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Successive Synthesis of Well-Defined Star-Branched Polymers by a New Iterative Approach Involving Coupling and Transformation Reactions

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ABSTRACT: Successive synthesis of well-defined star-branched polymers has been successfully achieved by a new iterative methodology based on living anionic polymerization. The methodology involves only two sets of reaction conditions for the entire iterative reaction sequence: (a) a coupling reaction of the benzyl bromide-functionalized polymer with poly(substituted styryl)lithium end-capped with 1-(3-*tert*-butyldimethylsilyloxymethylphenyl)-1-phenylethylene to link two polymer chains and introduce 3-*tert*-butyldimethylsilyoxymethylphenyl group(s) of benzyl bromide precursor(s) and (b) a transformation reaction of the introduced precursor(s) into benzyl bromide functionality (functionalities) by treatment with $(CH_3)_3SiCl-LiBr$. By repeating these two reactions, an array of asymmetric star-branched polymers were successively synthesized. They involved 3-arm ABC, 4-arm ABCD and A_2B_2, and 6-arm $A_2B_2C_2$ stars whose A, B, C, and D segments are polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), poly(methyl methacrylate), or poly(*tert*-butyl methacrylate), respectively. Their high degrees of compositional, molecular weight, and architectural homogeneity as well as narrow molecular weight distributions ($M_w/M_n < 1.05$) were confirmed by the analytical results of SEC, ^{1}H NMR, VPO, and SLS. The poly(*tert*-butyl methacrylate) segments of the $A_2B_2C_2$ star-branched polymer were readily and quantitatively hydrolyzed under the acidic conditions. As a result, a new ionic $A_2B_2C_2$ star having poly(methacrylic acid) segments was obtained.

Introduction

Star-branched polymers have been widely investigated from both experimental and theoretical viewpoints because their behaviors and properties in solution, melt, and solid state are quite distinct from those of the corresponding linear analogues.[1−8] Recently, asymmetric star-branched polymers having arms different in composition have received much attention. Because of their specific heterophase structures, in addition to branched architectures, asymmetric star-branched polymers may possibly induce microdomain arrangements to form novel and interesting nanoscopic objects with suprastructures.[9−14] However, well-defined asymmetric star-branched polymers are generally much more difficult in synthesis than the corresponding regular stars with the same arms because two or more quantitative nature of reactions and the isolation of intermediate polymers during the synthesis are often required. A number of asymmetric star-branched polymers have been synthesized so far, but the structural variation of well-defined asymmetric stars is still limited even at the present time.[13,15−40] Therefore, the development of new methodology is still an important challenge.

We have recently proposed the successive synthesis of star-branched polymers by an iterative methodology as a new concept.[41] The methodology involves only two sets of reaction conditions for the entire iterative synthetic sequence: an addition reaction of living anionic polymer to the 1,1-diphenylethylene (DPE) derivative or the produced DPE-chain-functionalized polymer and a coupling reaction of the newly generated 1,1-diphenylalkyl anions with 1-(4-(4-bromobutyl)phenyl)-1-phenylethylene to introduce DPE functionalities. A typical synthetic outline is illustrated in Scheme 1. The first addition reaction was carried out between two equiv of polystyryllithium (PSLi) and 1,3-bis(1-phenylethenyl)benzene consisting of a double DPE skeleton to link two polystyrene chains accompanying with two 1,1-diphenylalkyl anions newly generated at the linking points. Second, the generated two anions were in situ reacted with 1-(4-(4-bromobutyl)phenyl)-1-phenylethylene to introduce two DPE functionalities to afford an in-chain-functionalized polystyrene with two DPE moieties placed at the middle of the polymer chain. Because this DPE in-chain-functionalized polystyrene also had the DPE functionalities, the same process could be repeated. Actually, a core-functionalized 4-arm star-branched polystyrene with two DPE moieties, followed by a 6-arm star-branched polystyrene with two DPE moieties was successively synthesized by repeating the iterative process two more times. Fortunately, the two reactions in each iterative process proceeded virtually quantitatively to result in the formation of such stars in almost 100% yield. More importantly, the methodology can be readily applied to the synthesis of asymmetric star-branched polymers by using living anionic polymers different in composition. In fact, we were successful in synthesizing asymmetric 4-arm A_2B_2 and 6-arm $A_2B_2C_2$ star-branched polymers by using polystyryllithium (A), poly(α-methylstyryl)lithium (B), and polyisoprenyllithium (C), respectively. With 1,1-bis(3-(1-phenylethenyl)phenyl)ethylene consisting of a triple DPE skeleton in the same iterative methodology, regular A_3, A_6, A_9, A_{12}, and even A_{15} star-branched polystyrenes as well as asymmetric 6-arm A_3B_3 and 9-arm $A_3B_3C_3$ star-branched polymers could be successively synthesized in a similar manner.[42] The key point of this

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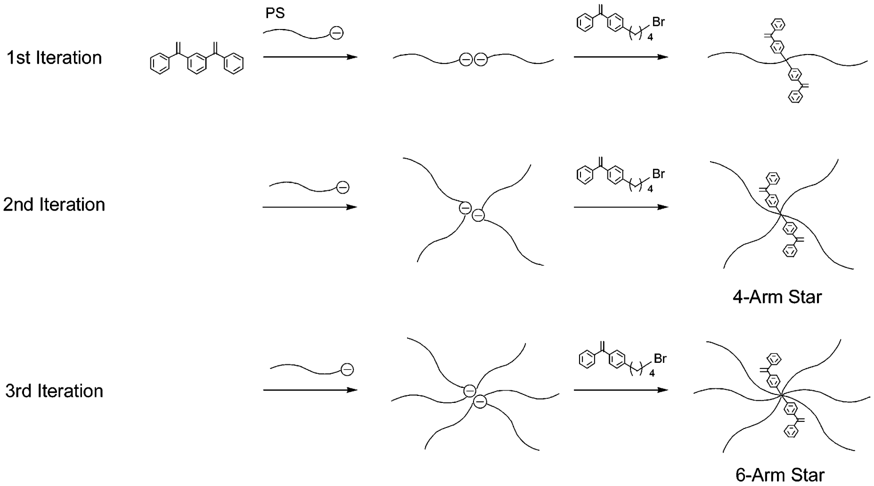
Scheme 1. Successive Synthesis of In-Chain-Functionalized Polystyrene with Two DPE Moieties and Core-Functionalized 4- and 6-Arm Star-Branched Polystyrenes with Two DPE Moieties by an Iterative Methodology Using 1,3-Bis(1-phenylethenyl)Benzene



methodology is that reaction sites can be always regenerated after each of the iterative processes and hence the same reaction sequence can be, in principle, limitlessly repeated to successively synthesize an array of star-branched polymers.

Herein, we report on an alternative iterative methodology for the successive synthesis of star-branched polymers. The methodology involves a coupling reaction of benzyl bromide-functionalized polymer with ω-functionalized living anionic polymer with benzyl bromide precursor(s) and a transformation reaction of the introduced precursor(s) into benzyl bromide functionality (functionalities). The two reactions are repeated in each iterative reaction sequence to successively synthesize star-branched polymers. The objective of the present study is to examine the synthetic possibility and potential of this new alternative methodology, especially for the synthesis of asymmetric star-branched polymers.

Experimental Section

Materials. All chemicals (>98% purities) were purchased from Aldrich, Japan and used as received unless otherwise stated. Tetrahydrofuran (THF) (99%, Mitsubishi Chemical Co., Ltd.) was refluxed over Na wire for 12 h and distilled over $LiAlH_4$ under nitrogen. It was finally distilled from its sodium naphthalenide solution on a high vacuum line (10^{-6} Torr). Diphenylmethylpotassium was prepared from diphenylmethane and potassium naphthalenide in THF according to the method previously reported.[43] Styrene, α-methylstyrene, and 4-methylstyrene (99%, Tokyo Kasei Kogyo Co., Ltd. Japan) were washed with 10% NaOH aq, dried over $MgSO_4$, and distilled over CaH_2 under reduced pressures. They were finally distilled over Bu_2Mg (~5 mol %) on the vacuum line into ampules equipped with break seals that were prewashed with potassium naphthalenide in THF. Methyl and *tert*-butyl methacrylates were washed with 5% NaOH aq and H_2O, dried over $MgSO_4$, and distilled over CaH_2 under reduced pressures. They were finally distilled over trioctylaluminum (>99%, Sumitomo Chemical Co., Ltd.) (~2 mol %) on the vacuum line into ampules equipped with break seals that were prewashed with 1,1-diphenylhexyllithium in heptane. α,α′-Dichloro-*p*-xylene (>99.5%) was recrystallized in hexane and dried under the vacuum line overnight. Acetophenone and *N,N*-dimethylformamide (DMF) were distilled over CaH_2 under reduced pressures. *tert*-Butyldimethylsilyl chloride (99%, Shinetsu Chemical Co., Ltd.) was used as received. Chloroform (99%, Nakarai Tesque Co., Ltd. Japan), acetonitrile (99%, Nakarai Tesque Co., Ltd. Japan), and trimethylsilyl chloride (98%, Tokyo Kasei Kogyo Co., Ltd.) were distilled over CaH_2 under a nitrogen atmosphere. Both LiCl and LiBr (99%, Koso Chemical Co., Ltd.) were dried under the vacuum line at 100 °C overnight. 1,1-Bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene was synthesized according to our procedures previously reported.[44]

Measurements. Size-exclusion chromatography (SEC) was performed on a TOSOH HLC 8020 instrument with UV (254 nm) and refractive index detection. THF was used as a carrier solvent at a flow rate of 1.0 mL/min at 40 °C. Three polystyrene gel columns (pore size (bead size): 650 Å (9 μm), 200 Å (5 μm), and 75 Å (5 μm)) were used. Measurable molecular weight ranges are $10^3-4 \times 10^5$. Calibration curves were made with polystyrene, poly(methyl methacrylate), and poly(*tert*-butyl methacrylate) samples synthesized by us for determining both M_n and M_w/M_n values. Both ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured in $CDCl_3$ using a BRUKER DPX spectrometer. Vapor pressure osmometry (VPO) measurements were made with a Corona 117 instrument in benzene at 40 °C with a highly sensitive thermoelectric couple (TM-32K, sensitivity: 35 000 μV ± 10%/1 M) and with equipment of very exact temperature control. Molecular weight can be measured up to 100 kg/mol with an error of less than 10%. The apparatus constant was obtained by measuring five standard polystyrenes samples and calibrating their values against M_n values. Static light scattering (SLS) measurements were performed with an Ohotsuka Electronics DLS-7000 instrument equipped with a He−Ne laser (633 nm) in THF at 25 °C. The refractive index increment (dn/dc) in THF at 25 °C was determined for each star-branched polymer with an Ohotsuka Electronics DRM-1020 refractometer operating at 633 nm. Intrinsic viscosities were measured with an Ubbelohde viscometer in toluene at 35 °C.

1-(3-*tert*-Butyldimethylsilyloxymethylphenyl)-1-phenylethylene (1). Under a nitrogen atmosphere, acetophenone (6.60 g, 54.9 mmol) in THF (5.0 mL) was added dropwise at 0 °C to a stirred solution of the Grignard reagent, prepared from 2-(3-bromophenyl)-1,3-dioxane (10.1 g, 44.1 mmol) and Mg (1.48 g, 60.9 mmol) in THF (80 mL), and the reaction mixture was stirred at 25 °C for 12 h. It was then acidified with 2 N HCl (100 mL), extracted with ether thrice, and dried over $MgSO_4$. The usual workup afforded crude 1-(3-formylphenyl)-1-phenylethanol as a yellow oil (9.78 g, 43.2 mmol, 98%) and was followed by dehydration with a catalytic amount of *p*-toluenesulfonic acid in benzene (50 mL) at 70 °C for 3 h. After usual workup, 1-(3-formylphenyl)-1-phenylethylene was obtained as an yellow oil (6.93 g, 33.3 mmol, 77%). It was reduced with $NaBH_4$ (2.52 g, 66.6 mmol) in ethanol (150 mL) at 25 °C for 12 h to afford 1-(3-hydroxymethylphenyl)-1-phenylethylene (6.73 g, 32.0 mmol, 96%). Under nitrogen, *tert*-butyldimethylsilyl chloride (5.31 g, 35.2 mmol) in DMF (20 mL) was added at 0 °C to a solution of 1-(3-hydroxymeth-

Table 1. Synthesis of BnBr Chain-End-Functionalized and In-Chain-Functionalized Polystyrenes, 3- and 4-Arm Star-Branched Polystyrenes Using 1 in THF at −78 °C[a]

	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	functionality[d]		$g' = [\eta]$star/$[\eta]$linear[e]	
type	calcd	SEC	VPO	calcd[b]	SLS[c]	SEC	calcd	^{1}H NMR	calcd[f]	exptl
chain-end	10.4	11.0	9.62	10.6	11.2[g]	1.02	1	1.05		
in-chain	22.4	23.6	20.4	22.8	24.1[g]	1.02	1	1.02		
3-arm	34.7	31.2	34.2	35.4	36.2	1.02	1	1.00	0.83	0.83
4-arm	45.2	38.2	44.9	46.1	45.7	1.02	1	1.02	0.71	0.72

[a] Yields of the isolated polymers were always more than 80%. [b] Calculated from M_n (calcd) and M_w/M_n (SEC) values. [c] Measured in toluene at 25 °C. dn/dc = 0.105−0.112 (mL/g). [d] Functionality of BnBr moiety. [e] Intrinsic viscosities of star-branched polystyrenes ($[\eta]_{\text{star}}$) were measured in toluene at 35 °C. Intrinsic viscosities of linear polystyrenes with the same molecular weights ($[\eta]_{\text{linear}}$) were calculated from the equation: $[\eta] = 1.29 \cdot 10^{-4} M_w(\text{SLS})^{0.71}$ values (ref 47). [f] Calculated from eq 1: $g' = [(3f-2)/f^2]^{0.58}[0.724 - 0.015(f-1)]/0.724$. f = arm number ($3 \le f \le 18$) (ref 46). [g] Measured by SEC.

ylphenyl)-1-phenylethylene (6.73 g, 32.0 mmol) and imidazole (6.54 g, 96.0 mmol) in dry DMF (50 mL). The mixture was allowed to stand with stirring at 25 °C for 6 h. After usual workup, flash column chromatography (hexane/benzene = 2:1, v/v) afforded 9.15 g (28.2 mmol, 88%) of the title compound, **1**, as a colorless syrup. A trace amount of water was removed completely by azeotropic distillation from its absolute benzene solution thrice.

^{1}H NMR ($CDCl_3$): δ 7.37−7.25 (9H, m, ArH), 5.49 and 5.47 (2H, ss, CH_2=), 4.76 (2H, s, Ar−CH_2−OSi), 0.940 (9H, s, Si−$C(CH_3)_3$), 0.103 (6H, s, $Si(CH_3)_2$).

^{13}C NMR ($CDCl_3$): δ 150.2 (*C*=CH_2), 141.6 (CH_2=C−*C*(Ar)-CH_2−), 141.4 (CH_2=C−*C*(Ar)), 128.4, 128.3, 128.2, 128.2, 127.7, 126.9, 126.1, and 125.5 (Ar), 114.3 (C=*C*H_2), 65.0 (Ar−*C*H_2−OSi), 26.0 (Si−C(*C*H_3)$_3$), 18.5 (Si−*C*(CH_3)$_3$), −5.2 ($Si(CH_3)_2$).

Preparation of Living Anionic Polymers. All polymerizations were carried out under a high vacuum condition ($<10^{-6}$ Torr) in sealed glass reactors with break seals. The reactors were always prewashed with the initiator solutions after being sealed off from the vacuum line. Polystyryllithium (PSLi), poly(α-methylstyryl)lithium (PαMSLi), and poly(4-methylstyryl)lithium (P4MSLi) were prepared by the *sec*-BuLi-initiated polymerization of the corresponding styrene derivatives in THF at −78 °C for 20 min, 4 h, and 1 h, respectively. The living polymer of methyl methacrylate was obtained by the polymerization of methyl methacrylate in THF at −78 °C for 0.5 h initiated with a 1:1 adduct anion prepared from *sec*-BuLi and a 1.5-fold excess of DPE in the presence of five equiv of LiCl (toward *sec*-BuLi). The living polymer of *tert*-butyl methacrylate was obtained by the polymerization of *tert*-butyl methacrylate with diphenylmethylpotassium in THF at −78 °C for 3 h. Monomers and initiators were used in the concentration ranges of ∼0.5−0.8 M and ∼0.04−0.06 M, respectively.

Successive Synthesis of Star-Branched Polymers by Iterative Methodology Using 1. Synthesis of Chain-End-Functionalized Polystyrene with BnBr Moiety: Under the high vacuum conditions ($<10^{-6}$ Torr), PSLi (2.16 g, 0.196 mmol, M_n (SEC) = 11.0 kg/mol) in THF (22.1 mL) was end-capped with **1** (0.266 mmol) in THF (4.70 mL) at −78 °C, and the mixture was allowed to stir for an additional 30 min at −78 °C. The mixture was quenched with degassed MeOH (5.0 mL) and poured into a large amount of MeOH (300 mL) to precipitate the polymer. It was reprecipitated two times from THF to MeOH and freeze-dried from its benzene solution for 24 h. The resulting polymer (2.12 g, 0.193 mmol) was then treated with trimethylsilyl chloride (1.50 g, 13.8 mmol) and LiBr (0.894 g, 10.3 mmol) in a chloroform/acetonitrile (80 mL/20 mL) mixed solution at 30 °C for 12 h under nitrogen. Then the reaction mixture was poured into water (80 mL), extracted with chloroform (30 mL) four times, and the combined organic layer was dried over $MgSO_4$. Removal of solvent under reduced pressure followed by precipitation into a large amount of MeOH (200 mL) and reprecipitating twice afforded the expected chain-end-functionalized polystyrene with BnBr moiety (1.89 g, 98%, M_n (SEC) = 11.2 kg/mol, M_w/M_n (SEC) = 1.02, and the degree of functionalization determined by ^{1}H NMR = 1.0_5).

First Iterative Process. PSLi (1.12 g, 0.112 mmol, M_n (SEC) = 10.0 kg/mol) in THF (11.5 mL) was end-capped with **1** (0.164 mmol) in THF (2.90 mL) at −78 °C for 30 min and in situ coupled with the chain-functionalized polystyrene with BnBr moiety (0.983 g, BnBr functionality = 0.0878 mmol) in THF (18.2 mL) at −78 °C for 12 h. The polymer mixture was quenched with degassed MeOH (5.0 mL) and poured into a large amount of MeOH (400 mL) to precipitate the polymers. The coupled polymer was isolated in 86% yield (1.81 g) by fractional precipitation where hexane was slowly added into cyclohexane solution of the polymer at 25 °C and the mixture was allowed to stand for 24 h at 5 °C to precipitate the polymer. The introduced 3-*tert*-butyldimethylsilyloxymethylphenyl (SMP) group at the middle of the polymer chain was quantitatively transformed into BnBr moiety under the condition identical with that mentioned above. The expected in-chain-functionalized polystyrene with BnBr moiety was obtained in 95% yield (1.71 g).

Second and Third Iterative Processes. Similarly, the second and third iterations were carried out to successively synthesize 3-, followed by 4-arm star-branched polystyrenes, respectively. A 1.2-fold excess of PSLi end-capped with **1** toward BnBr functionality was always employed in each coupling reaction. The resulting star-branched polystyrenes were isolated by fractional precipitation. Both 3- and 4-arm star-branched polystyrenes were obtained in 90 and 88% yields, respectively. Their detailed results are listed in Table 1.

Similarly, 3-arm ABC, followed by 4-arm ABCD asymmetric star-branched polymers where A, B, C, and D segments were polystyrene, poly (α-methylstyrene), poly(4-methystyrene), and poly(methyl methacrylate) segments, respectively, were successively synthesized starting from the same chain-end-functionalized polystyrene with BnBr moiety synthesized above. Detailed procedures and conditions are as follows:

First Iterative Process. Under the high vacuum conditions ($<10^{-6}$ Torr), PαMSLi (1.02 g, 0.108 mmol, M_n (^{1}H NMR) = 9.45 kg/mol) in THF (10.8 mL) was end-capped with **1** (0.139 mmol) in THF (2.35 mL) at −78 °C for 30 min and in situ coupled with the chain-functionalized polystyrene with BnBr moiety (0.720 g, BnBr functionality = 0.0720 mmol) in THF (7.85 mL) at −78 °C for 1 h. The polymer mixture was quenched with degassed MeOH (5.0 mL) and poured into a large amount of MeOH (200 mL) to precipitate the polymers. The coupled polymer was isolated in 82% yield (1.17 g) by fractional precipitation using a hexane/cyclohexane system. The introduced SMP group at the junction between polystyrene (A) and poly(α-methylstyrene) (B) segments was quantitatively transformed into BnBr moiety under the condition identical with that mentioned above. The expected in-chain-functionalized AB diblock copolymer with BnBr moiety was obtained in 95% yield (1.11 g).

Second Iterative Process. P4MSLi end-capped with **1** (0.793 g, 0.0714 mmol, M_n (^{1}H NMR) = 11.1 kg/mol) was coupled with the BnBr in-chain-functionalized AB diblock copolymer (0.987 g, BnBr functionality = 0.0476 mmol) in THF (22.5 mL) at −78 °C for 6 h. After quenching with MeOH, the coupled polymer was isolated in 88% yield (1.33 g) by fractional precipitation using a hexane/cyclohexane system. The intro-

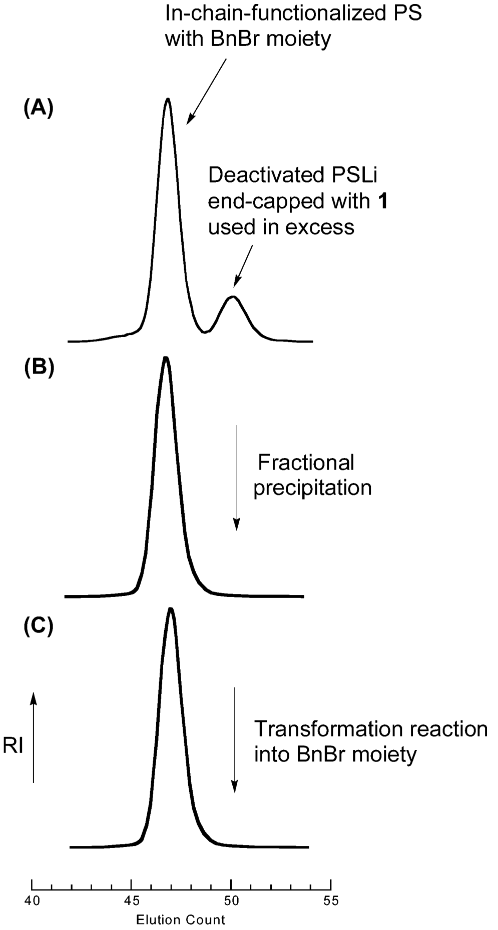


Figure 1. SEC profiles of the resulting polymers obtained by coupling reaction of BnBr chain-end-functionalized polystyrene with PSLi end-capped with **1** and by transformation reaction: (A) before fractionation, (B) after fractionation, and (C) after transformation reaction.

duced SMP group at the core of the ABC star-branched polymer was quantitatively transformed into BnBr moiety. The expected 3-arm ABC asymmetric star-branched polymer with BnBr moiety at the core was obtained in 95% yield (1.11 g).

Third Iterative Process. The living anionic polymer of methyl methacrylate initiated with 1,1-diphenyl-3-methylpentyllithium (0.438 g, 0.0381 mmol, M_n (^{1}H NMR) = 11.5 kg/mol) was coupled with the 3-arm ABC asymmetric star-branched polymer thus synthesized (0.820 g, BnBr functionality = 0.0238 mmol) in THF (15.2 mL) at −40 °C for 12 h. Quenching with MeOH (5.0 mL) followed by fractionally precipitating with a CH_3CN/MeOH (4:1, v/v) mixed solvent afforded the expected 4-arm ABCD asymmetric star-branched polymer in 91% yield (0.992 g).

Successive Synthesis of Star-Branched Polymers by the Same Iterative Methodology Starting from In-Chain-Functionalized Polystyrene with Two BnBr Moieties. First Iterative Process. PSLi (3.31 g, 0.288 mmol, M_n (SEC) = 11.5 kg/mol) in THF (35.0 mL) was end-capped with **1** (0.338 mmol) in THF (2.28 mL) at −78 °C for 30 min, followed by coupling with α,α′-dichloro-*p*-xylene (0.120 mmol) in THF (3.85 mL) at −78 °C. After 1 h, the reaction mixture was quenched with degassed MeOH (5.0 mL) and poured into a large amount of MeOH (400 mL) to precipitate the polymers. The coupled polymer was isolated in 90% yield by fractional precipitation using hexane/cyclohexane. Under nitrogen, the resulting polymer (2.83 g) was treated with trimethylsilyl chloride (1.42 g, 13.1 mmol) and LiBr (0.949 g, 10.9 mmol) in a chloroform/acetonitrile (80 mL/20 mL) mixed solution at 30 °C for 12 h. Then the reaction mixture was poured into water (80 mL), extracted with chloroform (30 mL) four times, and the combined organic layer was dried over $MgSO_4$. Removal of solvent under reduced pressure followed by precipitation into a large amount of MeOH (300 mL) afforded the expected in-chain-functionalized polystyrene with two BnBr moieties (2.78 g, 98%, M_n (SEC) = 24.7 kg/mol, M_w/M_n (SEC) = 1.02 and the degree of functionalization by ^{1}H NMR = 2.0_5).

Second Iterative Process. PαMSLi end-capped with **1** (1.78 g, 0.189 mmol, M_n (SEC) = 9.43 kg/mol) was reacted with the in-chain-functionalized polystyrene with two BnBr moieties (2.22 g, 0.0899 mmol, BnBr functionality = 0.0899 × 2 = 0.180 mmol) in THF (23.9 mL) at −78 °C for 1 h. The reaction mixture was quenched with degassed MeOH (5.0 mL) and poured into a large amount of MeOH (200 mL) to precipitate the polymers. After isolation by fractional precipitation using hexane/cyclohexane, the 4-arm A_2B_2 asymmetric star-branched polymer with two SMP groups at the core where A and B segments were polystyrene and poly(α-methylstyrene) segments, respectively, was obtained in 91% yield (3.53 g). The two SMP groups were quantitatively transformed into two BnBr moieties under the similar condition to that described above, resulting in the formation of the expected 4-arm A_2B_2 asymmetric star-branched polymer with two BnBr moieties at the core in 95% yield (3.33 g).

Third Iterative Process. The living polymer of *tert*-butyl methacrylate initiated with diphenylmethylpotassium (0.653 g, 0.0634 mmol, M_n (^{1}H NMR) = 10.4 kg/mol) was coupled with the 4-arm A_2B_2 asymmetric star-branched polymer thus synthesized (1.07 g, 0.0244 mmol, BnBr functionality = 0.0244 × 2 = 0.0488 mmol) in THF (12.2 mL) at −40 °C for 12 h. Quenching with MeOH (5.0 mL) followed by fractionally precipitating with a large amount of MeOH (200 mL) afforded the expected 6-arm $A_2B_2C_2$ asymmetric star-branched polymer in 85% yield (1.34 g).

Hydrolysis of 6-Arm $A_2B_2C_2$ Star-Branched Polymer. The 6-arm $A_2B_2C_2$ star polymer (0.504 g) synthesized herein was dissolved in a mixture of 12 N HCl (1.0 mL) and 1,4-dioxane (50 mL), and the mixture was allowed to stir at 80 °C for 24 h. It was then concentrated to ~5 mL and poured into a large amount of MeOH to precipitate the polymer (0.451 g, 100% yield). The polymer was reprecipitated twice from the THF solution to MeOH and freeze-dried from its benzene solution for 24 h. Complete hydrolysis of the *tert*-butyl ester function was confirmed by ^{1}H NMR and IR analyses.

^{1}H NMR: δ 7.20−6.20 (m, 1990 H, aromatic), 2.20−0.80 (m, 1246 H, $-CH_2CH(Ph)-$ and $-CH_2C(CH_3)(CO)-$), 0.80−0.60 (m, 24H, $-CH(CH_3)CH_2CH_3$), 0.60 to −0.90 (m, 551 H, $-CH_2C(CH_3)(Ph)-$).

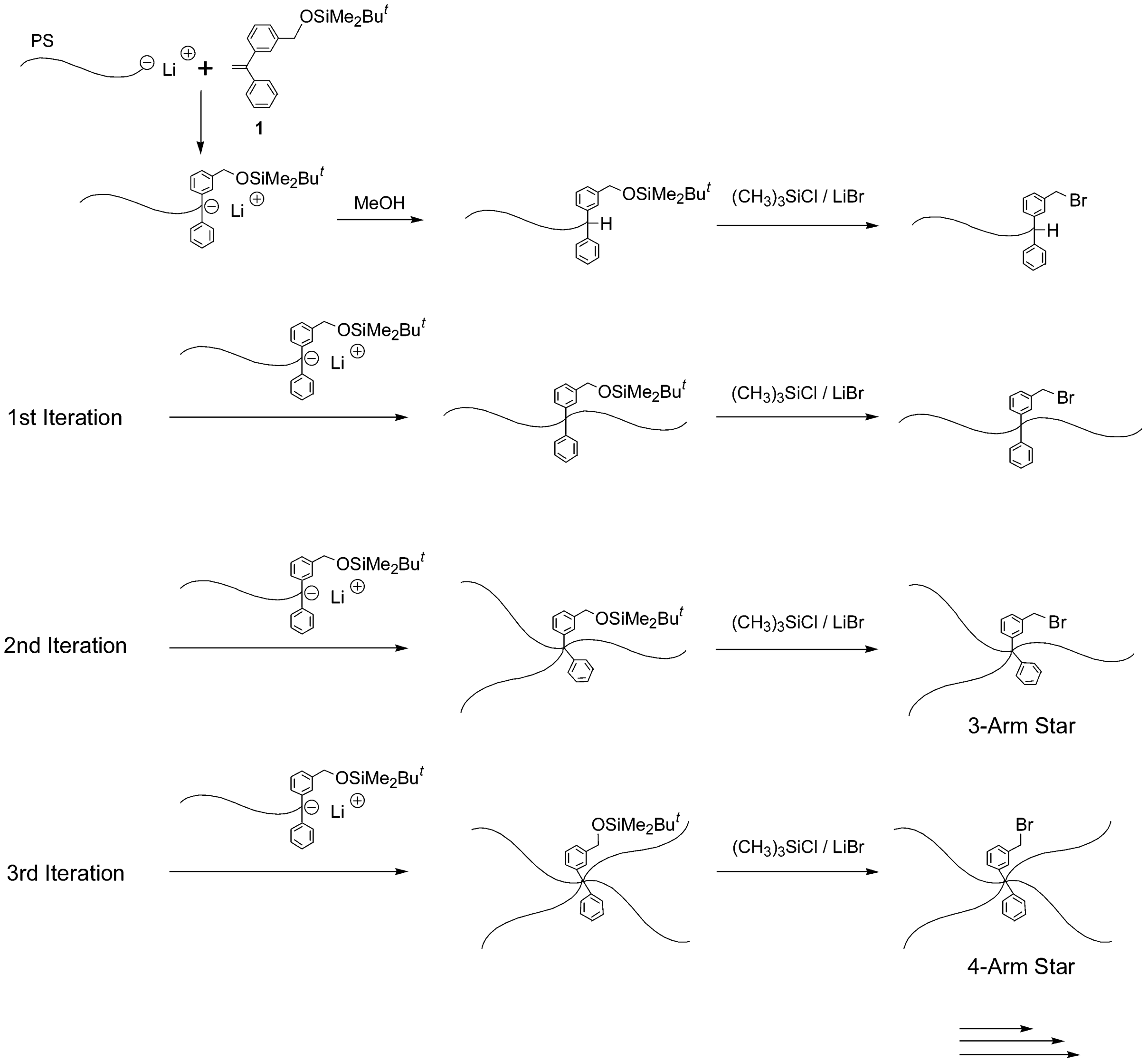
FT-IR (KBr, cm^{-3}): 3420 (O−H), 1720 (C=O).

Isolation and Purification of Polymers. The objective star-branched polystyrenes were effectively isolated from the resulting polymer mixtures by fractional precipitation using hexane/cyclohexane (2:3, v/v) at 5 °C. Hexane was added slowly to a cyclohexane solution of polystyrene (~1 g/150 mL) at 25 °C until the mixture became turbid, and the mixture was allowed to stand at 5 °C for 1 h. The precipitated polymer was recovered by carefully decanting the supernatant solution. The AB block copolymer, ABC, and A_2B_2 stars were also isolated in >80% yields in similar ways. On the other hand, ABCD and $A_2B_2C_2$ star-branched polymers were precipitated by pouring their THF solutions into acetonitrile/MeOH (4:1, v/v) and MeOH, respectively. The polymers all were purified by reprecipitating twice from THF into MeOH and then freeze-drying from their absolute benzene solutions for 6 h thrice.

Results and Discussion

Successive Synthesis of Star-Branched Polymers by Iterative Methodology Using 1-(3-*tert*-Butyldimethylsilyloxymethylphenyl)-1-phenylethylene (1). Scheme 2 shows the first proposed iterative methodology using **1** for the successive synthesis of star-branched polymers. As can be seen, the methodology involves only two sets of reaction conditions for the entire iterative reaction sequence: a coupling reaction

Scheme 2. Successive Synthesis of BnBr Chain-End- and In-Chain-Functionalized Polystyrenes and BnBr Core-Functionalized 3- and 4-arm Star-Branched Polystyrenes by an Iterative Methodology Using 1-(3-*tert*-Butyldimethylsilyloxymethylphenyl)-1-phenylethylene (1)

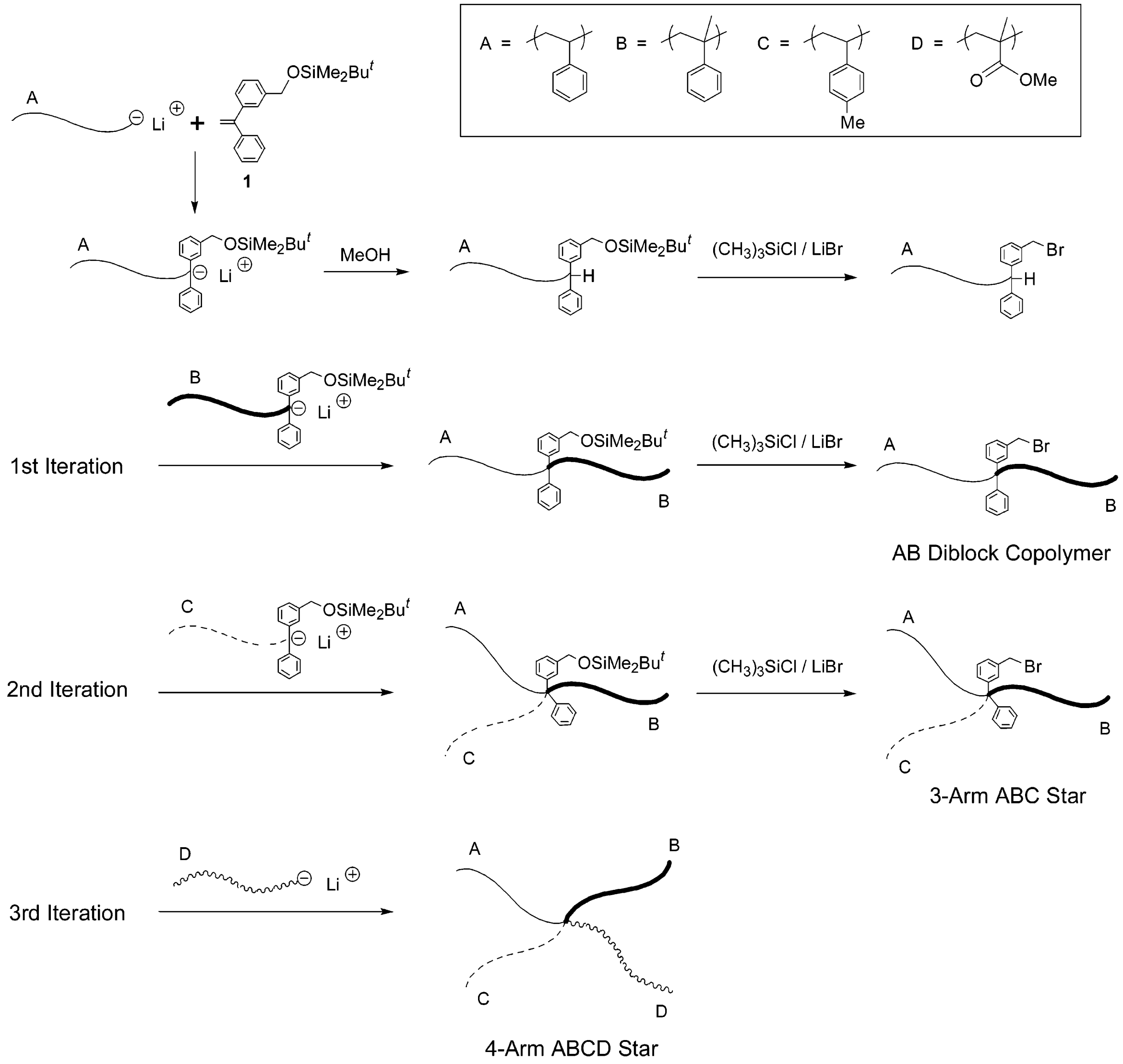


and a transformation reaction. First of all, we have intended to test the synthesis of regular star-branched polystyrenes to make sure whether the proposal methodology does work satisfactorily in terms of the successive star-branched polymer synthesis. Throughout the synthesis, the arm segment was designated to be ~10 kg/mol in M_n value. The starting chain-end-functionalized polystyrene with benzyl bromide (BnBr) moiety was prepared by the end-capping of PSLi with **1**, followed by treatment with $(CH_3)_3SiCl-LiBr$.

The first iterative process involves the coupling reaction of the PSLi end-capped with **1** with the BnBr chain-end-functionalized polystyrene, followed by transformation into a BnBr moiety with $(CH_3)_3SiCl-LiBr$. The SEC profile of the reaction mixture showed only two distinct sharp peaks corresponding to the coupled product and the deactivated PSLi end-capped with **1** used in excess in the reaction (see Figure 1A). The coupling efficiency was essentially quantitative on the basis of the two peak areas. The coupled product was isolated in 86% yield by fractional precipitation and then treated with $(CH_3)_3SiCl-LiBr$. The quantitative transformation of the *tert*-butyldimethylsilyloxymethylphenyl (SMP) group into BnBr functionality was confirmed by ^{1}H NMR spectra showing that the signals at 0.08, 0.94, and 4.66 ppm assigned to methyl protons of the $Si-CH_3$ and $Si-C(CH_3)_3$ groups and methylene protons of the benzyl silyl ether ($-C_6H_4-CH_2-OSi\equiv$) completely disappeared, and alternatively, a new signal at 4.35 ppm characteristic of methylene protons of the BnBr moiety appeared. The degree of BnBr functionalization was confirmed to be quantitative ($f = 1.0_2$) by comparing two signal intensities at 4.35 and 0.64 ppm characteristic to methylene and methyl protons of the BnBr moiety and the initiator fragment, respectively. SEC profiles of the polymers before and after treatment are very similar in shape and distribution as shown in Figure 1B and 1C. As was seen in Table 1, the M_n value of the resulting polymer measured by either SEC or VPO agreed well with that predicted. Thus, the objective in-chain-functionalized polystyrene with BnBr moiety was obtained by the first iteration.

Similarly, the second and third iterative processes were carried out under identical conditions. The SEC profile of the polymer isolated at each reaction stage exhibited a sharp monomodal peak and shifted to a higher molecular weight side as the iteration proceeded. In each case, the coupling efficiency was virtually

Scheme 3. Synthesis of BnBr Chain-End-Functionalized Polystyrene (A), AB Diblock Copolymer, 3-Arm ABC, and 4-Arm ABCD Asymmetric Star-Branched Polymers by the Iterative Methodology Using 1



quantitative on the basis of the SEC profiles. The characterization results are also summarized in Table 1. As expected from smaller hydrodynamic volumes attributable to their star-branched structures,[45] the M_n values of the polymers obtained at the second and third iterations estimated by SEC were somewhat smaller than the predicted values. On the other hand, both M_n and M_w values determined by VPO and SLS were in good agreement with those predicted. The star-branched architectures of the resulting stars could be supported by good agreement between the g′ values defined as $[\eta]_{star}/[\eta]_{linear}$, experimentally determined and predicted from the established eq 1, where f is the arm number for regular star-branched polymers.[46]

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

Overall, the successive synthesis of 3-arm, followed by 4-arm star-branched polystyrenes was successfully achieved without difficulty by repeating the iterative processes three times. Thus, the proposed methodology works satisfactorily.

On the basis of the successive synthesis of regular star-branched polystyrenes successfully achieved, the proposed methodology has been applied to the successive synthesis of asymmetric star-branched polymers with different arms. As illustrated in Scheme 3, the synthesis starts from the same chain-end-functionalized polystyrene with BnBr moiety. Poly(α-methylstyryl)lithium and poly(4-methylstyryl)lithium end-capped with **1** were used in the first and second iterations, respectively. The living anionic polymer of methyl methacrylate initiated with 1,1-diphenyl-3-methylpentyllithium was employed in the coupling reaction of the final iterative reaction sequence. Accordingly, the A, B, C, and D segments were polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), and poly(methyl methacrylate) chains, respectively. The coupling and transformation reactions in each of the iterations were carried out under conditions similar to those employed in the synthesis of regular star-branched polystyrenes. As shown in Figure 2, only two sharp peaks corresponding to the coupled product and the excess living polymer were observed in each of the iterations. No intermediate polymers were present in either case. The coupling efficiencies were virtually quantitative in all cases on the basis of SEC profiles using an UV detector. The coupled products were isolated by fractional precipitation. The characterization results are summarized in Table 2.

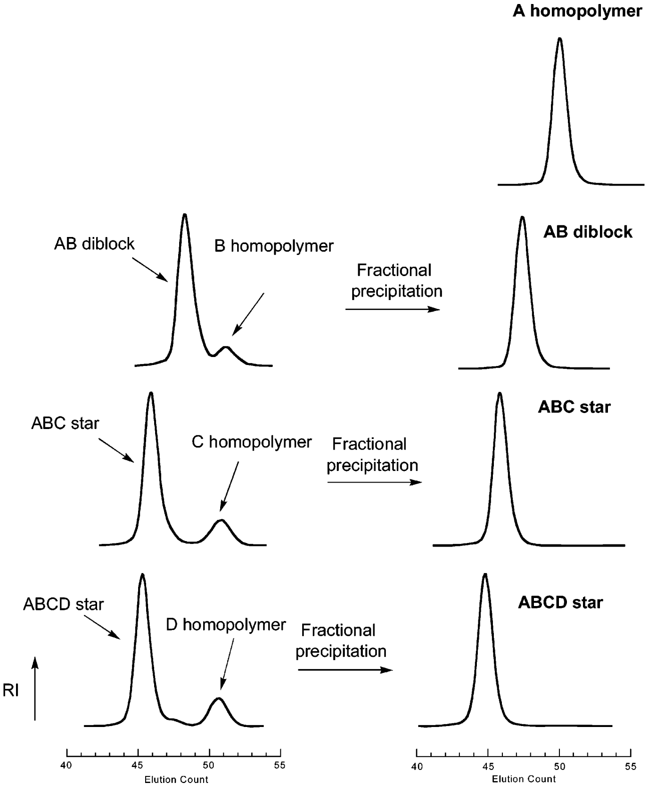


Figure 2. SEC profiles of the resulting reaction mixtures and the isolated polymers in the synthesis of A homopolymer, AB diblock copolymer, 3-arm ABC, and 4-arm ABCD asymmetric star-branched polymers.

The isolated polymers all possessed sharp monomodal SEC distributions without any shoulders and tailings (see also Figure 2). Their M_n and M_w values calculated from monomer-to-initiator ratios were in good agreement with those determined by ^{1}H NMR and SLS, respectively. ^{1}H NMR spectra of these polymers are shown in Figure 3. The resonances characteristic to polystyrene (A) (6.2−7.2 ppm for the phenyl protons), poly(α-methylstyrene) (B) (−0.95−0.5 ppm for the α-methyl protons), poly(4-methylstyrene) (C) (2.35 ppm for 4-methyl protons), and poly(methyl methacrylate) (D) (3.59 ppm for methoxy protons) segments are clearly observed. The compositions measured by ^{1}H NMR using these resonances agreed quite well with those predicted as listed in Table 2. Thus, we were able to successively synthesize in-chain-functionalized AB block copolymer, 3-arm ABC and 4-arm ABCD asymmetric star-branched polymers by repeating the iterative processes three times. Obviously, the proposed methodology is very effective for the successive synthesis of asymmetric star-branched polymers. Incompatibility of the different polymer segments caused by microphase separation seemed not to be affected under the conditions employed here. The successful synthesis of 4-arm ABCD asymmetric star-branched polymer is especially attractive because only two synthetic examples of similar ABCD asymmetric stars have been reported so far.[18b,40]

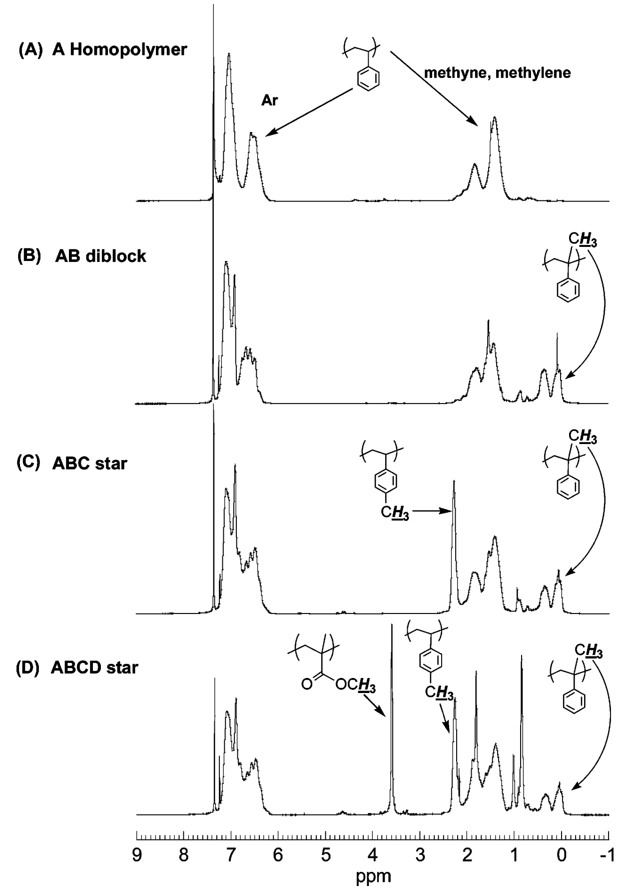


Figure 3. ^{1}H NMR spectra of the isolated (A) A homopolymer, (B) AB diblock copolymer, (C) 3-arm ABC, and (D) 4-arm ABCD asymmetric star-branched polymers.

Successive Synthesis of Star-Branched Polymers by the Same Iterative Methodology Starting with In-Chain-Functionalized Polystyrene with Two BnBr Moieties. To further examine the proposed methodology as a more general procedure, we have intended to synthesize one more series of asymmetric star-branched polymers starting from the newly synthesized in-chain-functionalized polystyrene with two BnBr moieties. The synthetic outline is illustrated in Scheme 4. With this methodology, two polymer segments can be introduced via the two BnBr functionalities in each iteration. The starting polymer was synthesized by the coupling reaction of α,α′-dichloro-*p*-xylene with two equiv of PSLi end-capped with **1** and the subsequent treatment with $(CH_3)_3SiCl-LiBr$ in the first iteration. With use of the in-chain-functionalized polystyrene with two BnBr moieties thus synthesized, the same iterative reaction sequence involving the coupling and transformation reactions was repeated two more times. Living anionic polymers of α-methylstyrene and *tert*-butyl methacrylate (~10 kg/mol) were used in the coupling reactions of the second and third iterative processes, respectively. Accordingly, A, B, and C segments were polystyrene, poly(α-methylstyrene), and poly(*tert*-butyl methacrylate) segments, respectively. The successive synthesis of 4-arm A_2B_2 and 6-arm $A_2B_2C_2$ asymmetric star-branched polymers is thus expected.

In the first iteration, α,α′-dichloro-*p*-xylene was coupled with a 2.4-fold excess of PSLi end-capped with **1** in THF at −78 °C for 1 h. Figure 4(A) shows the SEC profile of the reaction mixture. The coupled product was eluted as a major peak at a higher molecular weight and isolated in 90% yield by fractional precipitation (see Figure 4B). The isolated polymer was then treated with $(CH_3)_3SiCl-LiBr$. The complete transformation from two SMP groups into two BnBr functionalities was confirmed by ^{1}H NMR analysis. The M_n value determined by SEC agreed with that calculated, as was seen

Scheme 4. Successive Synthesis of BnBr In-Chain-Functionalized Polymer, BnBr Core-Functionalized 4-arm A_2B_2, and 6-Arm $A_2B_2C_2$ Asymmetric Star-Branched Polymers by the Iterative Methodology Using 1

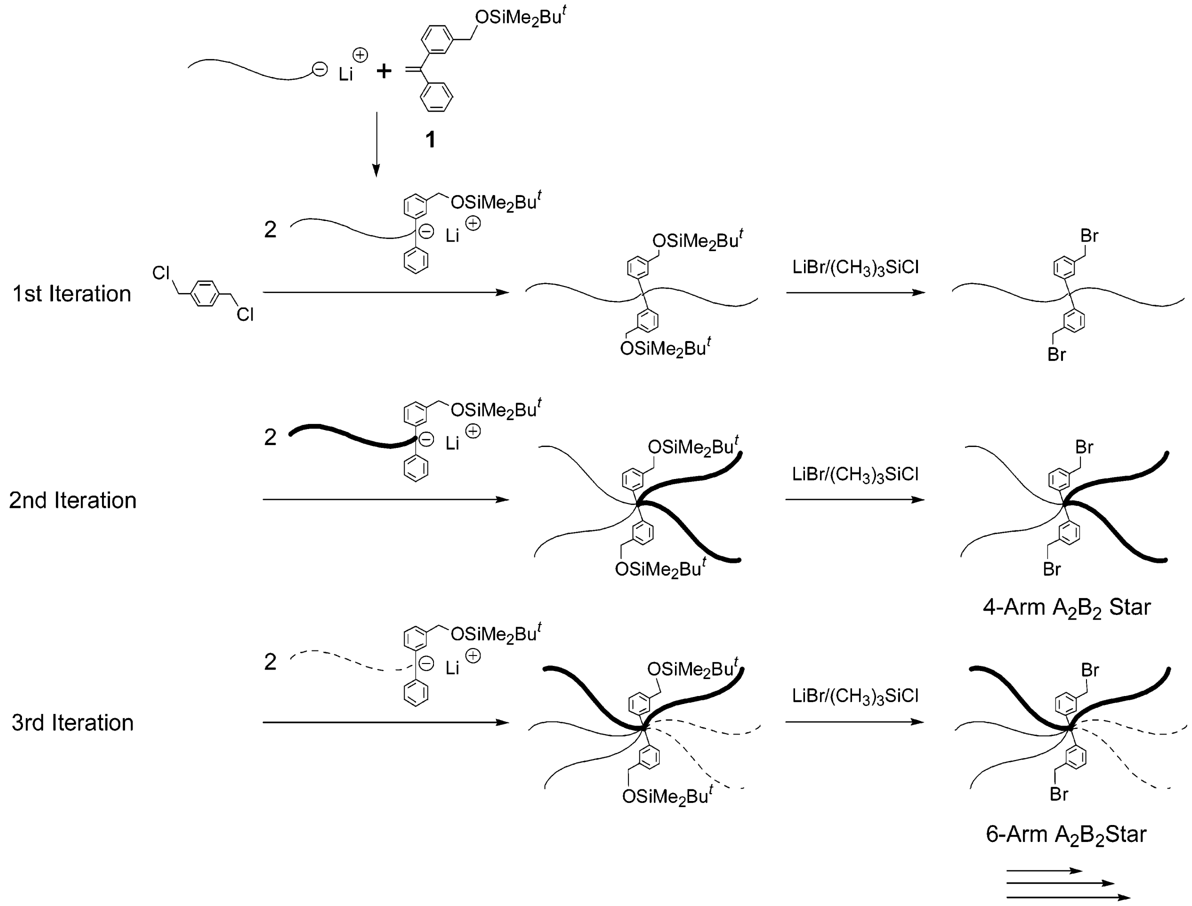


Table 2. Synthesis of BnBr Chain-End-Functionalized Polystyrene (A), AB Diblock Copolymer, 3-Arm ABC and 4-Arm ABCD Asymmetric Star-Branched Polymers Using 1 in THF at −78 °C[a]

	M_n (kg/mol)		M_w (kg/mol)		M_w/M_n	composition (wt %)[d]	
type	calcd	^{1}H NMR	calcd[b]	SLS[c]	SEC	calcd	^{1}H NMR
chain-end (A)	10.4	10.0	10.6	11.2[e]	1.02	100	100
AB diblock	19.8	20.8	20.2	21.2[f]	1.02	50/50	48/52
ABC star	31.7	34.4	32.3	35.7	1.02	32/34/34	34/32/34
ABCD star	45.8	46.5	46.7	48.8	1.02	26/24/25/25	27/23/25/25

[a] Yields of the isolated polymers were always more than 80%. A, B, C, and D segments were polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), and poly(methyl methacrylate), respectively. [b] Calculated from M_n (calcd) and M_w/M_n (SEC) values. [c] In THF at 25 °C. The d*n*/d*c* values were 0.182 and 0.167 mL/g for ABC and ABCD stars. [d] A/B, A/B/C, and A/B/C/D, respectively. [e] Measured by SEC. [f] Calculated from M_n (^{1}H NMR) and M_w/M_n (SEC) values.

Table 3. Synthesis of In-Chain-Functionalized Polystyrene (A_2), 4-Arm A_2B_2 and 6-Arm $A_2B_2C_2$ Asymmetric Star-Branched Polymers in THF at −78 °C[a]

	M_n (kg/mol)				M_w (kg/mol)		M_w/M_n	composition (wt %)[d]	
type	calcd	SEC	VPO	^{1}H NMR	calcd[b]	SLS[c]	SEC	calcd	^{1}H NMR
in-chain (A_2)	23.6	24.7			24.1	25.2[e]	1.02	100	100
A_2B_2 star	43.0	30.5	44.1	43.8	44.3	43.7	1.03	54/46	53/47
$A_2B_2C_2$ star	64.4	46.0	65.5	64.3	65.7	67.0	1.02	36/32/32	36/32/32

[a] Yields of the isolated polymers were always more than 85%. A, B, and C segments were polystyrene, poly(α-methylstyrene), and poly(*tert*-butyl methacrylate), respectively. [b] Calculated from M_n (calcd) and M_w/M_n (SEC) values. [c] In THF at 25 °C. d*n*/d*c* = 0.181 and 0.152 mL/g for types of A_2B_2 and $A_2B_2C_2$ star, respectively. [d] A/B and A/B/C. [e] Measured by SEC.

in Table 3. Thus, the starting in-chain-functionalized polystyrene with two BnBr moieties was obtained.

In the second iteration, the in-chain-functionalized polystyrene with two BnBr moieties was reacted with a 2.1-fold excess of poly(α-methylstyryl)lithium in THF at −78 °C for 1 h, followed by treatment with $(CH_3)_3SiCl-LiBr$ under the same conditions as the first iteration. The SEC profile of the reaction mixture shown in Figure 4C exhibited only two sharp peaks corresponding to the coupled product and the deactivated poly(α-methylstyryl)lithium used in excess in the reaction. The coupled product was isolated in 91% yield by fractional precipitation (see Figure 4D).

The M_n and M_w values of the resulting polymer determined by ^{1}H NMR, VPO, and SLS agreed well with those predicted. As shown in Figure 5B, the ^{1}H NMR

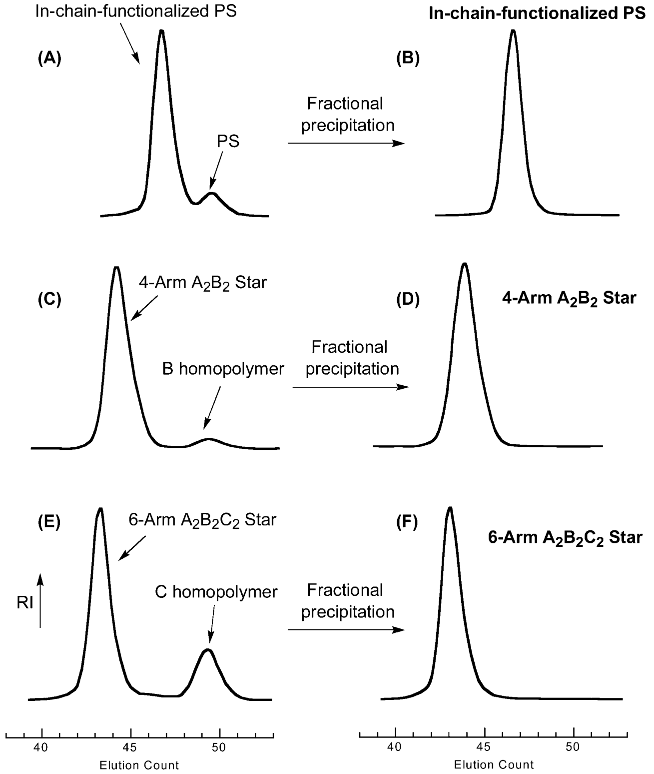


Figure 4. SEC profiles of the starting in-chain-functionalized polystyrene (A and B) and the resulting 4-arm A_2B_2 (C and D), and 6-arm $A_2B_2C_2$ asymmetric star-branched polymers (E and F) before and after fractionation, respectively.

spectrum shows the characteristic resonances at −0.95−0.5 ppm assigned to α-methyl protons of the B segment. The composition measured by the same spectrum was in good agreement with that calculated. Thus, obviously, the resulting polymer proved to be the expected 4-arm A_2B_2 asymmetric star-branched polymer.

Finally, a 6-arm $A_2B_2C_2$ asymmetric star was synthesized by the coupling of the BnBr core-functionalized A_2B_2 star with a 2.6-fold excess of living anionic polymer of *tert*-butyl methacrylate in THF at −40 °C for 12 h. As was observed in Figure 4E, the coupling reaction proceeded satisfactorily. The excess poly(*tert*-butyl methacrylate) was readily removed by washing the polymer mixture with methanol because it was soluble in methanol. The isolated polymer exhibits a sharp monomodal SEC distribution as shown in Figure 4F. As expected, overall SEC profiles shown in Figure 4 clearly demonstrate that each peak of the coupled polymer is narrow and monomodal and shifts to a higher molecular side as the iteration process proceeds. The M_n and M_w values determined by ^{1}H NMR, VPO, and SLS agreed well with those calculated from the feed ratios. As shown in Figure 5C, there are characteristic resonances at 6.2−7.2, −0.95−0.5 and 1.43 ppm assignable to the phenyl protons (polystyrene (A)), the α-methyl protons (poly(α-methylstyrene) (B)), and the methyl protons of the *tert*-butyl group (poly(*tert*-butyl methacrylate) (C)), respectively. The observed composition by ^{1}H NMR using such resonances was almost consistent with that predicted. Accordingly, all of the analytical results clearly indicate that the resulting polymer is the expected 6-arm $A_2B_2C_2$ asymmetric star-branched polymer with well-defined architecture. Again, incompatibility of the different segments was not affected in the synthesis.

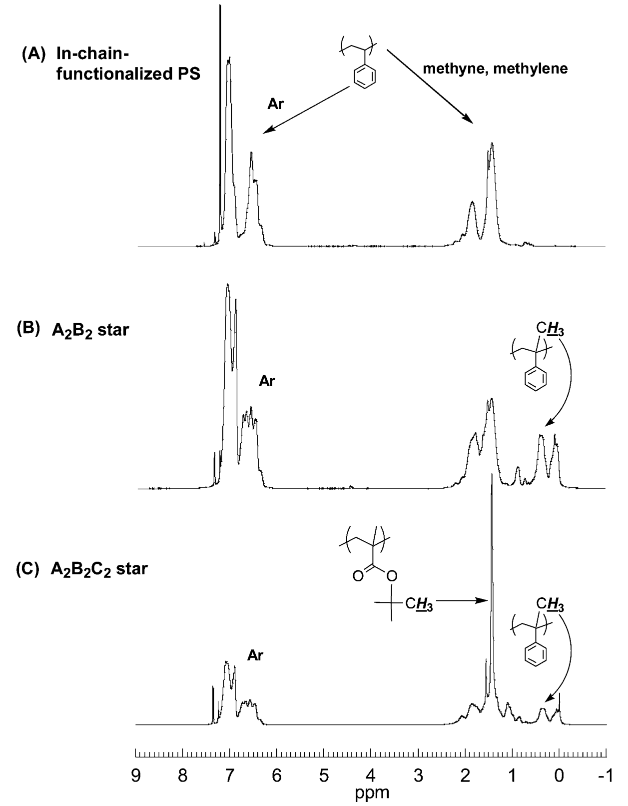


Figure 5. ^{1}H NMR spectra of the isolated (A) in-chain-functionalized PS, (B) 4-arm A_2B_2, and (C) 6-arm $A_2B_2C_2$ asymmetric star-branched polymers.

The iterative methodology proposed in this section works very satisfactorily to be able to successively synthesize 4-arm A_2B_2 and 6-arm $A_2B_2C_2$ asymmetric star-branched polymers. Importantly, the coupling efficiency was always virtually quantitative in each of the reactions, and the resulting polymers all were well-defined in architecture and precisely controlled in chain length.

Interestingly, the asymmetric $A_2B_2C_2$ star-branched polymer thus synthesized could be converted to a new ionic star-branched polymer by hydrolyzing the poly(*tert*-butyl methacrylate) segments to poly(methacrylic acid) segments with 0.2 N HCl in 1,4-dioxane. Table 4 lists solubilities of such $A_2B_2C_2$ stars before and after hydrolysis in usual solvents.

Conclusions

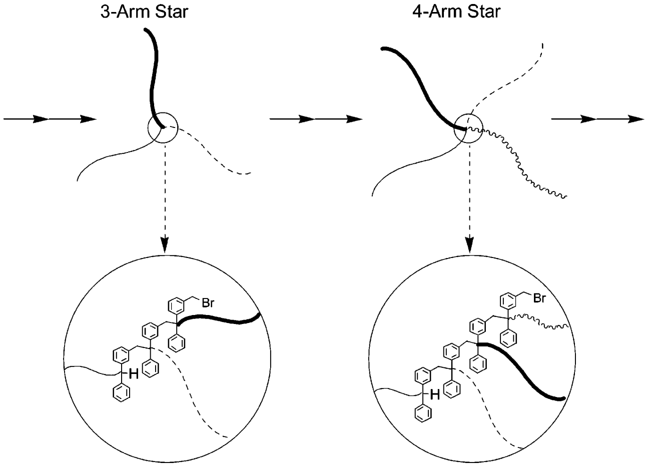
We have proposed a new alternative methodology on the basis of an iterative divergent approach for the successive synthesis of star-branched polymers. The methodology involves only two sets of reaction conditions: (a) a coupling reaction of the BnBr-functionalized polymer with living anionic polymer end-capped with **1** for linking polymer segments and the introduction of BnBr precursor(s) and (b) a transformation reaction of the introduced precursors into BnBr functionalities by treatment with $(CH_3)_3SiCl-LiBr$. The methodology works satisfactorily for the successive synthesis of a series of asymmetric star-branched polymers. In fact, 3-arm ABC, 4-arm ABCD, 4-arm A_2B_2, and 6-arm $A_2B_2C_2$ asymmetric stars were successfully synthesized by employing living anionic polymers of styrene, α-methylstyrene, 4-methylstyrene, methyl methacrylate, and *tert*-butyl methacrylate. One of the successful reasons for the successive star-branched polymer syn-

Table 4. Solubilities of 6-Arm $A_2B_2C_2$ Asymmetric Star-Branched Polymers before and after Hydrolysis[a]

solvent	before hydrolysis	after hydrolysis
hexane	I	I
cyclohexane	S	I
benzene	S	S
diethyl ether	S	I
1,4-dioxane	S	S
THF	S	S
acetone	S	I
ethyl acetate	S	S
methylene dichloride	S	S
chloroform	S	S
N,*N*-dimethylformamide	S	S
pyridine	S	S
acetonitrile	I	I
dimethyl sulfoxide	I	I
ethanol	I	I
methanol	I	I
water	I	I

[a] A, polystyrene; B, poly(α-methylstyrene); and C, poly(*tert*-butyl methacrylate) or poly(methacrylic acid) after hydrolysis. The symbols, S and I, indicate soluble and insoluble, respectively. The concentration of each polymer and the temperature were adjusted to be 10 mg/mL and 25 °C, respectively.

Scheme 5. Successive Synthesis of Star-Branched Polymers



theses may be due to the fact that the arm segments are not emanating from a single point core, but always separated at a regular interval of a connecting alkylphenyl group in the stars synthesized herein as illustrated in Scheme 5. Accordingly, the BnBr reaction sites may possibly be less sterically hindered even after repeating the iteration process and thereby make it possible to continue the iteration. Strictly defining the structures of the resulting polymers, they are more comparable with homopolymers and co-oligomers of macromonomers rather than star-branched polymers.

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