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Synthesis of Chain-End-Functionalized Poly(methyl methacrylate)s with a Definite Number of Benzyl Bromide Moieties and Their Application to Star-Branched Polymers

Akira Hirao* and Akira Matsuo

Polymeric and Organic Materials Department, Graduate School of Science and Technology,
Tokyo Institute of Technology, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152-8552, Japan

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ABSTRACT: The synthesis of well-defined chain-end-functionalized poly(methyl methacrylate)s with a definite number of benzyl bromide moieties via an iterative divergent approach starting from the living anionic polymer of methyl methacrylate is described. Only two sets of reactions involving coupling and transformation reactions are needed for the entire iterative reaction sequence. By repeating the iterative reaction sequence, chain-end-functionalized poly(methyl methacrylate)s with 2, 4, 8, and 16 benzyl bromide moieties were synthesized successfully. The resulting benzyl bromide-functionalized poly(methyl methacrylate)s underwent coupling reaction with living anionic polymers of methyl methacrylate, *tert*-butyl methacrylate, styrene, and isoprene to quantitatively afford well-defined regular 3-, 5-, 9-, and 17-arm star-branched poly(methyl methacrylate)s and asymmetric star-branched polymers containing poly(methyl methacrylate) segments.

Introduction

Recently, we have developed a new promising methodology based on an iterative divergent approach for the synthesis of chain-end-functionalized polystyrenes with a definite number of benzyl bromide moieties.[1] Only two sets of reactions are needed for the entire iterative reaction sequence as illustrated in Scheme 1.

The first reaction is a coupling reaction of the terminal benzyl bromide moiety with the functionalized 1,1-diphenylalkyl anion prepared from *sec*-BuLi and 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**) to introduce two 3-*tert*-butyldimethylsilyloxymethylphenyl groups at the chain end. The two 3-*tert*-butyldimethylsilyloxymethylphenyl groups thus introduced are transformed into two benzyl bromide moieties by treatment with a 1:1 mixture of LiBr and trimethylsilyl chloride in the second reaction. Since the resulting polymer has the same benzyl bromide moieties as the starting polymer, this reaction sequence involving coupling and transformation reactions can be repeated. Chain-end-functionalized polystyrenes with 4, 8, 16, and 32 benzyl bromide moieties could be synthesized by repeating the iterative reaction sequence four more times. Yields of such functionalized polymers were virtually quantitative.

The major problems of this promising methodology is that the polymer usable as a main chain segment is quite limited in number and chemical structure, since highly reactive reagents are in situ generated in the iterative reaction sequence.[1,2] Indeed, only polystyrene and poly(α-methylstyrene) have been so far employed as main-chain segments. Several attempts using various functionalized polystyrenes such as poly(4-trimethylsilylstyrene), poly(4-*tert*-butoxystyrene), poly(4-methoxymethoxystyrene), and poly(4-*tert*-butyldimethylsilyloxystyrene) have failed because of the instability of their functionalities toward $(CH_3)_3SiBr$ in situ generated in the transformation reaction.[3] With the use of polyisoprene in the methodology, high molecular weight polymers were formed in the transformation reaction, presumably due to the undesirable alkylation reaction among polymer chains.[3] To establish the developed methodology as a general synthetic procedure, it is important to find out other polymers stable enough under the conditions of the iterative reaction sequence.

We have focused on the possible use of poly(methyl methacrylate) (PMMA) as a main-chain segment in the methodology, since PMMA is one of the most widely utilized polymers with many industrial applications. Furthermore, we are strongly interested in synthesizing chain-end-functionalized PMMAs with benzyl bromide functionalities that can be used as functionalized prepolymers leading to various specially shaped polymers.[4−7] Herein, we report on the synthetic development of the iterative methodology for the synthesis of chain-end-functionalized PMMAs with a definite number of benzyl bromide moieties. We also report on the successful synthesis of well-defined star-branched polymers by the coupling reaction of such benzyl bromide chain-end-functionalized PMMAs with living anionic polymers of MMA, *tert*-butyl methacrylate, styrene, and isoprene.

Experimental Section

Materials. All chemicals were purchased from Tokyo Kasei Kogyo Co., Ltd., Japan, and used as received unless otherwise stated. Methyl methacrylate (MMA) (98%), ethyl methacrylate (EMA) (98%), isopropyl methacrylate (^iPMA) (98%), *tert*-butyl methacrylate (^tBMA) (98%), and styrene (98%) were washed with 5% NaOH and H_2O and dried over $MgSO_4$. After removal of $MgSO_4$, they were distilled twice from CaH_2 under reduced pressures. All methacrylates were finally distilled from trioctylaluminum (ca. 2 mol %) on a vacuum line into ampules equipped with break-seals that were prewashed with potassium naphthalenide in THF. Styrene was finally distilled from dibutylmagnesium (ca. 5 mol %) on a vacuum line into ampules equipped with break-seals that were prewashed with potassium naphthalenide in THF. Isoprene (99%) was washed with 10% NaOH and dried over $MgSO_4$. It was distilled from CaH_2 under nitrogen and finally distilled from *n*-BuLi (ca. 5 mol %)

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* Corresponding author: Tel +81-3-5734-2131; Fax +81-3-5734-2887; e-mail ahirao@polymer.titech.ac.jp.

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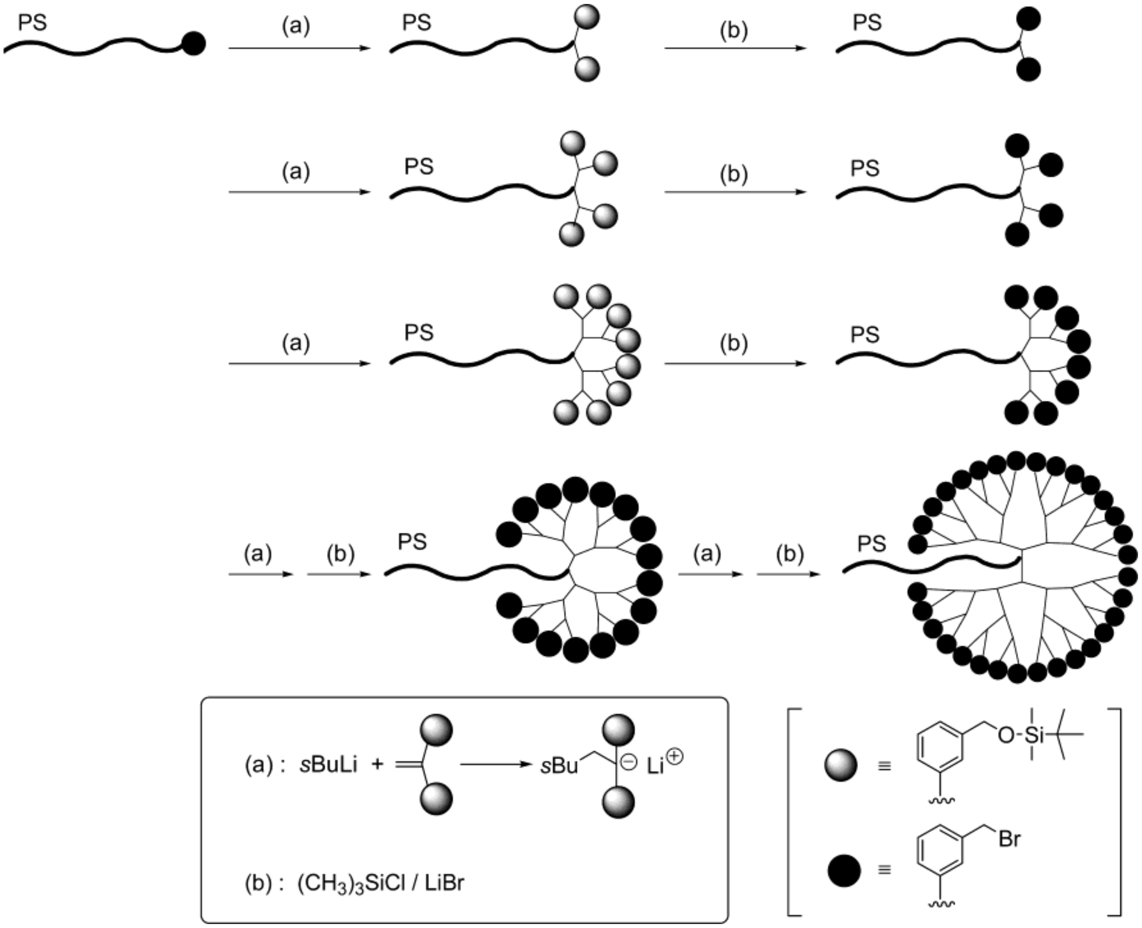
Scheme 1. Synthesis of Chain-End-Functionalized Polystyrenes with Benzyl Bromide Moieties Based on an Iterative Approach



at 0 °C on a vacuum line into ampules equipped with break-seals that were prewashed with 1,1-diphenylhexyllithium in heptane. 1,1-Diphenylethylene (DPE) (98%) was distilled twice from CaH$_2$ under reduced pressure and then distilled from its 1,1-diphenylhexyllithium solution on a vacuum line into ampules with break-seals that were prewashed with potassium naphthalenide in THF. THF (99%) was refluxed over sodium wire and distilled from LiAlH$_4$ under nitrogen. It was finally distilled from its sodium naphthalenide solution on a vacuum line. Heptane (99%) was washed with concentrated H$_2$SO$_4$, H$_2$O, dried over MgSO$_4$, and distilled from P$_2$O$_5$ under nitrogen. It was finally distilled from its 1,1-diphenylhexyllithium solution on a vacuum line. BCl$_3$ (1.0 M in CH$_2$Cl$_2$, Aldrich, Japan) and (C$_4$H$_9$)$_4$NF (1.0 M in THF, Aldrich, Japan) were used as received. LiCl (99%) and LiBr (99%, Koso Chemical Co., Ltd., Japan) were dried under a high vacuum (10^{-6} Torr) at 100 °C for 24 h. LiCl was then diluted with THF on a vacuum line. Chloroform (98%), acetonitrile (98%), and trimethylsilyl chloride (98%) were distilled from CaH$_2$ under nitrogen. 1,1-Bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**) was synthesized according to our procedures previously reported.[2c]

Measurements. Both ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX300 in CDCl$_3$. Chemical shifts were recorded in ppm downfield relative to chloroform (δ 7.26 ppm for ^{1}H NMR and δ 77.1 for ^{13}C NMR spectra). Size exclusion chromatograms (SEC) were measured with a TOSOH HLC-8020 at 40 °C with UV (254 nm) or refractive index detection. THF was used as carrier solvent at a flow rate of 1.0 mL/min. Three polystyrene gel columns (TSK$_{gel}$ G4000H$_{XL}$, G3000H$_{XL}$, G2000H$_{XL}$ or TSK$_{gel}$ G5000H$_{XL}$, G4000H$_{XL}$, G3000H$_{XL}$) were used. Measurable molecular weight ranges are $10^3-4 \times 10^5$ and $10^4-4 \times 10^6$ g/mol, respectively. Fractionation by HPLC was performed at 40 °C using a TOSOH HLC-8020 type fully automatic instrument equipped with a TSK-G4000H$_{HR}$ column (300 mm in length and 21.5 mm in diameter). The measurable molecular weight range is $10^3-5 \times 10^5$ g/mol. All runs for fractionation were made with THF as an eluent. The concentration of the polymer solution for fractionation was adjusted to 10−20% w/v, depending on the molecular weight of the sample. Calibration curves were made with standard PMMA to determine M_n and M_w/M_n values. Similarly, calibration curves for poly(*tert*-butyl methacrylate) and polyisoprene were made using M_n and M_w values determined by VPO and static light scattering (SLS), respectively. The measurements for SLS were performed with an Otsuka Electronics SLS-600R instrument equipped with a He−Ne laser (633 nm) in THF at 25 °C. A Berry plot was used to determine the M_w value of each star-branched polymer. The refractive index increment (dn/dc) in THF at 25 °C was determined with an Otsuka Electronics DRM-1020 refractometer operating at 633 nm. Vapor pressure osmometry (VPO) measurements were made with a Corona 117 instruments in benzene at 40 °C with a highly sensitive thermoelectric couple (TM-32K: sensitivity 35 000 μV $\pm$ 10%/1 M) and with equipment of very exact temperature control. Therefore, molecular weight can be measured up to 100 kg/mol with an error of about 5%. The apparatus constant was obtained by measuring standard polystyrene samples (M_n: 5.05, 10.2, 20.5, and 45.0 kg/mol) and calibrating their values against M_n values. Intrinsic viscosities were measured with an Ubbelohde viscometer in THF at 25 °C. A new intrinsic viscosity equation for linear PMMA was made with six PMMA samples prepared by living anionic polymerization. MALDI−TOF MASS spectra were taken on Shimadzu AXIMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser (337 nm) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV by linear-positive ion mode. The sample polymer solution (1 g/L) was prepared in THF. The matrix, 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol, Aldrich) (10 mg), and sodium trifluoroacetate (Aldrich) (1 mg) were dissolved in THF (1 mL). The polymer solution (50 μL) was then mixed with 50 μL of the matrix solution. A 1 μL portion of the final solution was deposited onto a sample target plate and allowed to dry in air at room temperature. Mass values were calibrated by the two-point method with insulin β plus H^+ at 3497.96 and α-cyano-hydroxycinnamic acid dimer plus H^+ at 379.35.

Synthesis of Chain-End-Functionalized Poly(methyl methacrylate)s with Benzyl Bromide Moieties by an Iterative Divergent Methodology. Herein, a series of chain-end-functionalized PMMAs with benzyl bromide moieties have been designated as PMMA(BnBr)$_n$, whose the subscript "*n*" corresponds to the number of the benzyl bromide moieties introduced. Chain-end-functionalized PMMA with two benzyl bromide moieties (designated as PMMA(BnBr)$_2$) used as a starting material was synthesized by the living anionic polymerization of MMA initiated with the 1,1-diphenylalkyl anion from **1** and *sec*-BuLi, followed by transformation with $(CH_3)_3SiCl-LiBr$. The terminal two benzyl bromide moieties introduced at the initiating chain end were coupled with the functionalized 1,1-diphenylalkyl anion prepared from **1** and *sec*-BuLi to introduce four 3-*tert*-butyldimethylsilyloxymethylphenyl groups. Then, the four 3-*tert*-butyldimethylsilyloxymethylpheny groups were transformed into four benzyl bromide moieties. Thus, PMMA(BnBr)$_4$ was synthesized. The reaction sequence involving the coupling and transfer reactions was repeated two more times to afford PMMA(BnBr)$_8$ and PMMA(BnBr)$_{16}$, respectively, in ca. 100% yields. Typical experiments are as follows: The functionalized initiator was prepared from *sec*-BuLi (0.351 mmol) in heptane (2.75 mL) and **1** (0.460 mmol) in THF (3.61 mL) at −78 °C for 0.5 h. After addition of LiCl (1.05 mmol) in THF (5.34 mL) solution to the reaction mixture, MMA (4.36 g, 43.6 mmol) in THF (18.3 mL) solution chilled at −78 °C was added to polymerize with vigorous stirring at −78 °C. After 0.5 h, the polymerization was terminated with degassed methanol (5 mL), and the reaction mixture was poured into hexane to precipitate the polymer. The resulting polymer was dissolved in benzene and filtrated through a Celite column to remove LiCl and $LiOCH_3$, reprecipitated twice from THF into hexane, and freeze-dried from its absolute benzene solution for 24 h (4.20 g, 96%). ^1H NMR: δ 7.2−6.9 (m, 8H, aromatic), 4.65 (s, 4H, $-C_6H_4-CH_2-O-$), 3.5−3.7 (m, 376H, $-COOCH_3$), 1.6−2.0 (m, 251H, $-CH_2-C(CH_3)-$), 0.6−1.1 (m, 372H, $-CH_2-C(CH_3)-$), 0.89 (m, 18H, $-Si(CH_3)_2C(CH_3)_3$), 0.03 (s, 12H, $-Si(CH_3)_2C(CH_3)_3$). The M_n values calculated and observed by SEC and ^1H NMR were 13.0, 12.2, and 13.1 kg/mol, respectively. The end-functionalization degree was determined to be 2.00 by ^1H NMR.

The 3-*tert*-butyldimethylsilyloxymethylphenyl groups were transformed into benzyl bromide moieties according to our procedure previously reported.[1] A chain-end-functionalized PMMA (4.00 g, 0.611 mmol for 3-*tert*-butyldimethylsilyloxymethylphenyl group) was dissolved in a mixed solvent of $CHCl_3$ (80 mL) and CH_3CN (20 mL). Then, LiBr (2.80 g, 32.2 mmol) and $(CH_3)_3SiCl$ (4.90 mL, 38.6 mmol) were added to the polymer solution, and the reaction mixture was allowed to stir at 40 °C for 24 h under nitrogen. The reaction was then terminated with water (5 mL). The reaction mixture was washed with water and dried over $MgSO_4$. After removal of solvent under reduced pressure, the expected polymer PMMA(BnBr)$_2$ was obtained. It was purified by reprecipitation twice from $CHCl_3$ to hexane and finally freeze-dried from its absolute benzene solution (3.94 g, 99%). ^1H NMR: δ 7.2−6.9 (m, 8H, aromatic), 4.45 (s, 4H, $-C_6H_4-CH_2Br$), 3.4−3.8 (m, $-COOCH_3$), 1.6−2.0 (m, $-CH_2-C(CH_3)-$), 0.6−1.1 (m, $-CH_2-C(CH_3)-$). The M_n values calculated and observed by SEC, VPO, and ^1H NMR were 13.0, 12.3, 13.5, and 13.0 kg/mol, respectively. The M_w/M_n value determined by SEC was 1.04. The end-functionalization degree of benzyl bromide moiety measured by ^1H NMR was 1.98. Anal. Calcd for $C_{646}H_{1025}O_{250}Br_2$: C, 59.91; H, 7.98; O, 30.88; Br, 1.23. Found: C, 60.88; H, 7.75; O, 30.12; Br, 1.25.

The terminal two benzyl bromide moieties of the resulting PMMA(BnBr)$_2$ coupled with the functionalized anion from **1** and *sec*-BuLi to introduce four 3-*tert*-butyldimethylsilyloxymethylphenyl groups. The four *tert*-butyldimethylsilyloxymethylphenyl groups were transformed into four benzyl bromide moieties by treatment with $(CH_3)_3SiCl-LiBr$. Experimental details are as follows: The functionalized anion was prepared by adding *sec*-BuLi (0.811 mmol) in heptane (3.20 mL) solution into **1** (0.995 mmol) in THF (5.75 mL) solution at −78 °C for 0.5 h. It was added to a THF (43.7 mL) solution of PMMA(BnBr)$_2$ (3.55 g, 0.545 mmol for 3-*tert*-butyldimethylsilyloxymethylphenyl group) at −78 °C. The reaction mixture was allowed to stir for an additional 30 min at −78 °C and terminated with degassed methanol. The reaction mixture was poured into hexane to precipitate the polymer. The resulting polymer was dissolved in benzene and filtrated through a Celite column to remove LiBr and $LiOCH_3$, reprecipitated twice from THF into hexane, and freeze-dried from its absolute benzene solution for 24 h (3.51 g, 99%). ^1H NMR: δ 7.2−6.9 (m, 16H, aromatic), 4.65 (s, 8H, $-C_6H_4-CH_2-O-$), 3.5−3.7 (m, $-COOCH_3$), 1.6−2.0 (m, $-CH_2-C(CH_3)-$), 0.6−1.1 (m, $-CH_2-C(CH_3)-$), 0.89 (m, 36H, $-Si(CH_3)_2C(CH_3)_3$), 0.03 (s, 24H, $-Si(CH_3)_2C(CH_3)_3$). The M_n values calculated and observed by SEC and ^1H NMR were 13.9, 12.6, and 13.8 kg/mol, respectively. The M_w/M_n value measured by SEC was 1.03. The end-functionalization degree determined by ^1H NMR was 4.04.

Table 1. Synthesis of Chain-End-Functionalized PMMAs with 2, 4, 8, and 16 Benzyl Bromide Moieties[a]

	$M_n \times 10^{-3}$					functionality[b]	
polymer	calcd	SEC	VPO	^1H NMR	M_w/M_n	calcd	^1H NMR
PMMA(BnBr)$_2$	13.0	12.3	13.5	13.0	1.04	2	1.9_8
PMMA(BnBr)$_4$	13.6	12.4	13.2	13.6	1.03	4	3.9_7
PMMA(BnBr)$_8$	15.0	12.9	14.7	15.1	1.03	8	8.5_0
PMMA(BnBr)$_{16}$	17.9	14.2	18.4	17.9	1.03	16	$16._8$

[a] Yields of polymers were quantitative in all cases. [b] Functionality of benzyl bromide moieties.

The resulting chain-end-functionalized PMMA (3.29 g, 0.944 mmol for 3-*tert*-butyldimethylsilyloxymethylphenyl group) was dissolved in a mixed solvent of $CHCl_3$ (60 mL) and CH_3CN (15 mL). Then, LiBr (2.99 g, 34.4 mmol) and $(CH_3)_3SiCl$ (5.00 mL, 39.4 mmol) were added to the polymer solution, and the reaction mixture was allowed to stir at 40 °C for 24 h under nitrogen. The reaction was then terminated with water. The reaction mixture was washed with water and dried over $MgSO_4$. After removal of solvent under reduced pressure, the resulting polymer was purified by reprecipitating twice from $CHCl_3$ to hexane and finally freeze-dried from its absolute benzene solution to afford PMMA(BnBr)$_4$ (3.19 g, 97%). ^1H NMR: δ 7.2−6.9 (m, aromatic), 4.45 (s, 8H, $-C_6H_4-CH_2Br$), 3.4−3.8 (m, $-COOCH_3$), 1.6−2.0 (m, $-CH_2-C(CH_3)-$), 0.6−1.1 (m, $-CH_2-C(CH_3)-$). The M_n values calculated and observed by SEC, VPO, and ^1H NMR were 13.6, 12.4, 13.2, and 13.6 kg/mol, respectively. The M_w/M_n value measured by SEC was 1.03. The end-functionalization degree of benzyl bromide moiety determined by ^1H NMR was 3.97. Anal. Calcd for $C_{686}H_{1071}O_{250}Br_4$: C, 60.39; H, 7.91; O, 29.36; Br, 2.34. Found: C, 61.62; H, 7.75; O, 28.29; Br, 2.35.

Similarly, chain-end-functionalized PMMAs with 8 and 16 benzyl bromide moieties were synthesized by repeating the iterative reaction sequence. Their analytical results are as follows:

PMMA(BnBr)$_8$. ^1H NMR: δ 7.2−6.9 (m, aromatic), 4.42 (m, 16H, $-C_6H_4-CH_2Br$), 3.4−3.8 (m, $-COOCH_3$), 1.6−2.0 (m, $-CH_2-C(CH_3)-$), 0.6−1.1 (m, $-CH_2-C(CH_3)-$). Anal. Calcd for $C_{766}H_{1163}O_{250}Br_8$: C, 61.29; H, 7.81; O, 26.65; Br, 4.26. Found: C, 61.46; H, 7.62; O, 25.77; Br, 4.15.

PMMA(BnBr)$_{16}$. ^1H NMR: δ 7.2−6.9 (m, aromatic), 4.38 (m, 32H, $-C_6H_4-CH_2Br$), 3.4−3.8 (m, $-COOCH_3$), 1.6−2.0 (m, $-CH_2-C(CH_3)-$), 0.6−1.1 (m, $-CH_2-C(CH_3)-$). Anal. Calcd for $C_{926}H_{1347}O_{250}Br_{16}$: C, 62.61; H, 7.64; O, 22.55; Br, 7.20. Found: C, 62.77; H, 7.41; O, 22.48; Br, 7.34.

Their M_n and M_w/M_n values and degrees of end-functionalization are listed in Table 1.

Table 2. Synthesis of Chain-End-Functionalized PMMAs with Two Benzyl Chloride, Iodide, and Benzyl Alcohol Moieties[a]

polymer	$M_n \times 10^{-3}$				M_w/M_n	functionality[b]	
	calcd	SEC	VPO	^{1}H NMR		calcd	^{1}H NMR
PMMA(BnCl)$_2$	12.7	13.4	12.0	12.7	1.04	2	1.9_4
PMMA(BnI)$_2$	12.9	13.5	11.9	12.9	1.04	2	1.9_4
PMMA(BnOH)$_2$	12.7	13.5	ND[c]	12.7	1.04	2	1.9_7

[a] Yields of polymers were quantitative in all cases. [b] Functionality of benzyl chloride, iodide, or benzyl alcohol moieties. [c] Not determined.

The transformation reaction into benzyl chloride was carried out by treating chain-end-functionalized PMMA with two 3-*tert*-butyldimethylsilyloxymethylphenyl groups with a 12-fold excess of BCl_3. A solution of BCl_3 (0.600 mmol, 0.600 mL, 1 M in CH_2Cl_2) was added via syringe at 20 °C to a CH_2Cl_2 (20.0 mL) solution of a chain-end-functionalized PMMA with two 3-*tert*-butyldimethylsilyloxymethylphenyl groups (0.330 g, 0.0500 mmol for 3-*tert*-butyldimethylsilyloxymethylphenyl group) under nitrogen. The mixture was stirred at 20 °C for an additional 2.5 h. The reaction was terminated with methanol (2 mL). The reaction mixture was washed with water and dried over $MgSO_4$. After removal of solvent under reduced pressure, the resulting polymer was purified by reprecipitating twice from CH_2Cl_2 to hexane and finally freeze-dried from its benzene solution (0.300 g, 91%). ^{1}H NMR: δ 6.9−7.2 (m, 8H, aromatic), 4.53 (s, 4H, $-C_6H_4-CH_2Cl$), 3.5−3.7 (m, 367H, $-COOCH_3$), 1.6−2.0 (m, 250H, $-CH_2-C(CH_3)-$), 0.6−1.1 (m, 375H, $-CH_2-C(CH_3)-$).

The reaction of chain-end-functionalized PMMA with two 3-*tert*-butyldimethylsilyloxymethylphenyl groups with $(CH_3)_3SiCl-NaI$ was performed under the conditions similar to those using $(CH_3)_3SiCl-LiBr$ mentioned above. In this case, however, the reaction was carried out at 15 °C for 24 h in order to avoid the cleavage of the methyl ester function. ^{1}H NMR: δ 7.2−6.9 (m, 8H, aromatic), 4.41 (m, 4H, $-C_6H_4-CH_2I$), 3.5−3.7 (m, 367H, $-COOCH_3$), 1.6−2.0 (m, 247H, $-CH_2-C(CH_3)-$), 0.6−1.1 (m, 371H, $-CH_2-C(CH_3)-$).

Chain-end-functionalized PMMA with two benzyl alcohol moieties was obtained by deprotecting the terminal two 3-*tert*-butyldimethylsilyloxymethylphenyl groups with $(C_4H_9)_4NF$. In a typical experiment, the chain-end-functionalized PMMA (0.300 g, 0.0455 mmol for 3-*tert*-butyldimethylsilyloxymethylphenyl group) dissolved in THF (20.0 mL) was treated with $(C_4H_9)_4NF$ (1.00 mL, 1.00 mmol, 1.0 M in THF) at 25 °C for 6 h. After the solvent was removed under reduced pressure, the residual polymer was purified by reprecipitation twice from THF to water and finally freeze-dried from its absolute benzene solution (0.270 g, 90%). ^{1}H NMR: δ 7.2−6.9 (m, 8H, aromatic), 4.42 (m, 4H, $-C_6H_4-CH_2-OH$), 3.5−3.7 (m, 367H, $-COOCH_3$), 1.6−2.0 (m, 250H, $-CH_2-C(CH_3)-$), 0.6−1.1 (m, 380H, $-CH_2-C(CH_3)-$). The M_n and M_w/M_n values and degrees of end-functionalization for these functionalized (PMMA)s with benzyl halide and benzyl alcohol moieties are listed in Table 2.

Synthesis of 3-, 5-, 9-, and 17-Arm Star-Branched PMMAs. The 3-, 5-, 9-, or 17-arm star-branched PMMA was synthesized by the coupling reaction of either of PMMA(BnBr)$_n$ with living anionic PMMA. The synthetic procedure for the 17-arm star-branched PMMA is as follows: A THF solution (12.0 mL) containing MMA (1.25 g, 12.5 mmol) was anionically polymerized with the initiator prepared from *sec*-BuLi (0.112 mmol) and DPE (0.175 mmol) in the presence of LiCl (0.337 mmol) in THF (3.60 mL) solution at −78 °C for 0.5 h. A THF (3.60 mL) solution of PMMA(BnBr)$_{16}$ (0.0742 g, 0.0668 mmol for benzyl bromide moiety) was added at once to the living PMMA at −78 °C. The reaction mixture was allowed to stand at −40 °C for an additional 6 h. After the reaction was terminated with degassed methanol (5 mL), the reaction mixture was poured into a large amount of hexane (300 mL) to precipitate the polymer. The resulting polymer was dissolved in benzene and filtrated through a Celite column to remove LiCl, LiBr, and $LiOCH_3$. The objective star-branched PMMA was isolated by fractional precipitation where hexane was slowly added to the benzene solution of polymer at room temperature to precipitate the star-branched polymer. The precipitated polymer was purified by reprecipitating twice from THF to hexane and freeze-dried from its absolute benzene solution for 24 h (0.770 g, 92%).

Synthesis of Asymmetric Star-Branched Polymers. The asymmetric AB_2 and AB_4 star-branched polymers were similarly synthesized by the coupling reaction of either PMMA(BnBr)$_2$ or PMMA(BnBr)$_4$ with living anionic polymers of ^{t}BMA, styrene, and isoprene.

The polymerization of ^{t}BMA was initiated with 1,1-diphenyl-3-methylpentyllithium in the presence of a 3-fold excess of LiCl or diphenylmethylpotassium in THF at −78 °C for 4 and 1 h, respectively. Styrene was polymerized with *sec*-BuLi in THF at −78 °C for 20 min, followed by end-capping with a 1.2-fold excess of DPE in THF at −78 °C for 0.5 h. Isoprene was polymerized with *sec*-BuLi in heptane at 40 °C for 2 h. Heptane was then removed under vacuum, and an equal amount of THF was added at −78 °C. The polyisoprenyllithium in THF thus prepared was end-capped with a 1.5-fold excess of DPE in THF at −78 °C for 24 h. The coupling reactions were conducted in THF at −78 °C for 1 h.

The resulting star-branched polymers containing P^{t}BMA segments and polystyrene segments were isolated by fractional precipitation with benzene−hexane and cyclohexane−hexane, respectively. The star-branched polymer having polyisoprene segments was isolated by HPLC fractionation. The star-branched polymers were purified by reprecipitating three times from THF to hexane or methanol and freeze-drying from their absolute benzene solutions.

Results and Discussion

Synthesis of Chain-End-Functionalized Poly(methyl methacrylate)s with a Definite Number of Benzyl Bromide Moieties. In the iterative methodology proposed herein, highly reactive $(CH_3)_3SiBr$ in the transformation reaction[8] and the functionalized 1,1-diphenylalkyl anion from **1** and *sec*-BuLi in the coupling reaction are in-situ generated. The methyl ester function of PMMA is susceptible to undergo cleavage reaction[9] and nucleophilic attack by such reactive reagents.[10] It is therefore essential to examine that PMMA remains completely stable under such reaction conditions for the possible use of PMMA as main-chain polymer in the iterative methodology. For this examination, a chain-end-functionalized PMMA with two 3-*tert*-butyldimethylsilyloxymethylphenyl groups was first prepared by the living anionic polymerization of MMA with the functionalized 1,1-diphenylalkyl anion prepared from **1** and *sec*-BuLi in THF at −78 °C. A 3-fold excess of LiCl was used to narrow molecular weight distribution.[11] The resulting polymer, after twice reprecipitation, was treated with $(CH_3)_3SiCl-LiBr$.

Figure 1A,B shows SEC profiles of the polymers obtained before and after treatment with $(CH_3)_3SiCl-LiBr$. The SEC profile of PMMA after the treatment exhibited a sharp monomodal distribution and was almost identical in shape and distribution to that of the polymer before the treatment. The ^{1}H NMR spectra of both polymers are shown in Figure 2A,B. The signals at 0.03 and 0.89 ppm assigned to $Si-CH_3$ and $Si-C(CH_3)_3$ methyl protons of the 3-*tert*-butyldimethylsilyloxymethylphenyl group could be clearly observed with the expected intensities in Figure 2A. A signal at 4.65 ppm assigned to CH_2 protons of the benzyl 3-*tert*-butyldimethylsilyl ether was also present in the same spectrum. After the treatment, these signals completely

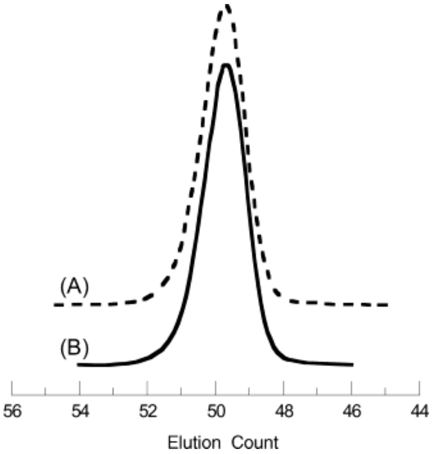


Figure 1. SEC profiles of chain-end-functionalized PMMAs before (A) and after transformation reaction (B).

disappeared, and alternatively a new signal at 4.45 ppm characteristic of CH_2 protons of the benzyl bromide moiety was observed in the expected peak intensity. Similarly, ^{13}C NMR spectra of both polymers provide confirmation that the 3-*tert*-butyldimethylsilyloxymethylphenyl groups were completely transformed into benzyl bromide moieties. In the spectrum of the polymer obtained after the transformation, the signals at −5.19 and 25.6 ppm characteristic of $Si-CH_3$ and $Si-C(CH_3)_3$ methyl carbons of the 3-*tert*-butyldimethylsilyloxymethylphenyl group and the signal at 68.0 ppm for CH_2 carbon of the benzyl *tert*-butyldimethylsilyl ether completely disappeared. Alternatively, the resonance assigned to the CH_2 carbon of the benzyl bromide moiety appeared at 33.5 ppm. Signals suggesting methyl ester cleavage could not be found in both ^1H and ^{13}C NMR spectra of the PMMA obtained after the treatment. These analytical results clearly indicate that the transformation reaction cleanly and quantitatively proceeds without any damages of PMMA to afford PMMA$(BnBr)_2$. The results are summarized in Table 1.

Next, the coupling reaction of PMMA$(BnBr)_2$ with a 1.5-fold excess of the functionalized 1,1-diphenylalkyl anion prepared from **1** and *sec*-BuLi was carried out in THF at −78 °C for 0.5 h. After the reaction, the SEC profile remained narrow in distribution and showed almost the same as that of the starting PMMA$(BnBr)_2$. Both ^1H and ^{13}C NMR analyses indicate that the benzyl bromide moieties had completely reacted to introduce four 3-*tert*-butyldimethylsilyloxymethylphenyl groups. The degree of end-functionalization was virtually quantitative ($f = 4.0_4$). Signals suggesting methyl ester attack by the 1,1-diphenylalkyl anion could not be detected in both NMR spectra. Accordingly, PMMA also remains stable under the conditions of coupling reaction.

As a further evidence for the stability of PMMA toward the 1,1-diphenylalkyl anion, the model reaction between PMMA (M_n = 4.96 kg/mol) and PSLi end-capped with **1** (M_n = 5.22 kg/mol) was carried out at 1:1 molar ratio in THF at −78 °C for 1 h. It should be mentioned that the terminal anion of PSLi end-capped with **1** is exactly the same in chemical structure as the functionalized 1,1-diphenylalkyl anion from **1** and *sec*-BuLi. Since both polymers possess sharp molecular weight distributions eluted at very similar counts, even a small amount of the coupled product, if any, can be readily detected by SEC. After mixing both polymers, a characteristic dark red color of the 1,1-diphenylalkyl anion appears to remain unchanged as long as the temperature is kept at −78 °C. The SEC profile of the reaction mixture exhibited no coupled product formation at all after 1 h. This indicates clearly that PMMA and the 1,1-diphenylalkyl anion can coexist under the conditions in THF at −78 °C.

The four 3-*tert*-butyldimethylsilyloxymethylphenyl groups thus introduced were completely transformed into four benzyl bromide moieties by the same treatment with $(CH_3)_3SiCl-LiBr$. Accordingly, PMMA$(BnBr)_4$ was synthesized from PMMA$(BnBr)_2$ via the reaction sequence involving coupling and transformation reactions.

With the use of PMMA$(BnBr)_4$ as a starting material, PMMA$(BnBr)_8$ and subsequently PMMA$(BnBr)_{16}$ were synthesized successively in similar manners in ca. 100% yields by repeating the reaction sequence two more times. The synthetic outline for PMMA$(BnBr)_n$ is illustrated in Scheme 2. The results are also listed in Table 1.[12] As can be seen in their SEC profiles of PMMA$(BnBr)_n$ (n = 2, 4, 8, and 16) (Figure 3), each of all SEC peaks possesses a sharp monomodal distribution and moves to higher molecular weight sides as the iteration proceeds.

In general, the M_n values estimated by SEC relative to PMMA were somewhat smaller than those calculated. This was more significant in PMMA$(BnBr)_8$ and PMMA$(BnBr)_{16}$. The similar trend was observed in the case of PS$(BnBr)_n$ previously reported, presumably due to the dendritic sphere structures of the end groups.[1] On the other hand, their M_n values determined by VPO and ^1H NMR agreed well with those calculated. Agreement

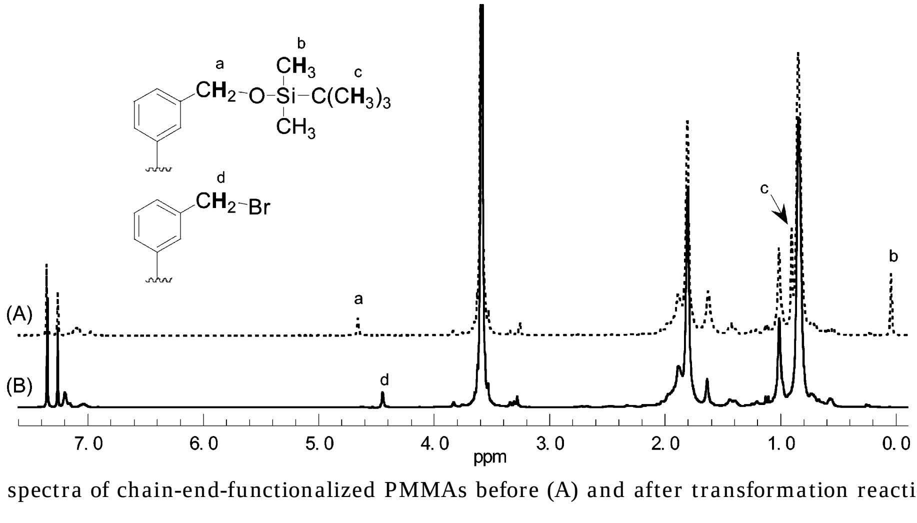
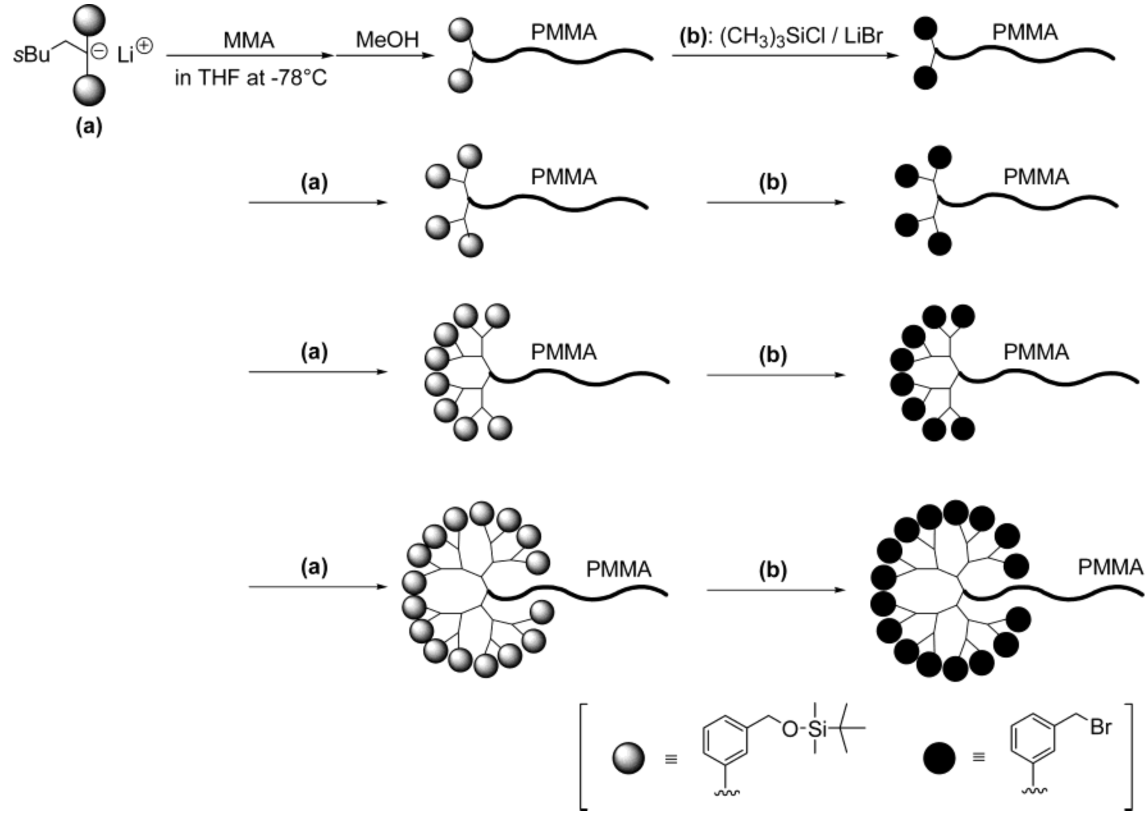


Figure 2. ^1H NMR spectra of chain-end-functionalized PMMAs before (A) and after transformation reaction (B).

Scheme 2. Synthesis of Chain-End-Functionalized PMMAs with Benzyl Bromide Moieties Based on an Iterative Approach



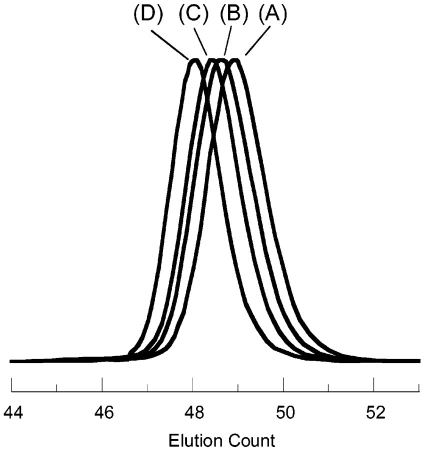


Figure 3. SEC profiles of PMMA(BnBr)$_2$ (A), PMMA(BnBr)$_4$ (B), PMMA(BnBr)$_8$ (C), and PMMA(BnBr)$_{16}$ (D).

between degrees of end-functionalization observed by ^{1}H NMR and calculated was satisfactory in each polymer sample.

To further check the structures of chain-end-functionalized PMMAs synthesized by the iterative methodology, we have newly prepared lower molecular weight chain-end-functionalized PMMAs with two and four 3-*tert*-butyldimethylsilyloxymethylphenyl groups that are precursory polymers of PMMA(BnBr)$_2$ and PMMA(BnBr)$_4$, respectively, and examined structures of these polymers by MALDI−TOF MASS spectroscopy. Figure 4A shows the MALDI−TOF MASS spectrum of chain-end-functionalized PMMA with two 3-*tert*-butyldimethylsilyloxymethylphenyl groups ($M_{n,SEC} = 6470$).

The spectrum exhibits a uniform series of peaks and the expected mass difference of 100.1 mass unit. The centered peak at 6363.7 exactly corresponds to the Na^+ adduct of 58-mer chain-end-functionalized PMMA initiated with the functionalized 1,1-diphenylalkyl anion prepared from **1** and *sec*-BuLi. Figure 4B shows the spectrum of chain-end-functionalized PMMA with four 3-*tert*-butyldimethylsilyloxymethylphenyl groups ($M_{n,SEC} = 7260$) synthesized by the iterative reaction sequence. Again, the spectrum consists of a similar single series of peaks and shifts to a higher mass. The observed shift was in good agreement with the mass of expected structure. Thus, we have also demonstrated by MALDI−TOF MASS spectroscopy that the chain-end-functionalized PMMAs synthesized here possess the expected homogeneous structures, and the iterative methodology works satisfactorily on PMMA main chains as desired. Very unfortunately, MALDI−TOF MASS spectra of a series of PMMA(BnBr)$_n$ could not be obtained.

As illustrated in Scheme 2, in the synthesis of PMMA(BnBr)$_n$ benzyl bromide moieties were introduced from the initiating chain end of PMMA main chain, while the terminating chain end was used for the same purpose in the synthesis of PS(BnBr)$_n$ (see Scheme 1).

In addition to benzyl bromide functionality, the terminal 3-*tert*-butyldimethylsilyloxymethylphenyl group could be transformed quantitatively into benzyl chloride (BnCl), benzyl iodide (BnI), and benzyl alcohol (BnOH) moieties by treatment with BCl_3, $(CH_3)_3SiCl-NaI$, and $(C_4H_9)_4NF$, respectively. Indeed, PMMA(BnCl)$_2$, PMMA(BnI)$_2$, and PMMA(BnOH)$_2$ could be synthesized as summarized in Table 2.

Among them, the successful transformation into benzyl iodide moieties is quite surprising, since it has been reported that alkyl esters are readily cleaved by either $(CH_3)_3SiCl-NaI$ or $(CH_3)_3SiI$.[9c,13,14]

Synthesis of Chain-End-Functionalized Poly(alkyl methacrylate)s with Benzyl Bromide Moi-

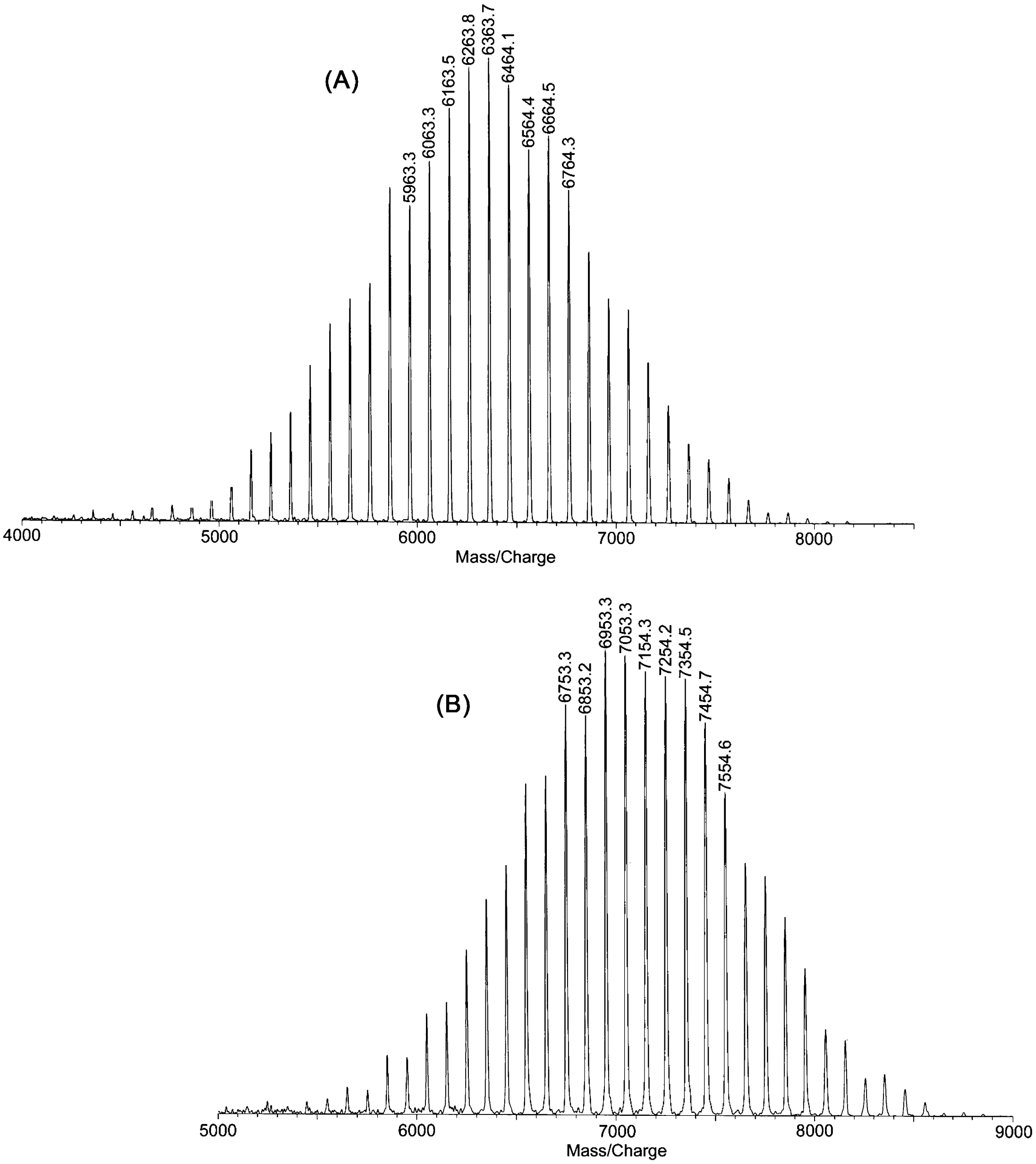


Figure 4. MALDI−TOF MASS spectra of chain-end-functionalized PMMA with two 3-*tert*-butyldimethylsilyloxymethylphenyl groups (A) and four 3-*tert*-butyldimethylsilyloxymethylphenyl groups synthesized via the iterative approach (B).

eties. In this section, we have examined the use of other poly(alkyl methacrylate)s in the iterative methodology. Three alkyl methacrylate monomers, ethyl, isopropyl, and *tert*-butyl methacrylates, were anionically polymerized with the functionalized 1,1-diphenylalkyl anion prepared from **1** and *sec*-BuLi in the presence of a 3-fold excess of LiCl to afford the corresponding three chain-end-functionalized poly(alkyl methacrylate)s with two 3-*tert*-butyldimethylsilyloxymethylphenyl groups. All of the resulting polymers possessed predictable molecular weights, narrow molecular weight distributions, and nearly quantitative degrees of end-functionalization. The results are summarized in Table 3.

Table 3. Synthesis of Chain-End-Functionalized Poly(alkyl methacrylate)s with Two and Four Benzyl Bromide Moieties and In-Chain-Functionalized Polystyrene-*block*-PMMA with Two Benzyl Bromide Moieties[a]

	$M_n \times 10^{-3}$				functionality[b]	
polymer	calcd	SEC	^{1}H NMR	M_w/ M_n	calcd	^{1}H NMR
PEMA(BnBr)$_2$	12.3	13.9	12.3	1.03	2	2.1_2
PEMA(BnBr)$_4$	13.0	14.9	13.0	1.03	4	4.2_0
P^{i}PMA(BnBr)$_2$	13.2	13.3	13.2	1.04	2	2.0_8
P^{i}PMA(BnBr)$_4$	13.9	13.8	13.9	1.03	4	4.2_0
PS(BnBr)$_2$PMMA[c]	20.6	20.0	20.6	1.04	2	2.0_5

[a] Yields of polymers were quantitative in all cases. [b] Functionality of benzyl bromide moieties. [c] In-chain-functionalized polystyrene-*block*-PMMA with two benzyl bromide moieties.

The resulting chain-end-functionalized poly(alkyl methacrylate)s were treated with (CH$_3$)$_3$SiCl−LiBr at 40 °C for 24 h. Before and after the treatment, SEC profiles of the functionalized poly(ethyl methacrylate) (PEMA) and poly(isopropyl methacrylate) (P^{i}PMA) revealed sharp monomodal distributions and remained unchanged in shape. Their two 3-*tert*-butyldimethylsilyloxymethylphenyl groups were completely transformed into two benzyl bromide moieties. On the other hand, difficulty arose in the transformation reaction of chain-end-functionalized poly(*tert*-butyl methacrylate) (P^t-

BMA). The resulting polymer was not soluble in THF, benzene, and hexane but swelled in these solvents. The ^{1}H NMR of the polymer in CD_3OD indicates that the *tert*-butyl ester function was significantly deprotected. Accordingly, P^{t}BMA could not be used in the iterative methodology under the conditions employed here.

In-chain-functionalized polystyrene-*block*-PMMA with two 3-*tert*-butyldimethylsilyloxymethylphenyl groups between the two blocks was prepared by the sequential addition of styrene, **1**, followed by MMA in THF at −78 °C. By treatment with $(CH_3)_3SiCl-LiBr$, a new in-chain-functionalized polystyrene-*block*-PMMA with two benzyl bromide moieties was obtained.

With the use of PEMA$(BnBr)_2$ and P^{i}PMA$(BnBr)_2$ as starting materials, the coupling and transformation reactions were carried out under the identical conditions as mentioned above. As expected, both reactions proceeded efficiently to afford chain-end-functionalized polymers with four benzyl bromide moieties, PEMA$(BnBr)_4$ and P^{i}PMA$(BnBr)_4$, respectively. The results are also listed in Table 3. Thus, PEMA and P^{i}PMA were also successfully used in the iterative methodology. Accordingly, this success may open a novel synthetic route for chain-end-functionalized poly(alkyl methacrylate)s with a definite number of benzyl bromide moieties with many potential application.

Synthesis of Regular Star-Branched Poly(methyl methacrylate)s. Recently, several star-branched PMMAs have been synthesized by means of group transfer polymerization[15] and living radical polymerization.[16−18] Since the multifunctional initiators are generally used for their syntheses, the question regarding the uniformity of the arms in the resulting star-branched polymers still remains. On the other hand, the synthesis of star-branched PMMA and poly(alkyl methacrylate)s by means of anionic polymerization has received little attention until recently. In 1999, Hadjichristidis and co-workers have reported the first successful synthesis of 4-arm star-branched PMMA and P^{t}BMA by the coupling reaction of 1,2,4,5-tetra(bromomethyl)benzene with the corresponding living anionic polymers.[19] Soon after, we have successfully synthesized several asymmetric star-branched polymers containing P^{t}BMA segments by the coupling reaction of PS$(BnBr)_n$ with living anionic polymers of ^{t}BMA.[20] It is thus obvious that the benzyl bromide functionality reacts efficiently with living anionic polymers of alkyl methacrylates. Therefore, a series of PMMA$(BnBr)_n$ synthesized here are expected to undergo coupling reaction with living anionic polymers of alkyl methacrylates to produce star-branched polymers.

Based on such successful coupling reactions, the coupling reaction of living anionic polymer of MMA with either of PMMA$(BnBr)_n$ was carried out in order to synthesize regular star-branched PMMAs. The living PMMA (M_n = ca. 11 kg/mol) was prepared by the living anionic polymerization of MMA with 1,1-diphenyl-3-pentyllithium in the presence of a 3-fold excess of LiCl in THF at −78 °C for 0.5 h and in situ used in the coupling reaction. As the PMMA main chain of PMMA$(BnBr)_n$ is also around 11 kg/mol in molecular weight, the resulting star-branched polymer is substantially regarded as a regular star-branched PMMA. A 2.0-fold excess of the living PMMA to each benzyl bromide moiety was usually used.

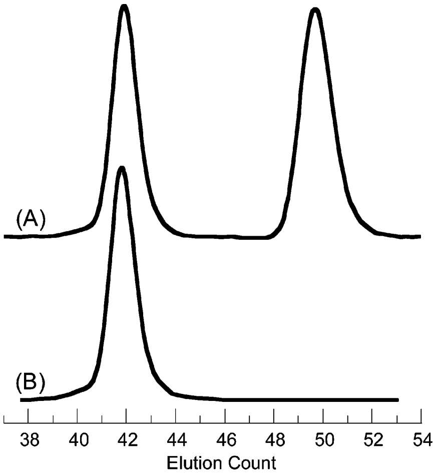


Figure 5. SEC profiles of crude reaction mixture (A) and the 17-arm star-branched PMMA isolated by fractional precipitation (B).

Table 4. Synthesis of 3-, 5-, 7-, and 17-Arm Star-Branched PMMAs[a]

	$M_n \times 10^{-3}$		$M_w \times 10^{-3}$			
type	calcd	SEC	calcd	SLS	d*n*/d*c*	M_w/M_n
A_3	39.1	38.0	39.9	40.5	0.0873	1.02
A_5	58.5	45.3	59.6	61.5	0.0877	1.02
A_9	97.6	58.6	99.6	105	0.0876	1.02
A_{17}	200	91.7	208	205	0.0880	1.04

[a] Linking reactions were carried out in THF at −40 °C for 6 h. Yields of polymers were quantitative in all cases. The M_n values of PMMA segments in PMMA$(BnBr)_n$ and living polymers of MMA were adjusted to be ca. 11 kg/mol in all cases.

The coupling reaction went to completion within 6 h in THF at −40 °C even with the use of PMMA$(BnBr)_{16}$. In each case, SEC profile of the reaction mixture exhibited only two sharp monomodal peaks corresponding to the objective coupled star product eluted at a higher molecular weight side and the deactivated PMMA used in excess in the reaction. The SEC profile of the reaction mixture of living PMMA with PMMA$(BnBr)_{16}$ is shown in Figure 5A. The objective star-branched polymer was isolated in 92% yield by fractional precipitation. The isolated polymer exhibited a sharp monomodal SEC distribution without shoulder and tailing as shown in Figure 5B.

Other star-branched polymers were also similarly isolated and characterized by ^{1}H NMR, SEC, SLS, and viscosity measurements. The results are summarized in Table 4. As expected from their branched architectures, the M_n values estimated by SEC using standard PMMA calibration were always smaller than those predicted in all cases. On the other hand, the absolute M_w values determined by SLS agreed quite well with those predicted within analytical limits. ^{1}H NMR analyses indicated that all of the benzyl bromide moieties had reacted completely. These results demonstrate clearly that the coupling reactions proceed efficiently to afford regular 3-, 5-, 9-, and 17-arm star-branched PMMAs with well-defined structures. As mentioned above, all of the coupling reactions were complete within 6 h in THF at −40 °C. Accordingly, it appears that no steric limitation is encountered in the coupling reaction under the conditions employed.

To further elucidate the star-branched architectures of the resulting polymers, their intrinsic viscosities, $[\eta]_{star}$, were measured in THF at 25 °C and compared

Table 5. Intrinsic Viscosities and g' Values for 3-, 5-, 9-, and 17-Arm Star-Branched PMMAs

		$[\eta]$ (mL/g)			g'		
			$[\eta]_{\mathrm{linear}}$			obsd	
no. of arms	$M_w \times 10^{-3}$ [a]	$[\eta]_{\mathrm{star}}$ [b]	eq 1[c]	eq 3[d]	calcd[e]	eq 1[c]	eq 3[d]
3	40.5	14.8	15.6	17.8	0.83	0.95	0.83
5	61.5	15.9	21.0	23.7	0.63	0.76	0.67
9	105	16.2	30.9	34.4	0.42	0.52	0.47
17	205	16.9	50.1	54.8	0.24	0.34	0.31

[a] Determined by SLS. [b] Measured in THF at 25 °C. [c] Calculated from $[\eta]_{\mathrm{linear}} = 7.5 \times 10^{-3} M_w^{0.72}$ (see text). [d] Calculated from $[\eta]_{\mathrm{linear}} = 1.11 \times 10^{-2} M_w^{0.695}$ (see text). [e] Calculated from $g' = [(3f - 2)/f^2]^{0.58}[0.724 - 0.015(f - 1)]/0.724$.

Table 6. Synthesis of AA′$_8$ Asymmetric Star-Branched PMMAs[a]

time (h)	A′ segment $M_n \times 10^{-3}$	$M_n \times 10^{-3}$ calcd	$M_n \times 10^{-3}$ SEC	$M_w \times 10^{-3}$ calcd	$M_w \times 10^{-3}$ SLS	M_w/M_n	CE[b] (%)
6	31.4	266	125	278	179	1.04	$62._7$
24	31.4	266	137	272	218	1.02	$79._3$
48	30.0	254	135	259	255	1.02	$98._2$

[a] Segment A: PMMA(BnBr)$_8$ (M_n = 15.0 × 10^3). [b] Coupling efficiency (CE) based on $M_{w,\mathrm{SLS}}$.

with $[\eta]_{\mathrm{linear}}$ values of linear PMMAs with the same molecular weights calculated by the following equation.

$$[\eta] = KM_w^{\alpha} \quad (\text{in THF at 25 °C, } K = 7.5 \times 10^{-3},\ \alpha = 0.72\text{; ref 22}) \quad (1)$$

The parameter g' value defined as $[\eta]_{\mathrm{star}}/[\eta]_{\mathrm{linear}}$ determined in each sample is listed in Table 5. Since the g' value has been well correlated to arm number of star-branched polymer based on the theoretical model and experimental results,[23−25] the g' values for 3-, 5-, 9-, and 17-arm star-branched polymers were also calculated from eq 2 proposed by Douglas, Roovers, and Freed and listed in this table.

$$g' = \{[(3f - 2)/f^2]^{0.58}[0.724 - 0.015(f - 1)]\}/0.724 \text{ (ref 25)} \quad (2)$$

As was seen in Table 5, the g' values experimentally determined were somewhat deviated from those calculated. We considered that the deviation might be attributed to the tacticity difference among PMMA samples used in eq 1 and PMMA segments of the star-branched polymers synthesized here. Therefore, we have newly prepared six PMMA samples by the living anionic polymerization of MMA under the same conditions used here and made a new eq 3 by calibrating their $[\eta]$ values against M_w values determined by SLS.

$$[\eta] = KM_w^{\alpha}$$
$$(\text{in THF at 25 °C, } K = 1.11 \times 10^{-2},\ \alpha = 0.695) \quad (3)$$

By using $[\eta]_{\mathrm{linear}}$ values calculated from eq 3, agreement between g' values calculated from eq 2 and experimentally determined became more satisfactory in each sample. Since eq 2 has been applicable to star-branched polymers with high molecular weight arms, good agreement between g' values in our samples with relative low molecular weight arms (M_n = ca. 11 kg/mol) may possibly be due to the less crowded dendritic core structures of star-branched polymers. The expected star-branched architectures of the resulting polymers are thus evident.

As mentioned above, the coupling reaction of either of PMMA(BnBr)$_n$ with living PMMA (M_n = ca. 11 kg/mol) was always complete within 6 h. Under the same conditions, however, the coupling reaction of PMMA(BnBr)$_8$ with living PMMA possessing a higher M_n value of 31.4 kg/mol was not complete. The coupling efficiency of this reaction was 63% based on the M_w value, as shown in Table 6. It was improved to be 79% with increasing the time to 24 h, but not quantitative. A longer reaction time up to 48 h and a 4.0-fold excess of living PMMA (M_n = 30.0 kg/mol) were required to go to near completion in the coupling reaction. The effect of molecular weight on the coupling reaction is thus critical. Taking into consideration of the stability of living PMMA bearing Li$^+$ in the presence of LiCl in THF at −40 °C, the reaction conditions should be reconsidered when living PMMAs with molecular weights higher than, for example, 50 kg/mol are employed.[26]

Synthesis of Asymmetric Star-Branched Polymers Having PMMA Segments. Several asymmetric ABC and A$_2$B$_2$ star-branched polymers having either P(^{t}BMA) or PMMA segments were previously synthesized by using the in situ generated polymer anions as macroinitiators of MMA or ^{t}BMA.[27−32] Recently, we have successfully synthesized asymmetric star-branched polymers with P^{t}BMA segments of the types AB$_2$, AB$_3$, AB$_4$, A$_2$B$_2$, ABC$_2$, and A$_2$B$_4$ by the coupling reaction of living anionic polymer of ^{t}BMA with chain-functionalized polymers with two, three, and four benzyl bromide moieties.[21] In this section, we have described the successful synthesis of new asymmetric stars possessing PMMA segment by using PMMA(BnBr)$_n$ (n = 2 and 4) in the coupling reaction with living anionic polymers of ^{t}BMA, styrene, and isoprene. The results are summarized in Table 7.

As the first attempt, the living P^{t}BMA was prepared by the anionic polymerization with 1,1-diphenyl-3-pentyllithium in the presence of a 3.0-fold excess of LiCl and in situ reacted with PMMA(BnBr)$_2$ in THF at −40

Table 7. Synthesis of Asymmetric Star-Branched Polymers[a]

			$M_n \times 10^{-3}$			$M_w \times 10^{-3}$			
type	segment B[b]	$M_n \times 10^{-3}$	calcd	SEC	^{1}H NMR	calcd	SLS	dn/dc	M_w/M_n
AB$_2$	P(^{t}BMA)	9.66	31.7	26.7	32.3	32.3	33.3	0.0844	1.02
AB$_4$	P(^{t}BMA)	11.3	58.5	37.2	59.6	60.9	62.7	0.0786	1.03
AB$_4$	PI	10.6	55.7	59.8	56.2	56.2	56.1	0.104	1.02
AB$_4$	PS	10.5	55.3	45.1	55.8	56.4	58.5	0.162	1.02

[a] The coupling reactions with living polymers of ^{t}BMA, styrene, and isoprene were carried out in THF at −78 °C for 1 h. Yields of polymers were quantitative in all cases. [b] Segment A: PMMA (M_n of PMMA ≅ 11 kg/mol) in all cases. P(^{t}BMA) = poly(*tert*-butyl methacrylate), PS = polystyrene, and PI = polyisoprene.

°C. Even after 48 h, however, the objective AB$_2$ star-branched polymer was obtained only in 33% yield. On the other hand, the living P^{t}BMA initiated with diphenylmethylpotassium completely coupled with PMMA(BnBr)$_2$ and PMMA(BnBr)$_4$ within 1 h in THF at −78 °C to afford AB$_2$ and AB$_4$ asymmetric star-branched polymers, respectively. With the use of polystyryllithium and polyisoprenyllithium, they were end-capped with DPE prior to the coupling reaction to avoid methyl ester attack by their propagating chain-end anions. The coupling reactions of such end-capped living polymers with PMMA(BnBr)$_4$ were complete in THF at −78 °C within 1 h to afford the corresponding AB$_4$ star-branched polymers. The resulting star-branched polymers were isolated by fractional precipitation or HPLC fractionation and characterized by ^{1}H NMR, SEC, and SLS measurements (see Table 7). All analytical results confirm that the asymmetric star-branched polymers synthesized are well-defined in architecture and well controlled in chain length and composition. Thus, a series of PMMA(BnBr)$_n$ synthesized in this study are very useful polymer coupling agents for the synthesis of both regular and asymmetric star-branched polymers with well-defined structures.

Conclusions

We have successfully extended the iterative divergent methodology previously developed for the synthesis of PS(BnBr)$_n$ to the synthesis of well-defined chain-end-functionalized PMMAs with 2, 4, 8, and 16 benzyl bromide moieties. During the synthesis, it has been demonstrated that PMMA remains stable under the conditions of the iterative reaction sequence involving coupling and transformation reactions where highly reactive basic and acidic reagents are in situ generated. The PMMA(BnBr)$_n$ thus synthesized efficiently coupled with living anionic polymers of MMA, ^{t}BMA, styrene, and isoprene to afford various regular star-branched PMMAs and asymmetric star-branched polymers having PMMA segments.

References and Notes

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