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Successive Synthesis of Well-Defined Many Arm Star-Branched Polymers by an Iterative Methodology Using a Specially Designed 1,1-Diphenylethylene

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ABSTRACT: The synthesis of well-defined regular and asymmetric star-branched polymers having as many as 63 arms, each of similar or different composition, is described. This synthesis has been achieved by developing a new, iterative methodology using a specially designed functionalized reagent, 3,5-bis(3-(4-(1-phenylethenyl)-phenyl)propoxy)benzyl bromide (**5**). This reagent is capable of introducing two 1,1-diphenylethylene (DPE) functions via one reaction site. The methodology involves only two sets of reactions for entire iterative reaction sequence: (a) an addition reaction of living anionic polymer(s) to DPE-chain-functionalized polymer to link polymer chain(s) and (b) an in situ substitution reaction of **5** with 1,1-diphenylalkylanions newly generated after the addition reaction. Two DPE functions are introduced per one anion. With this methodology, well-defined 3-, 7-, 15-, and 31-arm followed by 63-arm regular star-branched polystyrenes as well as 3-arm AB_2, 7-arm AB_2C_4, and 15-arm $AB_2C_4D_8$, followed by 31-arm $AB_2C_4D_8E_{16}$ asymmetric stars were successively synthesized. The A, B, C, D, and E segments were polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), poly(4-methoxystyrene), and poly(4-trimethylsilylstyrene) segments, respectively. All of the analytical results with ^{1}H NMR, SEC, SLS, and RALLS measurements revealed a high degree of structural and compositional homogeneity in each of all the stars synthesized in this study.

Introduction

Star-branched polymers have been widely investigated because of the synthetic challenges associated with preparing them and because they offer unique physical properties, quite different from the linear counterparts.[1−10] Furthermore, asymmetric star-branched polymers whose arms differ in composition have recently attracted much attention due to their abilities to either change the morphological map of their linear counterparts or to create novel morphological features with promising potential applications in nanotechnology.[11−18]

Although many well-defined star-branched polymers have so far been reported, most of these samples are usually composed of less than four arms and have two compositions. The syntheses of stars with many arms have been achieved only in a few cases even at the present time. With the most established methodology based on the linking reaction of living anionic polymers with multifunctional chlorosilane compounds, well-defined stars could be prepared with maximum arm numbers up to 18.[9,19−22] It was also reported that advances in the synthesis of carbosilane dendrimers led to the successful synthesis of poly(1,3-butadiene) stars having 32, 64, and as high as 128 arms.[23,24] However, validity of the chlorosilane linking agents for the synthesis of star-branched polymers with low molecular weight arms (M_n $\sim 10^3$) has recently been reevaluated by NMR and MALDI−TOF MS techniques.[25,26] For stars having theoretically 32 and 64 arms, the average functionalities of the chlorosilane linking agent were found to be 31 and 60, respectively, and the introduced arm numbers were 29 and 54, respectively. Obviously, these results demonstrate the steric requirements in the synthesis of stars with many arms.

The introduction of arms different in composition into star-branched polymers is also limited. For example, several 3-arm three-component ABC and the related asymmetric stars are now available,[12−17,27−37] but only four synthetic examples of 4-arm four-composition ABCD stars have been reported.[38−41] Very recently, we have successfully synthesized more complex 7-arm $A_2B_2C_2D$,[42] 13-arm $A_4B_4C_4D$,[43]and 5-arm ABCDE asymmetric star-branched polymers for the first time.[44,45] The synthetic limitation is attributed to the facts that three or more quantitative nature of reactions for the introducing of different arms and isolation of the intermediate products are often required during the synthesis.

Many-armed star-branched polymers can be readily prepared by linking living anionic polymers with divinyl compounds such as divinylbenzenes and ethylene glycol dimethacrylate. Since many anions were generated at the core of the resulting star-branched polymer by the linking reaction, it was possible to prepare asymmetric stars by adding additional monomers. However, this methodology lacks the precision and control necessary for the synthesis of polymers with well-defined structures and low degrees of compositional heterogeneity.[9c,46] Knauss and co-workers also reported a convenient synthesis of many-armed star-branched polymers by the controlled addition of a dual-functionalized 4-(chlorodimethylsilyl)styrene to poly-styryllithium to form star-branched polystyrene in a convergent fashion. Again, the number of introduced arm could not be precisely controlled by this technique.[47] Therefore, the development of the synthetic methodology for star-branched polymers with many arms, each of similar or different in composition, has been strongly desired.

In a recent few years, we have been developing a new methodology based on iterative approach using specially designed 1,1-diphenylethylene (DPE) derivatives. With this methodology, the successive synthesis of a series of well-defined regular and asymmetric star-branched polymers has been achieved.[40,44,45,48,49] The methodology involves only two sets

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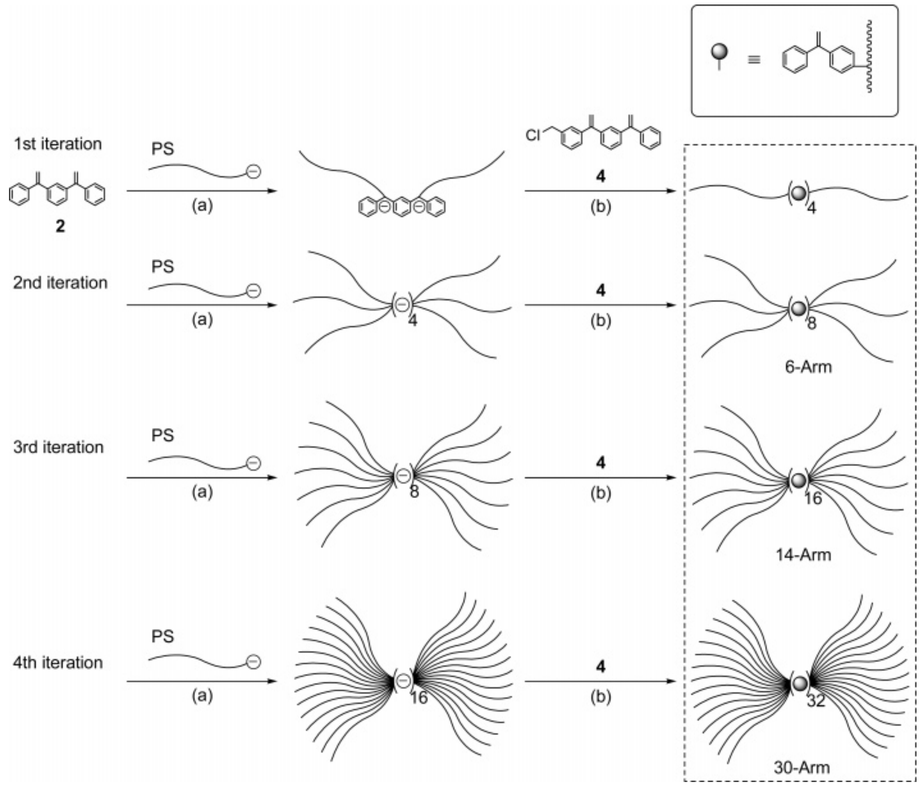
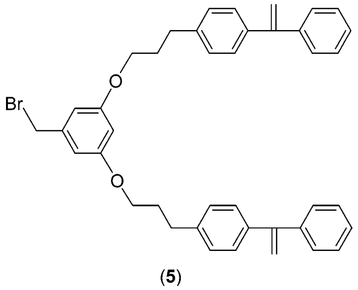
Scheme 1. Successive Synthesis of Regular Star-Branched Polystyrenes by Iterative Methodology Using 4



of reactions for the entire iterative synthetic sequence: (a) an addition reaction of living anionic polymer to a DPE derivative or chain-functionalized polymer with DPE function(s) to link polymer chain(s) and (b) an in situ substitution reaction of the newly generated 1,1-diphenylalkyl anion with 1-(4-(4-bromobutyl)phenyl)-1-phenylethylene (**1**) to introduce DPE functionality. The two reactions, a and b, were repeated four more times with use of a different living anionic polymer in each reaction step a, resulting in the successive formation of AB diblock copolymer, 3-arm ABC and 4-arm ABCD, followed by 5-arm ABCDE asymmetric star-branched polymers, whose A, B, C, D, and E segments were poly(4-trimethylsilylstyrene), poly(4-methoxystyrene), poly(4-methylstyrene), polystyrene, and poly(4-*tert*-butyldimethylsilyloxystyrene) segments, respectively.[40,45] It was also possible to synthesize 3- and 4-arm, followed by 5-arm, star-branched polystyrenes by repeating the two reactions with living polystyrene. Similarly, the successive synthesis of 2-arm A_2, 4-arm A_2B_2, and 6-arm $A_2B_2C_2$ series as well as 3-arm A_3, 6-arm A_3B_3, and more complex 9-arm $A_3B_3C_3$ series asymmetric stars was achieved with 1,3-bis(1-phenylethenyl)benzene (**2**) or 1,1-bis(3-(1-phenylethenyl)phenyl)ethylene (**3**) as a starting core agent.[48,49] Furthermore, 3-, 6-, 9-, and 12-arm, followed by even 15-arm regular star-branched polystyrenes could be synthesized by the same iterative methodology with **3**.[49] The key point of the iterative 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 star-branched polymers. Therefore, it is expected that similar or different arms in composition can be introduced into stars as many as possible until the reactions will be suppressed by the steric requirements.

Very recently, we have extended the above-mentioned methodology for the synthesis of star-branched polymers having more arms.[45] For this purpose, a new functionalized agent, 1-(3-chloromethylpheyl)-1-((3-(1-phenylethenyl)phenyl)ethylene (**4**), was synthesized and used in the reaction step b. This agent is capable of introducing two DPE functionalities via one reaction site. As illustrated in Scheme 1, the entire iterative reaction process is identical with that previously reported, except for the use of **4** in place of **1**. As can be seen, the drastic increment of arm number going from 2, 6, 14, and so on to 30 is expected. In practice, 2- and 6-arm, followed by 14-arm, regular star-branched polystyrenes could be quantitatively obtained without any problem by repeating the iterative process three times. However, it was found that the addition reaction at the fourth iterative process was not complete. The average arm number introduced into the star was 25 less than the theoretical number of 30. The incomplete introduction of arm may possibly be due to the steric hindrance and/or the electrostatic repulsion between PSLi and several 1,1-diphenylalkyl anions generated at the core of the star. It is therefore essential to change the molecular structure **4** in such a way that steric hindrance and electrostatic repulsion around the reaction sites are reduced.

Herein, we report on the improved synthesis of star-branched polymers having many arms similar or different in composition by developing the iterative methodology using a new functionalized agent, 3,5-bis(3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl bromide (**5**):



(**5**)

Experimental Section

Materials. All chemicals (>98% purities) were purchased from Aldrich, Japan, and used as received unless otherwise noted.

Tetrahydrofuran (THF) (99%, Mitsubishi Chemical Co., Ltd.) was refluxed over Na wire for 12 h and then distilled from $LiAlH_4$ under nitrogen. It was finally distilled from its sodium naphthalenide solution on a high vacuum line (10^{-6} Torr). *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) was distilled over CaH_2 twice under nitrogen and then distilled in the presence of BuLi (ca. 5 mol %) on a high vacuum line. *tert*-Butylbenzene was washed with concentrated H_2SO_4, followed by water three times, dried over $CaCl_2$ overnight, and then dried over P_2O_5 for an additional 24 h. It was distilled twice from its BuLi solution under reduced pressure and finally distilled from *sec*-BuLi under high vacuum conditions. DPE, styrene, α-methylstyrene, 4-methylstyrene, and 4-methoxystyrene were washed with 10% NaOH(aq), dried over $MgSO_4$, and distilled over CaH_2 under reduced pressure. 4-Trimethylsilylstyrene was synthesized and purified as previously reported.[50] All monomers were finally distilled over Bu_2Mg (ca. 5 mol %) on the vacuum line into ampules equipped with break-seals that were prewashed with the initiator solutions.

Measurements. Both ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured in $CDCl_3$ or $(CD_3)_2SO$ using a Bruker DPX spectrometer. 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 between 10^3 and 4×10^5. A calibration curve was made with standard polystyrene samples for determining both M_n and M_w/M_n values. Fractionation with SEC was performed with a flow rate of 5.0 mL/min at 40 °C using a Tosoh HLC 8020 fully automatic instrument equipped with a $TSK_{gel}G5000H_{HR}$ column. All runs for fractionation were made with THF as an eluent. 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 refract meter operating at 633 nm. Right angle laser light scatterings (RALLS) were measured on an Asahi Techneion Viscotek model 302 TDA with triple detector software. Three polystyrene gel columns, a TSK_{gel} $G2000H_{HR}$ and two TSK_{gel} GMH_{HR-H}, were used. THF was used as a carrier solvent at a flow rate 1.0 mL/min. Intrinsic viscosities were measured with an Ubbelohde viscometer in toluene at 35 °C.

1-(4-(3-Bromopropyl)phenyl)-1-phenylethylene. Under a nitrogen atmosphere, a mixture of 3-bromopropylbenzene (24.7 g, 124 mmol), benzoyl chloride (32.5 mL, 279 mmol), and $AlCl_3$ (20.1 g, 151 mmol) was heated at 60 °C and stirred for 4 h. After the mixture was cooled to 0 °C, 2 N HCl was added to the mixture, followed by neutralization with solid NaOH. The organic layer was extracted with CH_2Cl_2 three times and dried over $MgSO_4$. After removal of the solvent, the crude product was carefully purified by flash column chromatography on silica gel (hexanes/$CH_3COOC_2H_5$ = 40/1, R_f = 0.2) to afford 4-(3-bromopropyl)benzophenone (24.6 g, 81.1 mmol, 65%) as a yellow liquid. ^1H NMR (300 MHz, $CDCl_3$), δ: 7.81−7.19 (m, 9H, *H*Ar), 3.42 (t, 2H, $-CH_2-$Br), 2.88 (t, 2H, $-CH_2-$Ar), 2.21 (pentad, 2H, $-CH_2-CH_2-$Ar). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 145.7, 137.8, 135.7, 132.3, 130.5, 130.1, 130.0, 128.6, 128.3, 34.0, 33.8, 32.8.

Under a nitrogen atmosphere, 4-(3-bromopropyl)benzophenone (15.7 g, 51.7 mmol) dissolved in THF (20 mL) was added slowly to an ice-cooled THF solution (100 mL) containing methyltriphenylphosphonium bromide (24.3 g, 68.1 mmol) and potassium *tert*-butoxide (6.93 g, 61.9 mmol). The mixture was stirred at 25 °C for 6 h and then quenched with water, extracted with ethyl acetate, and dried over $MgSO_4$. Removal of the solvents by evaporation followed by purification using flash column chromatography on silica gel (hexanes/ $CH_3COOC_2H_5$ = 50/1, R_f = 0.3) gave 1-(4-(3-bromopropyl)phenyl)-1-phenylethylene (7.25 g, 24.1 mmol, 47%) as a colorless viscous liquid. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.33−7.15 (m, 9H, *H*Ar), 5.44 (s, 1H, $CH_2{=}C$), 5.42 (s, 1H, $CH_2{=}C$), 3.41 (t, 2H, $-CH_2-$Br), 2.79 (t, 2H, $-CH_2-$Ar), 2.18 (pentad, 2H, $-CH_2-CH_2-CH_2-$); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 150.2, 142.0, 140.6, 139.8, 129.2, 128.8, 128.7, 128.6, 128.4, 128.1, 126.7, 114.4, 34.5, 34.1, 33.6. Anal. Calcd for $C_{17}H_{17}Br$: C, 67.78; H, 5.69; Br, 26.53. Found: C, 67.92; H, 5.70; Br, 26.50.

3,5-Dihydroxybenzyl Alcohol. Under a nitrogen atmosphere, H_2SO_4 (3 mL) diluted with methanol (10 mL) was slowly added to an ice-cooled methanol solution (100 mL) containing 3,5-dihydroxybenzoic acid (10.3 g, 66.5 mmol) over a period of 10 min. The mixture was refluxed at 95 °C for 4 h. After cooling to room temperature, the solvent was removed. The residue was dissolved in ethyl acetate, washed with brine, and dried over $MgSO_4$. After filtration, the solvent was removed to afford pure methyl 3,5-dihydroxybenzoate (10.1 g, 60.2 mmol, 91%) as a white powder. ^1H NMR (300 MHz, $(CD_3)_2SO$), δ: 9.64 (s, 2H, Ar−O*H*), 6.81 (s, 2H, *H*Ar), 6.44 (s, 1H, *H*Ar), 3.79 (s, 3H, $-O-CH_3$). ^{13}C NMR (75 MHz, $(CD_3)_2SO$), δ: 166.3, 158.6, 131.3, 107.2, 107.1, 52.1.

Under a nitrogen atmosphere, methyl 3,5-dihydroxybenzoate (4.00 g, 23.8 mmol) in THF (30 mL) was slowly added to an ice-cooled THF (100 mL) containing $LiAlH_4$ (4.52 g, 119 mmol) over a period of 20 min. The mixture was stirred at 60 °C for 6 h. After being cooled to 0 °C, ethyl acetate, ethanol, water, and 2 N HCl were successively added to carefully decompose excess $LiAlH_4$. After evaporation of the solvents, the residue was extracted with ethyl acetate and dried over $MgSO_4$. Removal of the solvents, followed by purification with flash column chromatography on silica gel gave 3,5-dihydroxybenzyl alcohol (2.60 g, 18.6 mmol, 78%) as a white powder. ^1H NMR (300 MHz, $(CD_3)_2SO$), δ: 9.12 (s, 2H, Ar−O*H*), 6.20 (s, 2H, *H*Ar), 6.09 (s, 1H, *H*Ar), 5.03 (t, 1H, $Ar-CH_2-OH$), 4.33 (d, 2H, $Ar-CH_2-OH$). ^{13}C NMR (75 MHz, $(CD_3)_2SO$), δ: 159.1, 145.7, 105.2, 101.7, 63.9.

3,5-Bis(3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl Bromide (5). Under a nitrogen atmosphere, a mixture of 1-(4-(3-bromopropyl)phenyl)-1-phenylethylene (5.00 g, 16.6 mmol), 3,5-dihydroxybenzyl alcohol (0.950 g, 6.78 mmol), K_2CO_3 (3.00 g, 21.7 mmol), and *N*,*N*-dimethylformamide (100 mL) was stirred at 68 °C for 18 h, followed by quenching with water. The organic layer was extracted with ethyl acetate and dried over $MgSO_4$. After removal of the solvents by evaporation, the residue was purified by flash column chromatography on silica gel (hexanes/$CH_3COOC_2H_5$ = 5/1, R_f = 0.20) to afford 3,5-bis(3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl alcohol (3.02 g, 5.15 mmol, 76%) as a viscous syrup. ^1H NMR (300 MHz, $CDCl_3$), δ: 7.33−7.15 (m, 18H, HAr), 6.51 (s, 2H, HAr), 6.39 (s, 1H, HAr), 5.44 (s, 2H, $CH_2{=}C-$Ar), 5.41 (s, 2H, $CH_2{=}C-$Ar), 4.61 (s, 2H, $Ar-CH_2-OH$), 3.96 (t, 4H, $Ar-O-CH_2-$), 2.81 (t, 4H, $Ar-CH_2-CH_2-$), 2.10 (pentad, 4H, $-CH_2-CH_2-CH_2-$). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 160.4, 149.8, 143.3, 141.6, 141.1, 139.2, 128.4, 128.2, 127.7, 113.9, 105.2, 100.6, 67.0, 65.4, 31.9, 30.8. Anal. Calcd for $C_{41}H_{40}O_3$: C, 84.79; H, 6.94. Found: C, 84.82; H, 6.95.

Under a nitrogen atmosphere, 3,5-bis(3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl alcohol (3.02 g, 5.15 mmol), triphenylphosphine (2.60 g, 9.91 mmol), and carbon tetrabromide (3.30 g, 9.95 mmol) were dissolved in dry THF (20 mL). The mixture was stirred at 30 °C for 40 min and then carefully quenched with water. The organic layer was extracted with ethyl acetate and dried over $MgSO_4$ for overnight. After evaporation of the solvents, the residue was purified by flash column chromatography on silica gel (hexanes/ $CH_3COOC_2H_5$ = 50/1, R_f = 0.20) to give the objective **5** (1.71 g, 2.66 mmol, 52%). The product was freeze-dried several times from its absolute benzene solution to remove trace of water. ^1H NMR (300 MHz, $CDCl_3$), δ: 7.33−7.16 (m, 18H, *H*Ar), 6.53 (s, 2H, *H*Ar), 6.39 (s, 1H, *H*Ar), 5.45 (s, 2H, CH2 = C−Ar), 5.42 (s, 2H, $CH_2{=}C-$Ar), 4.40 (2, 2H, $Ar-CH_2-Br$), 3.97 (t, 4H, $Ar-O-CH_2-$), 2.82 (t, 4H, $Ar-CH_2-CH_2-$), 2.11 (pentad, 4H, $-CH_2-CH_2-CH_2-$). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 160.3, 149.9, 141.7, 141.1, 139.7, 139.2, 128.4, 128.2, 127.7, 113.9, 107.6, 101.6, 67.1, 33.8, 31.9, 30.7. Anal. Calcd for $C_{41}H_{39}BrO_2$: C, 76.51; H, 6.11; Br, 12.41. Found: C, 76.60; H, 6.15; Br, 12.40.

Preparation of Living Anionic Polymers. All polymerizations and reactions were carried out under high vacuum conditions (10^{-6}

Table 1. Synthesis of Star-Branched Polystyrenes by Iterative Methodology Using 5

type	reaction conditions[a]			M_n (kg/mol)		M_w (kg/mol)		M_w/M_n	g′[d]	
	solvent	temp (°C)	time (h)	calcd	SEC	calcd[b]	SLS[c]	SEC	calcd	exptl
linear	THF	−78		11.5	11.5			1.03		
3-arm	THF	−78	1	31.1	29.3	32.2	33.7	1.03	0.83[e]	0.85
7-arm	THF	−78	24	76.1	59.1	79.4	79.0	1.04	0.51[e]	0.53
15-arm	THF	−78	24	155	75.4	163	166	1.05	0.27[e]	0.28
25/31-arm	THF	−78	48	331	108	344	273	1.04		
31-arm	^{t}BuBz	30	168	314	104	330	330	1.05	0.15[f]	0.16
33/63-arm	^{t}BuBz	30	168	634	115	666	352	1.05		
63-arm	^{t}BuBz[g]	40	72	607	129	625	623	1.03	0.083[f]	0.10
113/127-arm	^{t}BuBz[g]	40	72	1220	156	1280	1130	1.05		

[a] For the addition reaction a. [b] Calculated from M_n(calcd) and M_w/M_n(SEC) values. [c] Measured in toluene at 25 °C. dn/dc = 0.104−0.106 (mL/g). [d] $[\eta]_{star}$ was measured in toluene at 35 °C. $[\eta]_{linear}$ was calculated from the following equation: $[\eta] = 1.29 \times 10^{-4} M_w(\mathrm{SLS})^{0.71}$ values.[55] [e] Calculated from eq 1. [f] Calculated from eq 2. [g] A 2-fold excess of TMEDA toward PSLi was added.

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) was prepared by the *sec*-BuLi-initiated polymerization of styrene in THF at −78 °C for 20 min or in *tert*-butylbenzene at 25 °C for 2 h. Poly(α-methylstyryl)lithium (PαMSLi), poly(4-methylstyryl)lithium (PMSLi), and poly(4-methoxystyryl)lithium (PMOSLi) were prepared by the *sec*-BuLi-initiated polymerization of the corresponding monomers in THF at −78 °C for 3, 1, and 1 h, respectively. These living polymers as well as poly(4-trimethylsilylstyryl)lithium (PSiSLi) were also prepared under the conditions initiated with *sec*-BuLi in *tert*-butylbenzene at 25 °C for 2 h.

Successive Synthesis of Star-Branched Polystyrenes by Iterative Methodology Using 5. Synthesis of Chain-End-Functionalized Polystyrene with Two DPE Moieties. Under high vacuum conditions, PSLi (0.110 mmol) in THF solution (12.0 mL) was added to a THF (3.20 mL) solution containing DPE (0.150 mmol) at −78 °C and the mixture was allowed to stir for 0.5 h. The resulting DPE-end-capped PSLi was reacted in situ with **5** (0.210 mmol) in THF (5.50 mL) at −78 °C for 10 min. Prior to the reaction, Bu_2Mg (0.0540 mmol) was added in order to scavenge impurities in **5**. The reaction mixture was poured into a large amount of methanol (300 mL) to precipitate the polymer. The objective chain-end-functionalized PS with two DPE moieties was purified by reprecipitation twice from THF to methanol, followed by freeze-drying from its absolute benzene solution for 24 h (1.05 g, 89%, M_n(SEC) = 11.5 kg/mol, M_w/M_n(SEC) = 1.03).

First Iterative Process. After PSLi (0.124 mmol, M_n(SEC) = 10.0 kg/mol) in THF (15.0 mL) was added to a THF solution (7.5 mL) containing chain-end-functionalized PS with two DPE moieties (0.590 g, 0.0513 mmol, 0.103 mmol for total DPE moieties) at −78 °C, the mixture was allowed to stand for at −78 °C for an additional 1 h. To avoid the unwanted attack of PSLi, DPE (0.0896 mmol) in THF (3.0 mL) was added to end-cap the excess PSLi, followed by in situ addition of **5** (0.208 mmol) in THF at −78 °C for 10 min. Prior to the reaction, **5** was treated with Bu_2Mg (0.0850 mmol) to scavenge impurities. The mixture was poured into a large amount of methanol to precipitate the polymers. The requisite 3-arm star-branched PS was isolated by fractional precipitation using cyclohexane and hexane at 5 °C and reprecipitated twice (1.27 g, 80%, M_w(SLS) = 33.7 kg/mol, M_w/M_n(SEC) = 1.03).

Second and Third Iterative Processes. The second and third iterative processes were carried out by the same procedure as that employed in the first iteration. A 1.2-fold excess of PSLi was reacted with each of the DPE-chain-functionalized star (PS)s obtained by the first and second iterations in THF at −78 °C for 24 h. The resulting stars were isolated by fractional precipitation with cyclohexane and hexane at 5 °C and reprecipitated twice from their THF solutions to methanol. Thus, both 7-arm and 15-arm star-branched (PS)s were obtained in ~80% yields, respectively. Their detailed results are listed in Table 1.

Fourth Iterative Process. PSLi (0.0753 mmol, M_n(SEC) = 9.96 kg/mol) in *tert*-butylbenzene (10.0 mL) was added to the 15-arm star-branched PS (0.244 g, 0.00157 mmol, 0.0251 mmol for total 16 DPE functions) dissolved in *tert*-butylbenzene (3.05 mL) at 0 °C and the mixture was allowed to stand for at 30 °C for 168 h. After cooling the system to −78 °C, the mixture was diluted with THF (13.5 mL) followed by addition of a THF solution (1.55 mL) of DPE (0.0576 mmol) to end-cap the excess PSLi. Then, the mixture was added in situ to **5** (0.175 mmol) in THF (1.05 mL) for 10 min. Prior to the above reaction, Bu_2Mg (0.0578 mmol) was added to **5** to scavenge impurities. The polymer mixture was precipitated in methanol. The objective 31-arm star-branched PS was isolated by fractional precipitation and reprecipitated twice to afford 0.345 g (71% isolated yield, M_w(SLS) = 330 kg/mol, M_w/M_n(SEC) = 1.05).

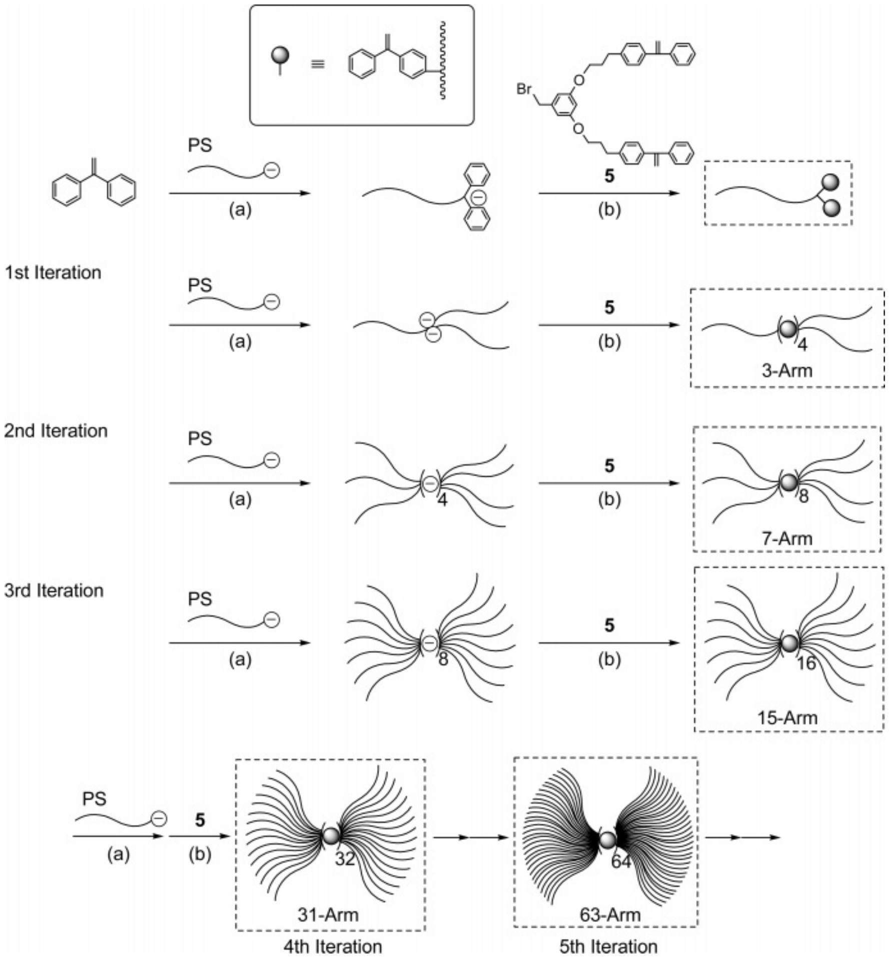
Fifth Iterative Process. A *tert*-butylbenzene solution (10.5 mL) containing PSLi (0.121 mmol, M_n(SEC) = 9.33 kg/mol) was added to the 31-arm star-branched PS (0.455 g, 0.00145 mmol, 0.0464 mmol for total 32 DPE functions) dissolved in *tert*-butylbenzene (4.50 mL) at 0 °C, followed by addition of TMEDA (0.243 mmol) in *tert*-butylbenzene (1.05 mL) at 0 °C. The mixture was allowed to stand for at 40 °C for 72 h. After the system was cooled to −78 °C, the reaction mixture was diluted with THF (12.0 mL) and a THF solution (0.56 mL) of DPE (0.146 mmol) was added to end-cap the excess PSLi. The mixture was added in situ to **5** (0.164 mmol) prepurified with Bu_2Mg (0.0621 mmol) in THF (1.55 mL) at −78 °C for 10 min. The polymers were precipitated in methanol. The objective 63-arm star-branched PS was isolated by fractional precipitation and reprecipitation twice to afford 0.716 g (81% isolated yield, M_w (SLS) = 623 kg/mol, M_w/M_n(SEC) = 1.03).

Sixth Iterative Process. A *tert*-butylbenzene solution (9.55 mL) containing PSLi (0.114 mmol, M_n(SEC) = 9.73 kg/mol) was added to the 63-arm star-branched PS (0.400 g, 0.000658 mmol, 0.0211 mmol for total 32 DPE functions) dissolved in *tert*-butylbenzene (4.55 mL) at 0 °C. TMEDA (0.222 mmol) in heptane (2.90 mL) was subsequently added at 0 °C and the mixture was allowed to stand for at 40 °C for 72 h. After cooling the system to −78 °C, the reaction mixture was diluted with THF (14.4 mL) followed by in situ addition of **5** (0.151 mmol) prepurified with Bu_2Mg (0.0665 mmol) in THF (2.00 mL) at −78 °C for 10 min. The polymers were precipitated in methanol. The star-branched PS was isolated by fractional precipitation using cyclohexane and hexane and reprecipitated twice to afford 0.585 g (83% isolated yield, M_w(SLS) = 1130 kg/mol, M_w/M_n(SEC) = 1.05).

Successive Synthesis of Asymmetric Star-Branched Polymers by Iterative Methodology Using 5. By developing the same iterative methodology under the similar conditions, 3-arm AB_2, 7-arm AB_2C_4, and 15-arm $AB_2C_4D_8$, followed by 31-arm $AB_2C_4D_8E_{16}$, asymmetric star-branched polymers were successively synthesized The A, B, C, D, and E segments of the stars were polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), poly(4-methoxystyrene), and poly(4-trimethylsilylstyrene), respectively. Detailed procedures and conditions are as follows.

First Iterative Process. Poly(α-methylstyryl)lithium (PαMSLi) (0.252 mmol, M_n(obsd) = 10.4 kg/mol) in THF (26.5 mL) was reacted with the chain-end-functionalized PS with two DPE moieties (1.04 g, 0.0873 mmol, 0.175 mmol for total two DPE moieties) in THF (11.0 mL) at −78 °C for 24 h. After adding DPE (0.137 mmol) in THF (1.05 mL) to end-cap the excess PαMSLi, the mixture was

Scheme 2. Successive Synthesis of Star-Branched Polystyrenes with Many Arms by Iterative Methodology Using 5



added in situ to **5** (0.332 mmol) prepurified with Bu_2Mg (0.0502 mmol) in THF (1.01 mL). After 20 min, the resulting polymers were precipitated in methanol. The objective 3-arm AB_2 asymmetric star-branched polymer was isolated by fractional precipitation with cyclohexane and hexane and reprecipitated twice to afford 2.18 g (79% isolated yield, M_w (RALLS) = 35.7 kg/mol, M_w/M_n(SEC) = 1.02).

Second and Third Iterative Process. Both 7-arm AB_2C_4 and 15-arm $AB_2C_4D_8$ asymmetric star-branched polymers were synthesized by the second and third iterative processes under the similar conditions in which poly(4-methylstyryl)lithium and poly(4-methoxystyryl)lithium were used, respectively. A 1.5-fold excess of living anionic polymer toward the DPE functionality was always employed in each addition reaction. The 7-arm AB_2C_4 asymmetric star-branched polymer was isolated by fractional precipitation using cyclohexane and hexane and reprecipitated twice to afford 1.54 g (80% isolated yield, M_w (RALLS) = 79.2 kg/mol, M_w/M_n(SEC) = 1.02). Similarly, the 15-arm $AB_2C_4D_8$ asymmetric star-branched polymer was isolated by fractional precipitation using toluene and methanol and reprecipitated twice to afford 0.846 g (74% isolated yield, M_w (RALLS) = 172 kg/mol, M_w/M_n(SEC) = 1.02).

Fourth Iterative Process. A *tert*-butylbenzene solution (7.55 mL) containing poly(4-trimethylsilylstyryl)lithium (PSiSLi) (0.0770 mmol, M_n(obsd) = 10.3 kg/mol) was added to the 15-arm $AB_2C_4D_8$ star (0.301 g, 0.00189 mmol, 0.0303 mmol for total 16 DPE functions) dissolved in *tert*-butylbenzene (3.15 mL) at 0 °C and the mixture was allowed to stand for at 30 °C for 168 h. After cooling the system to −78 °C, the mixture was diluted with THF (11.5 mL), followed by addition of DPE (0.110 mmol) in THF solution (0.50 mL) to end-cap the excess PSiSLi. The reaction mixture was added in situ to **5** (0.203 mmol) prepurified with Bu_2Mg (0.0892 mmol) in THF (1.55 mL) at −78 °C for 10 min. The polymers were precipitated in methanol. The objective 31-arm $AB_2C_4D_8E_{16}$ asymmetric star-branched polymer was isolated by fractionation with SEC (M_w (RALLS) = 363 kg/mol, M_w/M_n(SEC) = 1.02).

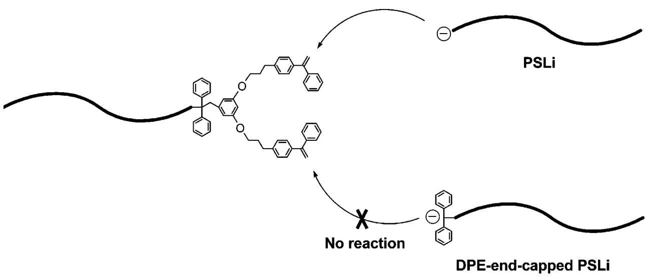
Results and Discussion

Successive Synthesis of Regular Star-Branched Polystyrenes by Iterative Methodology Using 5. We have first synthesized regular star-branched polystyrenes (PS)s to examine whether the iterative methodology using **5** does satisfactorily work. The two DPE moieties of **5** are separated each other by the $C_6H_4O(CH_2)_3$ linkage in order to reduce steric hindrance and electrostatic repulsion around the reaction sites. Throughout the synthesis, PS arm was adjusted to be around 10 kg/mol in M_n value to directly compare the effectiveness of the methodology with those previously reported.

The synthetic outline of regular star-branched (PS)s by the iterative methodology using **5** is illustrated in Scheme 2. Similar to Scheme 1, the methodology involves only two reaction steps for the entire iterative reaction sequence: (a) an addition reaction of PSLi to DPE-chain-functionalized PS to link the polymer chains and (b) an in situ substitution reaction of **5** with the 1,1-diphenylalkyl anions generated after the addition reaction. By this reaction, two DPE moieties can be introduced via one anion. The number of PS arm of the resulting star will increase from 3, 7, 15, and so on to 31.

The first iterative process involves the addition reaction of a 2.4-fold excess of PSLi to the chain-end-functionalized PS with two DPE moieties (a 1.2-fold excess of PSLi over each DPE function), followed by treatment with **5** to introduce four DPE functionalities. The two reactions were carried out under the

Scheme 3. Unwanted PSLi Attack on DPE Moieties



conditions in THF at −78 °C for 1 h and 10 min, respectively. Prior to the treatment with **5**, DPE was added to end-cap the excess PSLi in order to avoid the unwanted PSLi attack on the DPE moieties introduced into the polymer as illustrated in Scheme 3. SEC profile of the reaction mixture shows only two distinct sharp peaks corresponding to the linked product and the PSLi used in excess in the reaction (Figure 1A). The linking efficiency was complete on the basis of the two peak areas. As shown in Figure 1B, the product isolated in 80% yield by fractional precipitation exhibits a sharp monomodal SEC distribution, the M_w/M_n value being 1.03. The results are summarized in Table 1. The ^{1}H NMR spectrum showed the quantitative introduction of four DPE groups into the polymer. The absolute M_w value of 33.7 kg/mol determined by SLS agreed with that predicted ($M_w = 32.2$ kg/mol). Thus, a 3-arm star-branched PS core-functionalized with 4 DPE moieties was obtained.

The second and third iterative processes were carried out under the similar conditions. The reaction time for the step (a) was extended from 1 to 24 h to complete the reaction in either case. SEC profiles of the reaction mixtures showed two distinct sharp peaks (Figure 1, parts C and E). In addition, small peaks corresponding to dimers of the original (PSLi)s were observed between two peaks. They may be formed by the elimination of LiH from PSLi, followed by the addition reaction of the resulting styryl terminus with another PSLi as reported previously.[51,52] In fact, such a dimer formation is usually observed by allowing PSLi to stand for 5 h or longer times under the conditions in THF at −78 °C. SEC profile of the polymer isolated at each stage exhibits a sharp monomodal peak and shifts to a higher molecular weight side as the iteration proceeds as shown in Figure 1, parts D and F. In each case, the linking reaction proceeded virtually completely as confirmed by comparing two SEC peak areas. The characterization results are also summarized in Table 1. The M_n values of the polymers estimated by SEC were smaller than the predicted values as expected from their star-branched architectures. On the other hand, both the M_w values determined by SLS were in good agreement with those predicted. Unfortunately, the DPE functionalities introduced into stars could not be accurately determined due to the signal broadening in both cases.

The star-branched architectures of the resulting stars were also supported by comparing the g' values (defined as $[\eta]_{\text{star}}/[\eta]_{\text{linear}}$) experimentally observed with those calculated from the following established eq 1[53] where f is the arm number for regular star-branched polymers:

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

Indeed, agreement of the g' values between experimentally determined and calculated from eq 1 was very satisfactory in each star, strongly indicating that the resulting polymers possessed 3-, 7-, and 15-arm star-branched architectures (also see Table 1).

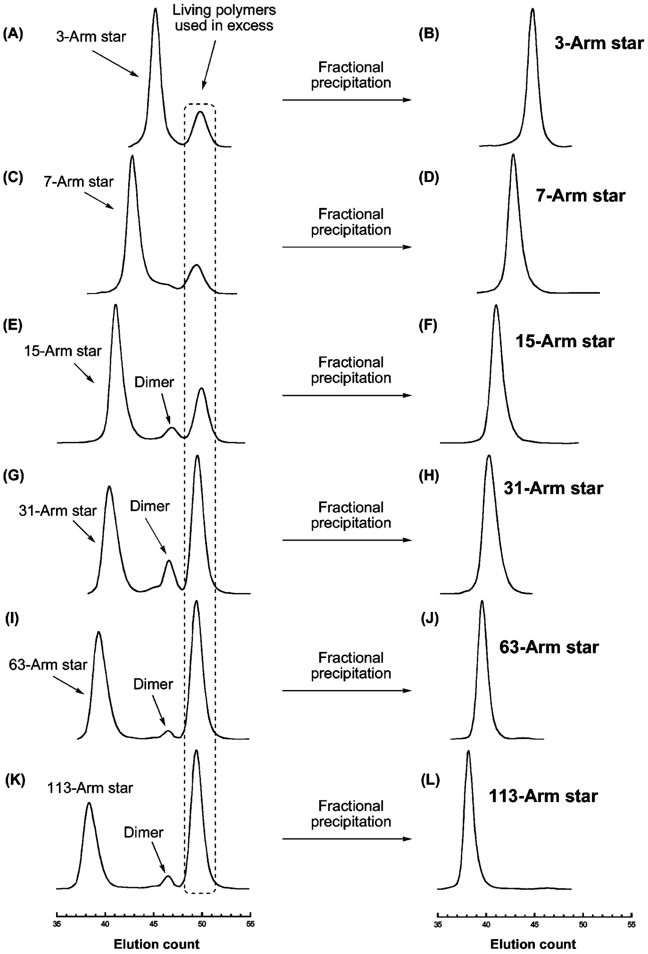
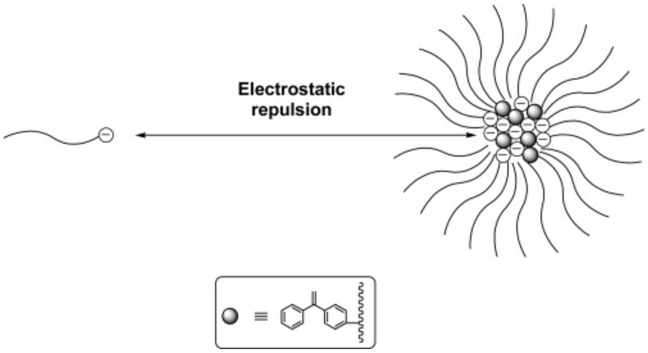


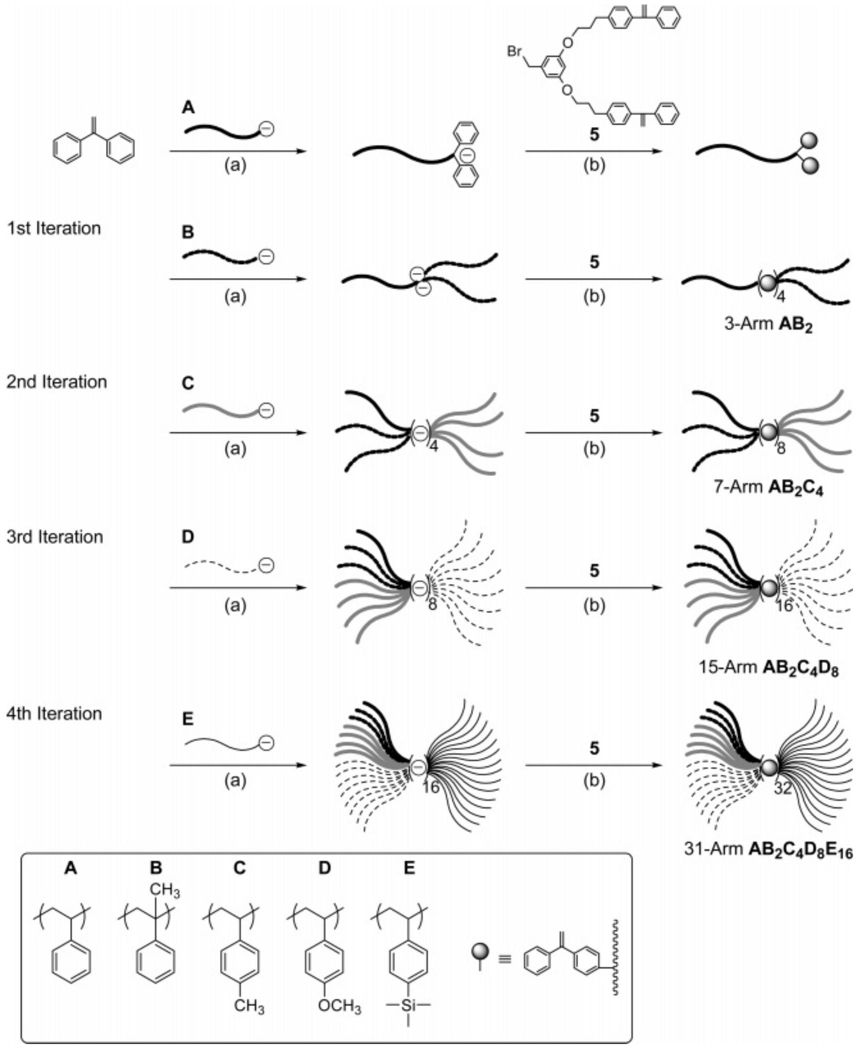
Figure 1. SEC profiles of the reaction mixtures and the isolated regular star-branched polystyrenes.

Scheme 4. Electrostatic Repulsion between PSLi and Many 1,1-Diphenylalkyl Anions Generated on Intermediate Star-Branched Polystyrene



In the fourth iteration, however, the linking reaction of PSLi with the 15-arm star-branched PS with 16 DPE functions was not complete under the conditions in THF at −78 °C for 48 h. For the star-branched PS having theoretically 31 arms, 25 arms were introduced under such conditions. By changing the reaction conditions in *tert*-butylbenzene at 30 °C for 168 h with a 3-fold excess of PSLi, the linking reaction was found to proceed completely. Prior to the in situ treatment with **5**, the reaction system was cooled to −78 °C to add an equal amount of THF, since THF is an essential solvent to suppress the occurring of Li−Br exchange reaction. As can be seen in Figure 1G, two sharp SEC peaks are observed along with a small peak of dimer and the reaction efficiency is quantitative based on these peak areas. The product was isolated by fractional precipitation and

Scheme 5. Successive Synthesis of Asymmetric Star-Branched Polymers by Iterative Methodology Using 5



characterized by SEC, ^{1}H NMR, and SLS, respectively. The SEC profile shown in Figure 1H exhibits a sharp monomodal distribution, the M_w/M_n value being 1.05. The absolute M_w value of 330 kg/mol determined by SLS was in accord with that predicted ($M_w = 330$ kg/mol). In addition, the experimentally observed g' value agreed well with that calculated by the following empirical eq 2 proposed by Roovers,[54] since eq 1 is not suitable for star-branched polymers having more than 17 arms:

$$\log g' = 0.36 - 0.80 \log f \quad (f\text{: arm number}) \qquad (2)$$

Thus, the objective 31-arm star-branched PS could be successfully synthesized by changing the reaction conditions. As mentioned in introduction, the reaction of PSLi with the 16 DPE functions of 14-arm star was not complete under the identical conditions in the same iterative methodology using **4**.[45] Thus, obviously, the use of **5** in place of **4** is effective to facilitate the reaction.

With use of the DPE-core-functionalized 31-arm star-branched PS, the fifth iterative process was carried out under the same conditions. However, the linking reaction proceeded only to a little extent even after 168 h. On the basis of the M_w value determined by SLS, the star having only 33 arms was obtained in this case. To facilitate the linking reaction, 2 equiv of TMEDA to PSLi was added and the reaction was carried out by raising the temperature to 40 °C. Very fortunately, the reaction proceeded completely under such conditions. SEC profile of the reaction mixture exhibits two main sharp peaks and the efficiency is estimated to be quantitative (Figure 1I). After the product was isolated by fractional precipitation, it was characterized by SEC, ^{1}H NMR, and SLS, respectively. The isolated polymer showed a sharp monomodal SEC distribution (see Figure 1J). Agreement of the M_w values between targeted and determined by SLS is quite satisfactory. The g' value was close to that calculated from eq 2. Thus, the fifth iterative process works efficiently to afford a 63-arm star-branched PS. The addition of TMEDA was drastically effective to facilitate the linking reaction, possibly due to the ion dissociation of PSLi to more extent.

With use of the DPE-core-functionalized 63-arm star-branched PS, the sixth iteration was attempted under the same conditions. The reaction mixture shows two main sharp SEC peaks corresponding to the linked product and the excess PSLi (see Figure 1K). The reaction efficiency was estimated to be ca. 80% based on the peak areas, but not quantitative. The objective polymer could be isolated by fractional precipitation with SEC as shown in Figure 1L and characterized by ^{1}H NMR, SEC, and SLS, respectively. On the basis of the SLS result, the introduced arms were 113, but not the expected 127 in number. Thus, the complete introduction of PS arm was not achieved under the best conditions employed in this study, but a narrowly distributed ($M_w/M_n = 1.05$) star-branched PS having many arms

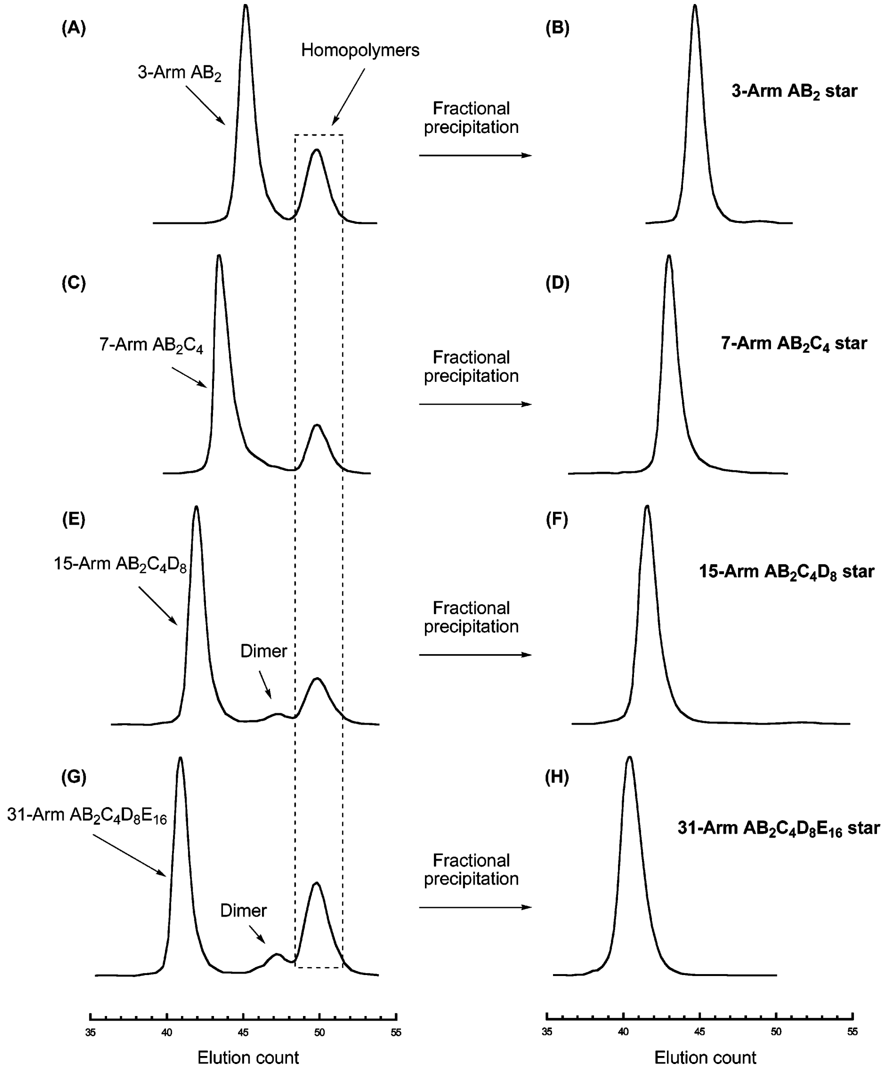


Figure 2. SEC profiles of the reaction mixtures and the isolated asymmetric star-branched polymers.

over 100 arms could be obtained. This result may possibly demonstrate the steric requirements of the linking reaction at the sixth iterative process. In addition, the influence of electrostatic repulsion among PSLi and many 1,1-diphenylalkyl anions generated around the core should also be considered as illustrated in Scheme 4.

In summary, the iterative methodology using **5** works satisfactorily to repeat the iterative process at least five times. As a result, well-defined regular star-branched polystyrenes having 3, 7, 15, and 31 arms, followed by 63 arms, were successively synthesized. The linking reaction conditions are important and critical to complete the reaction. The star-branched (PS)s having 3, 7, and 15 arms were obtained in THF at −78 °C for 1−24 h, while the conditions in *tert*-butylbenzene at 30 °C for 168 h were needed for the synthesis of the star-branched PS having 31 arms. Furthermore, the addition of TMEDA is required to facilitate the linking reaction in *tert*-butylbenzene at 40 °C for 72 h in order to synthesize the star-branched PS having 63 arms. The linking reaction of PSLi with the DPE-core-functionalized 63-arm star-branched PS proceeded efficiently, but not completely, resulting in the formation of the star-branched PS having 113 arms (target: 127 arms).

Successive Synthesis of Asymmetric Star-Branched Polymers by Iterative Methodology Using 5. Similar to the iterative methodology previously reported,[40,44,45,48,49] the methodology developed herein may be applicable to the successive synthesis of asymmetric star-branched polymers whose arms differ in chemical structure. In the preceding section, we demonstrated the synthetic utility of the iterative methodology using **5**. Therefore, the synthesis of asymmetric stars by the same methodology has been examined in this section.

The synthetic outline of asymmetric star-branched polymers is illustrated in Scheme 5. The chain-end-functionalized PS with two DPE moieties was used as a starting polymer. In the first iterative process, the DPE-chain-end-functionalized PS was reacted with a 2.9-fold excess of poly(α-methylstyryl)lithium (PαMSLi) (a 1.4-fold excess over each DPE function) in THF at −78 °C for 24 h, followed by treatment with **5** to introduce four DPE functions. Figure 2A shows SEC profile of the reaction mixture. The product was eluted as a major peak at a higher molecular weight side along with a small low molecular weight peak corresponding to the deactivated PαMSLi used in excess. The efficiency was estimated to be quantitative using UV detector. The product was isolated in a 79% yield by fractional precipitation using cyclohexane/hexane (3/2 by volume) at 5 °C. SEC profile of the isolated product shows a sharp monomodal peak (see Figure 2B). The results are summarized in Table 2. The M_n and M_w values determined by ^{1}H NMR and RALLS agreed with those predicted. The same ^{1}H NMR spectrum showed the expected composition of PS and PαMS segments and the presence of four DPE functions introduced into the polymer (see Figure 3B). Thus, a 3-arm AB_2 asymmetric

Table 2. Synthesis of Asymmetric Star-Branched Polymers by Iterative Methodology Using 5[a]

type	M_n (kg/mol) calcd	M_n (kg/mol) SEC	M_n (kg/mol) ^{1}H NMR	M_w (kg/mol) calcd[b]	M_w (kg/mol) SLS	M_w/M_n SEC	composition[c] calcd	composition[c] ^{1}H NMR
A	11.9	11.6	11.7			1.02		
AB_2	31.5	26.4	31.3	32.1	35.7	1.02	36/64	38/62
AB_2C_4	75.5	55.5	73.3	77.0	79.2	1.02	16/28/56	17/27/56
$AB_2C_4D_8$	159	67.6	161	162	172	1.02	8/12/27/53	8/10/30/52
$AB_2C_4D_8E_{16}$	332	97.9	309	339	363	1.02	4/6/13/27/50	4/7/15/29/46

[a] A, B, C, D, and E segments were polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), poly(4-methoxystyrene), and poly(4-trimethylsilylstyrene), respectively. [b] Calculated from M_n(calcd) and M_w/M_n(SEC) values. [c] A/B, A/B/C, A/B/C/D, and A/B/C/D/E, respectively.

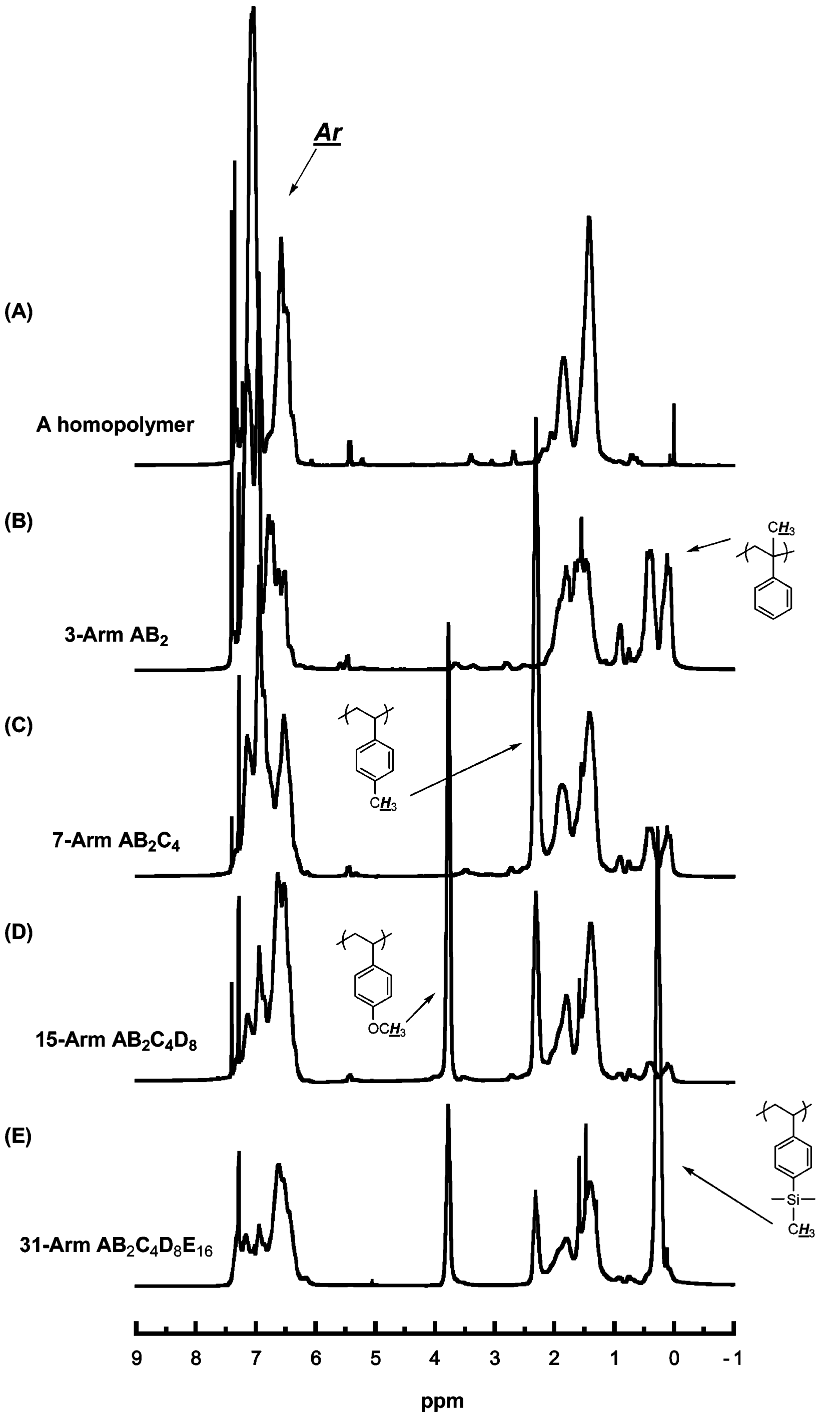


Figure 3. ^{1}H NMR spectra of asymmetric star-branched polymers synthesized by iterative methodology using **5**.

star-branched polymer core-functionalized with 4 DPE moieties was successfully synthesized by the first iteration.

In the second iterative process, the four DPE functions of the core-functionalized 3-arm star were reacted with poly(4-methylstyryl)lithium (PMSLi) (a 1.6-fold excess over each DPE function), followed by treatment with **5** under the same conditions. As is observed in SEC profile of the reaction mixture (Figure 2C), there are two sharp peaks corresponding to the linked product and the deactivated PMSLi used in excess in the reaction. The product was isolated in 80% yield by fractional precipitation and characterized by ^{1}H NMR, SEC, and RALLS, respectively. As shown in Figure 2D, the isolated star possesses a sharp monomodal and symmetrical SEC distribution. The M_n (73.3 kg/mol) and M_w values (79.2 kg/mol) determined by ^{1}H NMR and RALLS agreed well with those calculated ($M_n = 75.5$ kg/mol and $M_w = 77.0$ kg/mol). The molecular weight distribution was quite narrow ($M_w/M_n = 1.02$). The ^{1}H NMR spectrum showed a new resonance at 2.35 ppm assigned to 4-methyl protons of the PMS (C segment) together with those at 6.2−7.2 and −0.95 to −0.5 ppm corresponding to phenyl protons of the A, B, and C segments and α-methyl protons of the PαMS (B segment), respectively (see Figure 3C). It was found that agreement of the compositions between determined by ^{1}H NMR (17/27/56, A/B/C by weight) and calculated from the feed ratios (16/28/56) was excellent by comparing these resonance peak areas. The same spectrum also showed the quantitative introduction of 8 DPE functions. Thus, we could successfully synthesize a 7-arm AB_2C_4 asymmetric star with 8 DPE moieties at the core by the second iterative process.

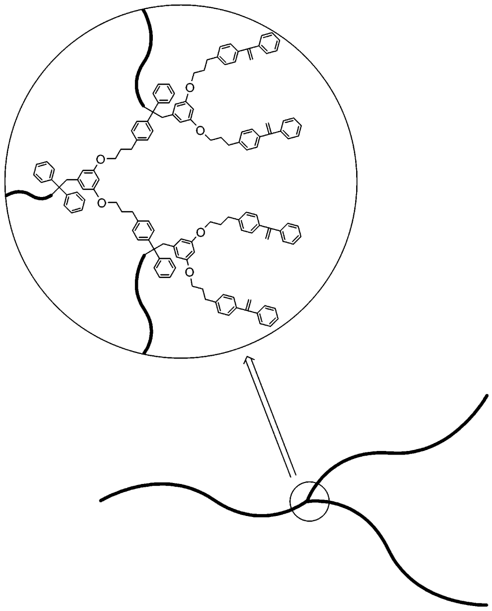
By using poly(4-methoxystyryl)lithium (PMOSLi) as a fourth D segment, the same iterative process was repeated with the DPE-core-functionalized 7-arm AB_2C_4 star-branched polymer. SEC profile of the reaction mixture showed two distinct peaks along with a small peak of the dimer as shown in Figure 2E. The star isolated in 80% yield by fractional precipitation possessed a sharp monomodal SEC distribution (Figure 2F). The M_n and M_w values determined by ^{1}H NMR and RALLS agreed well with those targeted. As shown in Figure 3D, the resonances characteristic of A, B, C, and D (6.2−7.2 ppm, Ar), B (−0.95 to −0.5 ppm, α-CH_3), C (2.35, Ar−CH_3), and D (3.73 ppm, OCH_3) segments are clearly observed. The composition of A/B/C/D (8/10/30/52) determined by this spectrum was very similar to that (8/12/27/53) calculated from the feed ratio. Thus, the third iterative process resulted in the successful formation of a 15-arm $AB_2C_4D_8$ asymmetric star-branched polymer (see also Table 2).

A more complex asymmetric star-branched polymer comprised of five different segments was synthesized by further repeating the iterative process using the DPE-core-functionalized $AB_2C_4D_8$ asymmetric star. In this synthesis, poly(4-trimethylsilylstyryl)lithium (PSiSLi) is used as the E segment of choice, since the silyl proton becomes a convenient probe to determine the composition and M_n value by ^{1}H NMR analysis. As mentioned in the preceding section, the linking reaction at the fourth iteration stage was not complete under the conditions in THF at −78 °C. Therefore, the reaction was carried out in *tert*-butylbenzene at 30 °C for 168 h with use of a 2.5-fold excess of PSiSLi over each DPE function.

As shown in Figure 2G, the SEC profile of the reaction mixture exhibits two main sharp peaks. The product was isolated by fractionation with SEC (see Figure 2H). All of the characterization results (M_n, M_w, and composition) clearly indicate the successful formation of the expected 31-arm $AB_2C_4D_8E_{16}$ asymmetric star-branched polymer. Figure 3E shows the ^{1}H NMR spectrum of the resulting polymer, in which characteristic resonances to A, B, C, D, and E segments are observed.

Thus, DPE-core-functionalized 3-arm AB_2, 7-arm AB_2C_4, and 15-arm $AB_2C_4D_8$, followed by 31-arm $AB_2C_4D_8E_{16}$, asymmetric star-branched polymers were successively synthesized by repeating the iterative processes four times. Combined characterization results revealed a high degree of structural and compositional homogeneity in each of all polymer samples. Obviously, the iterative methodology developed in this study is also effective for the synthesis of asymmetric star-branched polymers having arms comprised as many as five different segments. Incompatibility of such different polymer segments seems not to be affected on the synthesis under the conditions.

Scheme 6. Core Structure of 3-Arm Star-Branched Polymer



Conclusions

Herein, we have demonstrated a possible extension of the iterative methodology for the successive synthesis of star-branched polymers having many arms similar or different in composition. The methodology developed herein is in principle the same as that previously reported. Only an exception in the extended methodology is that **5** capable of introducing two DPE functions via one reaction site is employed in reaction step b. In practice, the iterative methodology using **5** works quite satisfactorily to successively synthesize 3-, 7-, 15-, and 31-arm, followed by 63-arm, regular star polystyrenes as well as 3-arm AB_2, 7-arm AB_2C_4, and 15-arm $AB_2C_4D_8$, followed by 31-arm $AB_2C_4D_8E_{16}$, asymmetric star-branched polymers. The A, B, C, D, and E segments were polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), poly(4-methoxystyrene), and poly(4-trimethylsilylstyrene) segments, respectively. A high degree of structural and compositional homogeneity in each of all the samples is confirmed by analytical results with ^{1}H NMR, SEC, SLS, and RALLS. The success is undoubtedly attributed to the use of **5** whose two DPE moieties are separated by the C_6H_4O-$(CH_2)_3$ linkage to reduce steric requirement and electrostatic repulsion. Furthermore, the success may also 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 spacer in the stars, for example, as illustrated in Scheme 6. Accordingly, the DPE reaction sites are always less sterically hindered in location even after repeating the iteration process.

Since each of all the stars still possesses DPE functions at the core, it may be possible to further repeat the iterative process to synthesize stars having more arms and different polymer segments. At the present time, however, the linking reaction stage at the sixth iterative process was found to proceed efficiently, but not completely under the best conditions employed in this study. The conditions should be more optimized to facilitate the linking reaction.

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