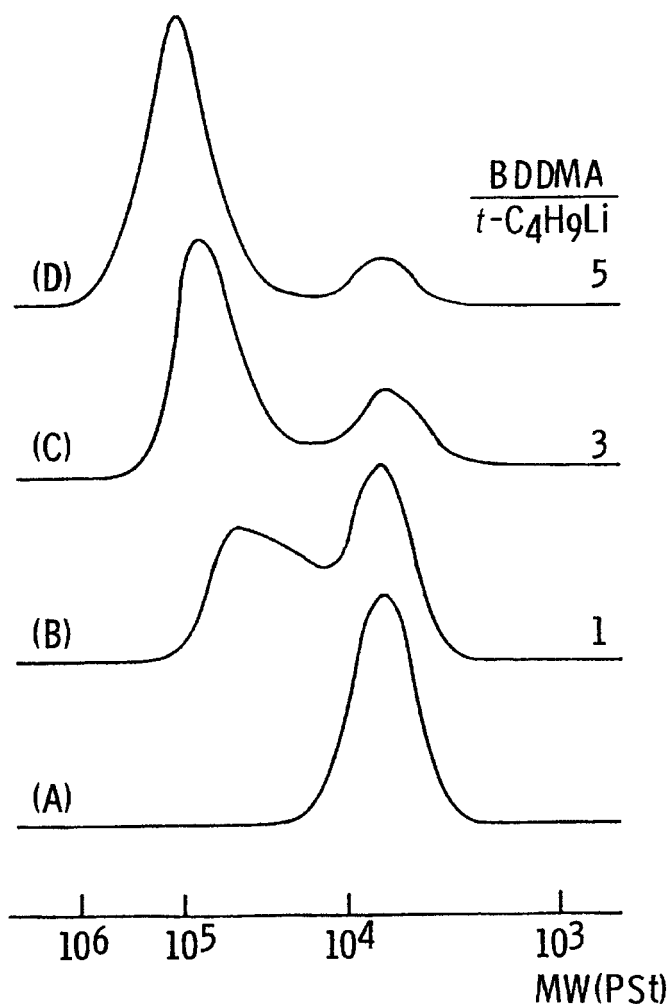


Figure 4. SEC curves of st -PMMA (A) and the reaction products of BDDMA and st -PMMA anion formed with $t\text{-C}_4\text{H}_9\text{Li}/(n\text{-C}_4\text{H}_9)_3\text{Al}$ (1/3 mol/mol) in toluene at -78°C (B, C, D, and E) (MMA 10 mmol, $t\text{-C}_4\text{H}_9\text{Li}$ 0.2 mmol).

chromatogram. \bar{M}_n and \bar{M}_w of star polymer molecule were determined by SEC-LALLS method. Since the low molecular weight fraction (Fig. 3B) consisted of only MMA units, the number of MMA units incorporated into the star polymer molecule (N_{MMA}) could be estimated as $\{(\text{weight of high molecular weight fraction}) - (\text{weight of dimethacrylate consumed})\} / (\text{molecular weight of MMA})$ by assuming the conversion of MMA to be 100%. The number of star polymer molecules in the fraction (N_{star}) was calculated from the yield and the \bar{M}_n of the star polymer and the number of MMA unit per star polymer molecule (n_{MMA}) was calculated as $N_{\text{MMA}} /$

Table 2. Characterization of Isotactic and Syndiotactic PMMA Star Polymers

	Isotactic ^a		Syndiotactic ^b	
	High ^c	Low ^c	High ^c	Low ^c
\bar{M}_w^d	240,000	—	1,260,000	—
\bar{M}_n^d	220,000	5230	960,000	5930
Yield (g)	0.981	0.219	1.013	0.177
N_{MMA}^e (mmol)	7.81	2.19	8.22	1.77
N_{star}^f (mmol)	0.0044	—	0.0010	—
n_{MMA}^g (mmol)	1775	52	8220	59
n_{arm}^h (mmol)	34.1	—	139	—
n_{DMA}^i (mmol)	214	—	610	—

^aMMA 10 mmol, *t*-C₄H₉MgBr 0.20 mmol, EGDMA 1.0 mmol, yields 100%.

^bMMA 10 mmol, *t*-C₄H₉Li/(*n*-C₄H₉)₃Al 0.20 mmol/0.60 mmol, BGDMA 1.0 mmol, yields of MMA and BGDMA: 100 and 84.0%, respectively.

^cHigh and low molecular weight fractions of the reaction product, which correspond to star polymer and unreacted PMMA, respectively. \bar{M}_n value for the latter was used as \bar{M}_n of the arm.

^dDetermined by SEC-LALLS method.

^eNumber of MMA unit in the fraction.

^fNumber of star polymer molecules in the fraction = (Yield of star polymer)/(\bar{M}_n of the star polymer).

^gNumber of MMA unit per molecule = $N_{\text{MMA}}/N_{\text{star}}$.

^hNumber of arm per molecule = $n_{\text{MMA}}(\text{star})/n_{\text{MMA}}(\text{prepolymer})$.

ⁱNumber of dimethacrylate unit per molecule = $\{(\bar{M}_n \text{ of the star polymer}) - n_{\text{MMA}} \times (\text{molecular weight of MMA})\} / (\text{molecular weight of dimethacrylate})$.

N_{star} . Dividing n_{MMA} by DP of the arm, one obtains the number of arm per star polymer molecule.

The number of core-forming monomer unit (EGDMA or BDDMA) per star polymer molecule could also be estimated as shown in Table 2. If one assumes that the core is fully consisted of dimethacrylate unit, the molecular weight of the core part are 42,500 for *it*-star polymer and 138,000 for *st*-star polymer. It is clearly seen from the table that the number of arms of the *it*-star polymer is smaller than that of the *st*-one. Although, this is partly due to the reactivity difference of EGDMA and BDDMA, the main reason is the lower reactivity of the *it*-star polymer anion.^[21]

Figure 5 shows the SEC chromatograms of star polymer with *it*-PMMA arms and a linear *it*-PMMA, both of which showed similar elution volumes. In other words, the hydrodynamic volumes of these polymers are similar to each other. Peak height of the RI-detected chromatograms were almost the same, indicating that the concentrations of the samples were almost the same. The peak height of the LALLS-detected chromatogram for the star polymer was two times as high as that for the linear PMMA. The results

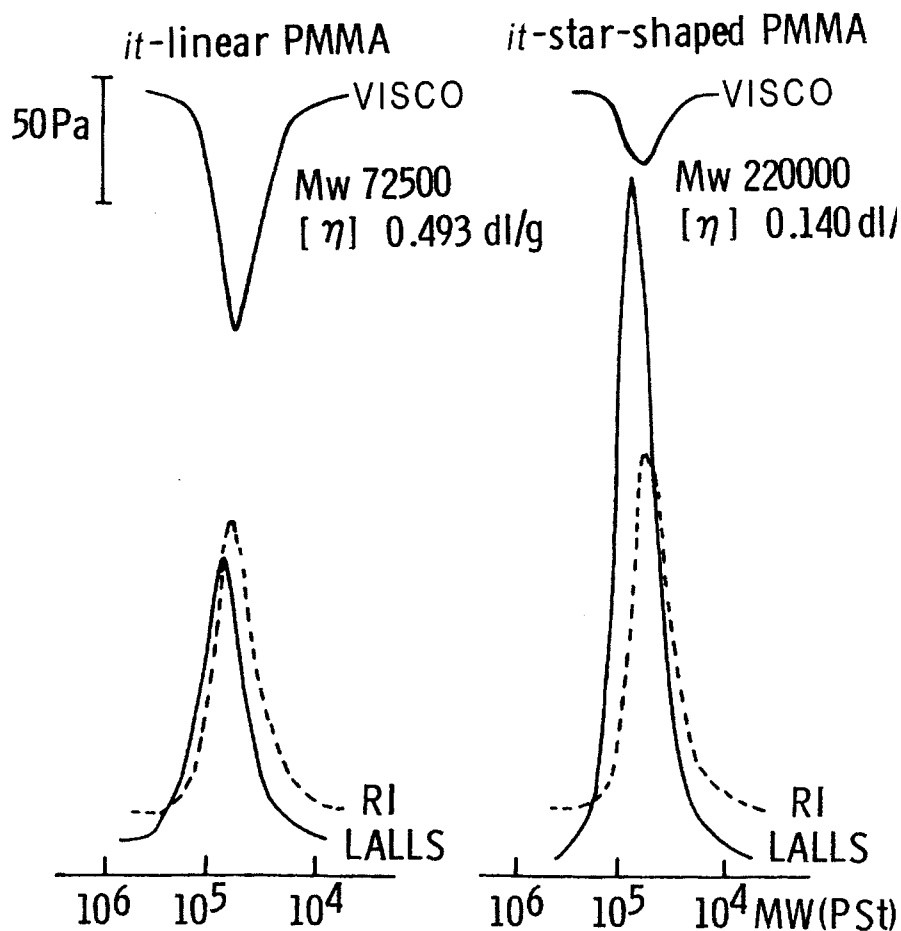


Figure 5. SEC curves of linear *it*-PMMA and star polymer with *it*-PMMA arms observed with refractive index (RI), LALLS and differential viscometer (VISCO) detectors.

means that the segmental density of the star polymer in solution is much larger than that of the linear polymer. On the other hand, the response in differential viscometric detection of the star polymer was much smaller than that of the linear PMMA, that is, even with the similar hydrodynamic volume the star polymer exhibits smaller viscosity than the linear polymer. Intrinsic viscosities $[\eta]$ of the star polymer and linear PMMA measured in THF at 40°C are indicated in the figure. The $[\eta]$ value of the star polymer was $1/3.5$ of that of the linear PMMA, and \bar{M}_w of the star polymer was 3.3 times larger than that of the linear PMMA. Thus the products $\bar{M}_w[\eta]$ for these polymers are close to each other. The results are consistent with the universal calibration theorem,^[22] which claims that the elution volume in SEC is proportional to $\bar{M}_w[\eta]$ regardless of polymer structure. The relationship between $[\eta]$ values of the star polymer with *st*-PMMA arms and linear

st-PMMA also showed similar results. The detailed results will be published in a separate article.^[21]

Star polymers having *it*-PMMA arms can be used as effective cross-linking materials for the triblock copolymer of polyisobutylene having *st*-PMMA blocks at both ends. When the triblock copolymer is mixed with a small amount of the *it*-PMMA star shaped polymer, physical crosslinking occurs between the copolymer molecules through stereocomplex formation between *st*-PMMA blocks and *it*-PMMA arms to form a thermoplastic elastomer.^[23]

CONCLUSION

Isotactic and syndiotactic star-shaped PMMAs were prepared by the reaction of the corresponding stereoregular PMMA living anions with ethylene glycol dimethacrylate in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene or with butane-1,4-diol dimethacrylate in toluene at -78°C , respectively. ^1H NMR and SEC analyses revealed that the isotactic star-shaped PMMA has 34 arms per molecule and the syndiotactic one 139 arms on average. The segmental density of the star polymers in THF estimated by SEC-LALLS and SEC-DV (differential viscometry) was found to be much larger than that of the linear polymer.

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