Synthesis of Branched Polymers by Means of Living Anionic Polymerization. 13. Synthesis of Well-Defined Star-Branched Polymers via an Iterative Approach Using Living Anionic Polymers

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ABSTRACT: We have developed a new iterative methodology for the synthesis of both regular and asymmetric star-branched polymers. The methodology involves only two sets of reactions for the entire iterative synthetic sequence: a living linking reaction of either 1,1-bis[3′-(1″-phenylethenyl)phenyl]ethylene or 1,1-diphenylethylene (DPE) functionalized polymers with living anionic polymers and an in-situ reaction for introducing DPE moieties into the polymers. By repeating the two reactions in the iteration, a series of regular star-branched polystyrenes of A_3, A_6, A_9, A_{12}, and A_{15} types and asymmetric star-branched polymers of A_3B_3 and $A_3B_3C_3$ types were successfully synthesized. There does not seem to be a steric limitation even in the fifth iteration. The A and B segments in these star-branched polymers were polystyrene and poly(4-methoxystyrene), respectively, and the C segment was poly(4-*tert*-butyldimethylsilyloxystyrene), poly(4-trimethylsilylstyrene), or polyisoprene. Their arm segments were precisely controlled in chain length, with well-defined architectures, and high degrees of compositional homogeneity, as confirmed by ^{1}H NMR, SEC, VPO, SLS, and viscosity measurements.

Introduction

Star-branched polymers are one of the most important classes in the field of fundamental science and technology.[1−8] Many regular star-branched polymers with well-defined architectures have been synthesized mainly by terminating living anionic polymers with multifunctional chlorosilanes.[9−15] The influence of chain branching on various polymer properties has been elucidated to considerable extents using these well-defined star-branched polymers. Currently, more complex asymmetric star-branched polymers whose arms differ in molecular weight or chemical composition are gaining attention, since these polymers should exhibit unique physical properties and morphologies due to both their branched architectures and heterophase structures. Indeed, Hadjichristidis et al.[16,17] and Abetz et al.[18] have recently demonstrated that the morphology and microphase behavior of asymmetric star-branched polymers and the compositionally similar linear block copolymers are dramatically different.

The synthesis of asymmetric star-branched polymers is generally more difficult than that of the regular star-branched polymers with the same number of arms in which all arms can be simultaneously introduced in a single reaction. In the synthesis of asymmetric star-branched polymers, two or more high-yielding reactions are usually required to introduce the different arms. Moreover, the intermediate polymers must often be isolated. Although several successful synthetic examples of asymmetric star-branched polymers have been reported,[18−27] general and systematic methodologies have not been well-established yet.

We recently developed a new iterative methodology for synthesizing both regular and asymmetric star-branched polymers.[28] It involves only two sets of reactions for the entire iterative synthetic sequence: a living linking reaction of either 1,3-bis(1′-phenylethenyl)benzene or 1,1-diphenylethylene (DPE) functionalized polymers with living anionic polymers and an in-situ reaction for introducing DPE moieties into the polymer chains. As illustrated in Scheme 1, well-defined star-branched polymers can successively be synthesized by repeating the two reactions at each stage of the iteration.

In the first iteration, 2 equiv of polystyryllithium was reacted with a starting core material of 1,3-bis(1′-phenylethenyl)benzene to produce the linked dimeric product with two anions at the linking point. Two DPE moieties were then introduced at the middle of the polymer chain via the two anions by an in-situ reaction with 1-[4′-(4″-bromobutyl)phenyl]-1-phenylethylene (**1**). In the second iteration, 2 equiv of polystyryllithium was again reacted with the polymer thus synthesized, followed by treatment in-situ with **1** under the same conditions, thus synthesizing a 4-arm star-branched polystyrene with two DPE moieties at the core. In the third iteration, a 6-arm star-branched polystyrene was synthesized by repeating the same two reactions on the resulting 4-arm star-branched polystyrene. Similarly, both 4-arm A_2B_2 and 6-arm $A_2B_2C_2$ asymmetric star-branched polymers can be synthesized by using different living anionic polymers at each stage in the iteration. The advantage of this iterative methodology is that the two reactions proceed cleanly and quantitatively to synthesize well-defined A_2, A_4, A_6, A_2B_2, and $A_2B_2C_2$ type star-branched polymers by repeating only the two reactions in the iteration. In principle, a series of star-branched polymers with more arms may be synthesized by repeating the iteration reaction sequence further.

This contribution reports the synthesis of different star-branched polymers by extending the iterative methodology to 1,1-bis[3′-(1″-phenylethenyl)phenyl]ethylene (**2**) as the starting core compound, which consists of three DPE moieties. The objective of this study is to establish the generality and versatility of the proposed iterative methodology from a synthetic viewpoint of both regular A_{3n} ($n = 1-5$) and asymmetric A_3B_3 and $A_3B_3C_3$

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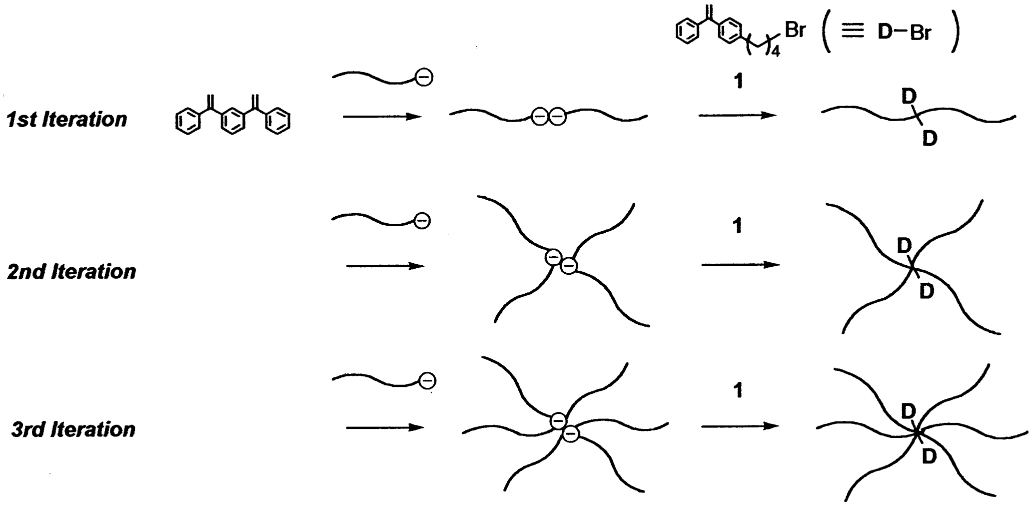
Scheme 1. Synthesis of A_2, A_4, and A_6 Star-Branched Polystyrenes by an Iterative Methodology Using 1,3-Bis(1-phenylethenyl)benzene



star-branched polymers. We focus on how many times the iteration is practically possible for the synthesis of star-branched polymers, since steric hindrance should increase with each iteration.

Experimental Section

Materials. All chemicals (>98% purities) were purchased from Tokyo Kasei Co. Ltd., Japan, and used as received unless otherwise noted. Dibutylmagnesium (99%, Aldrich, Japan) and *sec*-BuLi (99%, Nakarai Chemical Co. Ltd., Japan) were used without purification. Both 4-*tert*-butyldimethylsilyloxystyrene[29] and 4-trimethylsilylstyrene[30] were synthesized as previously reported. Styrene (99%) and 4-methoxystyrene (98%) were washed with 10% NaOH and water and dried over $MgSO_4$. Styrene, 4-methoxystyrene, 4-*tert*-butyldimethylsilyloxystyrene, and 4-trimethylsilylstyrene were distilled from CaH_2 under reduced pressure and finally distilled from dibutylmagnesium (ca. 5 mol %) on a vacuum line into ampules that were prewashed with 1,1-diphenylhexyllithium in heptane. *tert*-Butylbenzene was washed with concentrated H_2SO_4 and water and dried over P_2O_5. It was distilled from CaH_2 and finally distilled from its BuLi solution under reduced pressure. 1-[4′-(4″-Bromobutyl)phenyl]-1-phenylethylene (**1**) was synthesized according to our previously reported procedure.[28]

Measurements. Both ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured in $CDCl_3$ using a Bruker DPX spectrometer. Size-exclusion chromatography (SEC) was performed on a TOSOH HLC 8020 instrument with UV (254 nm) or 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 of bead size 5 μm and pore size of 200, 75, and 20 Å or 650 (bead size 9 μm), 200, and 75 Å were used. Measurable molecular weight ranges are $10^3-4 \times 10^5$ and $10^4-4 \times 10^6$, respectively. Calibration curves were made to determine M_n and M_w/M_n values with standard polystyrene samples. Calibration curves for poly(4-methoxystyrene), poly(4-*tert*-butyldimethylsilyloxystyrene), poly(4-trimethylsilylstyrene), and polyisoprene were constructed using M_n values from VPO. Fractionation by SEC was performed with a flow rate of 5.0 mL/min at 40 °C using a TOSOH HLC 8020 type fully automatic instrument equipped with a $TSK_{gel}G5000H_{HR}$ column (measurable molecular weight range: $10^3-4 \times 10^6$). All runs for fractionation were made with THF as an eluent. The concentration of the polymer solution for fractionation was adjusted to 1.5 wt %. Static light scattering (SLS) measurements were performed with an Ootsuka Electronics SLS-600R instrument equipped with a He−Ne laser (633 nm) in THF or benzene at 25 °C. The refractive index increment (dn/dc) in THF or benzene at 25 °C was determined for each star-branched polymer with an Ootsuka Electronics DRM-1020 refractometer operating at 633 nm. 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. Therefore, molecular weight can be measured up to 100 kg/mol with an error of about 5%. Intrinsic viscosities were measured with an Ubbelhode viscometer in toluene at 35 °C.

1,1-Bis[3′-(1″-phenylethenyl)phenyl]ethylene (2). In typical experiment, a solution of phenylmagnesium bromide prepared from bromobenzene (16.4 g, 104 mmol) and magnesium (3.74 g, 154 mmol) in dry THF (100 mL) was added dropwise to an ice-cooled dry THF solution (30 mL) containing 3-bromoacetophenone (20.1 g, 101 mmol) over a period of 20 min. The resulting mixture was then stirred at 25 °C for 20 h. It was acidified with 2 N HCl, extracted with ether, and dried over $MgSO_4$. Removal of the solvent under reduced pressure yielded crude 1-(3′-bromophenyl)-1-phenylethanol (17.5 g, 63.1 mmol, 61%). It was then dehydrated with a catalytic amount of *p*-toluenesulfonic acid in benzene (150 mL) at 80 °C for 4 h. After cooling to room temperature, saturated aqueous $NaHCO_3$ was added to the solution, and the resulting mixture was extracted with ether and dried over $MgSO_4$. Removal of the solvent followed by fractional distillation over CaH_2 under reduced pressure yielded 1-(3′-bromophenyl)-1-phenylethylene (6.76 g, 26.1 mmol, 41%) as a colorless liquid (110−112 °C/0.15 Torr). ^1H NMR δ: 7.49−7.16 (m, 9H, HAr), 5.48 (s, 1H, $C{=}CH_2$), 5.44 (s, 1H, $C{=}CH_2$). ^{13}C NMR δ: 148.9 ($-C{=}C$), 143.8, 140.8, 131.3, 130.8, 129.8, 128.4, 128.2, 128.1, 127.0, and 122.4 (Ar), 115.4 ($-C{=}C$).

Under a nitrogen atmosphere, dry ethyl acetate (0.570 mL, 5.83 mmol) in THF (5 mL) was added dropwise to an ice-cooled dry THF solution (30 mL) containing the Grignard reagent prepared from 1-(3′-bromophenyl)-1-phenylethylene (3.02 g, 11.7 mmol) and magnesium (0.565 g, 23.3 mmol) over a period of 20 min. The resulting mixture was then stirred at 25 °C for 20 h. It was acidified with 2 N HCl, extracted with ether, and dried over $MgSO_4$. Removal of the solvent under reduced pressure yielded crude 1,1-bis[3′-(1″-phenylethenyl)phenyl]ethanol (2.35 g, 5.83 mmol, 100%). It was then dehydrated with *p*-toluenesulfonic acid in benzene (30 mL) at 80 °C for 4 h. After cooling to room temperature, saturated aqueous $NaHCO_3$ (80 mL) was added to the solution, and the resulting mixture was extracted with ether and dried over $MgSO_4$. After evaporation, the residue was purified by flash column chromatography on silica gel eluting with hexanes to afford **2** (1.23 g, 3.20 mmol, 55%) as a colorless liquid which crystallized on standing. It was recrystallized twice from hexanes and freeze-dried several times to remove traces of water from its absolute benzene solution prior to use; mp 53−54 °C. ^1H NMR δ: 7.40−7.05 (m, 18H, HAr), 5.46−5.43 (m, 4H, $C{=}CH_2$). ^{13}C NMR δ:

150.0 and 149.8 (Ar−*C*=C), 141.5, 141.4, 141.3, 128.3, 128.1, 128.0, and 127.8 (Ar), 114.7 and 114.5 (Ar−C=*C*).

Preparation of Anionic Living Polymers. Polymerizations and reactions were carried out under 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 and used for polymerizations and reactions. Styrene, 4-methoxystyrene, 4-*tert*-butyldimethylsilyloxystyrene, and 4-trimethylsilylstyrene were polymerized with *sec*-BuLi in THF at −78 °C for 10 min, 1 h, 1 h, and 1 h, respectively. Polystyryllithium used in the living linking reaction with **2** in the first iteration was prepared by polymerizing styrene with *sec*-BuLi in *tert*-butylbenzene at 25 °C for 3 h. Isoprene was polymerized with *sec*-BuLi in heptane at 40 °C for 2 h. Prior to the living linking reaction, an equal volume of THF was added to the polymerization mixture at −78 °C. Monomers and initiators were used in the concentration ranges of ca. 0.5−1.0 and 0.02−0.4 M, respectively. The concentration of styrene in *tert*-butylbenzene was exceptionally adjusted to ca. 3 M.

Synthesis of Star-Branched Polymers. Star-branched polymers were synthesized via the iterative approach by a similar procedure described in our previous paper.[28] Procedures for the synthesis of 3-, 6-, 9-, 12-, and 15-arm star-branched polystyrenes are as follows.

First Iteration: Styrene (11.9 g, 114 mmol) in *tert*-butylbenzene (39.0 mL) was polymerized with *sec*-BuLi (0.360 M in heptane, 3.14 mL, 1.13 mmol) at 25 °C for 3 h. A portion of the resulting polystyryllithium (1.40 g, 0.133 mmol) was taken to characterize M_n and M_w/M_n values, and the remainder (10.6 g, 0.997 mmol) was reacted with **2** (0.302 mmol) in *tert*-butylbenzene (3.78 mL) at 25 °C for 1 h. After the reaction mixture was cooled to −78 °C, THF (40.0 mL) chilled at −78 °C was added, and then **1** (1.27 mmol) in THF (5.47 mL) was added. The reaction mixture was stirred at −78 °C for an additional 1 h and poured into a large excess of methanol to precipitate the polymer. The polymer was obtained in 99% yield (10.6 g). The 3-arm star-branched polystyrene (8.45 g, 85%) was isolated by fractional precipitation and three reprecipitations from THF into methanol and finally freeze-dried three times from its absolute benzene solution on the vacuum line (10^{-6} Torr) for 24 h.

Second Iteration. Polystyryllithium (0.197 mmol) in THF (21.4 mL) was added to a THF solution (17.1 mL) of the 3-arm star polystyrene (1.69 g, 0.154 mmol per DPE moiety) at −78 °C, and the reaction mixture was stirred at −78 °C for 10 min. A THF solution (2.83 mL) of **1** (0.236 mmol) was then added, and the reaction mixture was stirred at −78 °C for 1 h. The resulting polymer was precipitated and isolated by fractional precipitation. It was reprecipitated three times and freeze-dried three times from its absolute benzene solution. The 6-arm star-branched polystyrene (3.02 g) was obtained in 88% yield.

Third Iteration. Polystyryllithium (0.0603 mmol) in THF (6.76 mL) was added to a THF solution (10.1 mL) of the 6-arm star polystyrene (0.876 g, 0.0393 mmol per DPE moiety) at −78 °C, and the reaction mixture was stirred at −78 °C for 10 min. Then a THF (1.59 mL) solution of **1** (0.0854 mmol) was added, and the reaction mixture was stirred at −78 °C for 1 h. The 9-arm star-branched polystyrene (1.15 g, 88%) was obtained by the same method used for the 6-arm star-branched polystyrene.

Similarly, the fourth and fifth iterations were carried out to synthesize 12- and 15-arm star-branched polystyrenes. The isolate yields of polymers were 92% and 90%, respectively.

Isolation of Star-Branched Polymers. The resulting star-branched polymers were isolated by fractional precipitation or by SEC fractionation. All of the star-branched polystyrenes were isolated by fractional precipitation with cyclohexane/hexanes (4/1, v/v) at 5 °C. The A_3B_3 star-branched polymer where A and B were polystyrene and poly(4-methoxystyrene) was isolated by SEC fractionation. The $A_3B_3C_3$ star polymers were isolated by fractional precipitation with hexanes/ethanol (1/1, v/v) at room temperature.

Results and Discussion

Living Linking Reaction of Polystyryllithium with 2. We first attempted the living linking reaction of polystyryllithium with **2** in THF, since THF is a better solvent for the next in-situ reaction with **1**. A 3.0-fold molar excess (or 3.0 mol) of polystyryllithium ($M_n = 10.4$ kg/mol) was reacted with **2** in THF at −78 °C for 24 h. As soon as the first aliquot of **2** was added to polystyryllithium, a dark reddish color characteristic of the 1,1-diphenylalkyl anion derived from **2** was observed and remained unchanged during the reaction.

The SEC profile of the reaction mixture showed two sharp single peaks corresponding to the diaddition product and the monoaddition product and/or the unreacted polystyrene in the reaction. No evidence for the presence of the expected triaddition product was detected at all. Based on the peak areas, the diaddition product was formed in 75% yield. Raising the reaction temperature to −40 °C and extending the reaction time to 48 h increased the yield of the diaddition product to 92% along with the triaddition product of only 8% yield. The diaddition product was isolated in ca. 85% yield by fractional precipitation. The ^{1}H NMR spectrum showed a resonance at 5.4 ppm assigned to the DPE vinylene protons and the presence of one DPE moiety in the isolated polymer based on this resonance integration. The M_n value of 19.7 kg/mol observed by SEC corresponded exactly to the molecular weight of the diaddition product. Accordingly, polystyryllithium reacted predominantly with two of the three DPE moieties of **2** to form the diaddition product under the conditions employed. Further addition of polystyryllithium to the diaddition product appears to be very sluggish. The yield of triaddition product was not improved very much at longer reaction times.

In contrast to the results in THF, the linking reaction of a 4.0-fold excess of polystyryllithium ($M_n = 10.3$ kg/mol) with **2** proceeded quantitatively in *tert*-butylbenzene at 25 °C. As shown in Figure 1A−C, the reaction continues with time and is essentially complete after 1 h based on the peak areas. The final SEC profile (Figure 1C) showed a high molecular weight single peak and a small low molecular weight peak corresponding to the unreacted polystyrene used in excess in the reaction. The high molecular weight fraction was isolated nearly quantitatively by fractional precipitation. Its SEC and SLS characterization is summarized in Table 1.

As expected from the branched structure of the resulting polymer, the M_n value ($M_n = 27.8$ kg/mol) measured by SEC relative to polystyrene was somewhat smaller than that calculated. In contrast, the absolute molecular weights determined by VPO (M_n) and SLS (M_w) agreed quite well with those calculated for the triaddition product. The ^{1}H NMR analysis indicates that all of the DPE moieties of **2** had reacted completely with polystyryllithium since no resonance at 5.4 ppm for the DPE vinylene protons were detected. These results demonstrate that polystyryllithium quantitatively reacts with all three of the DPE moieties of **2** in *tert*-butylbenzene in 1 h at 25 °C to afford the living linking triaddition product, which is a 3-arm star-branched polystyrene with three anions at the core. Further evidence for the 3-arm branched architecture of the resulting product will be provided by the viscosity measurement discussed in the next section. Recently, Quirk and Tsai reported that the living linking reaction of polystyryllithium with 1,3,5-tris(1′-phenylethenyl)-

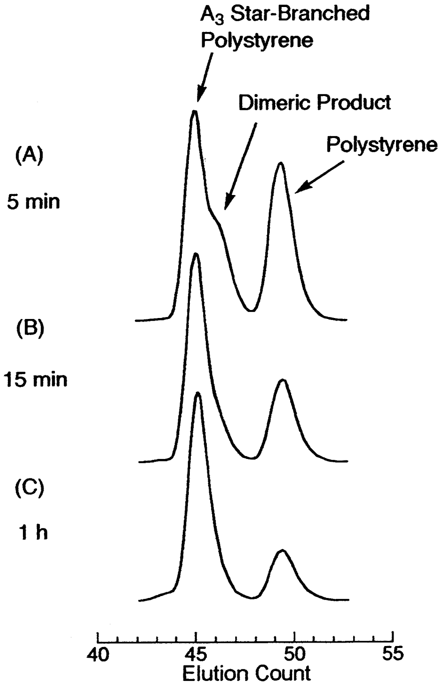


Figure 1. SEC RI traces of the products by the living linking reactions of polystyryllithium with **2** in *tert*-butylbenzene at 25 °C for 5 min, 15 min, and 1 h.

Table 1. Living Linking Reaction of Polystyryllithium with 2 in *tert*-Butylbenzene at 25 °C for 1 h[a]

M_n (kg/mol)			M_w (kg/mol)		M_w/M_n
calcd	SEC	VPO	calcd[b]	SLS	SEC
31.3	27.8	31.1	32.2	32.8	1.03

[a] The M_n value of polystyryllithium was 10.3 kg/mol. [b] Calculated from M_n(calcd) and M_w/M_n(SEC).

benzene proceeds quantitatively in benzene to afford a 3-arm star-branched polystyrene.[31] The result herein obtained is very similar to their result.

The solvent effect of the living linking reaction can be rationalized by the greater ion dissociation of ionic species in THF than *tert*-butylbenzene and therefore stabilization of the reactants. Quirk and co-workers[6,24] and later we[28] previously observed a similar solvent effect in the linking reaction of polystyryllithium with 1,3-bis(1′-phenylethenyl)benzene.

Successive Synthesis for 3-, 6-, 9-, 12-, and 15-Arm Star-Branched Polystyrenes Having Two DPE Moieties at Their Cores by an Iterative Methodology. The synthetic route for the 3-, 6-, 9-, 12-, and 15-arm star-branched polystyrenes is outlined in Scheme 2. Since the reaction of polystyryllithium with **2** was complete in *tert*-butylbenzene at 25 °C for 1 h, the living linking reaction in the first iteration was carried out under the same conditions. After the reaction mixture was cooled to −78 °C, an equal amount of THF was added to the mixture. The in-situ reaction was followed by addition of 1.1 equiv of **1** to the mixture at −78 °C for 1 h. The SEC profiles of the polymers obtained before and after the addition of **1** were almost the same. The polymer eluted at the higher molecular weight side was isolated by fractional precipitation. The results are summarized in Table 2.

The isolated polymer showed a sharp monomodal SEC distribution. The observed M_n value by SEC was somewhat smaller than that calculated. On the other hand, the absolute molecular weights determined by VPO and SLS agreed quite well with those calculated of the expected product. The ^{1}H NMR analysis showed that three DPE moieties were introduced into the polymer chain by comparing the integrals of the two resonances at 5.4 and 0.6−0.8 ppm assigned to the methyl protons of the initiator residue. The expected 3-arm star-branched polystyrene with three DPE moieties at the core was thus obtained in the first iteration.

In the second iteration, the living linking reaction was carried out in THF at −78 °C between a 3.8-fold excess of polystyryllithium and the resulting 3-arm star-branched polystyrene with three DPE moieties. The subsequent in-situ reaction of the living linking product with **1** was performed under the same conditions as mentioned above. In a separate experiment, the linking reaction was observed to be unexpectedly fast and complete within 5 min in THF at −78 °C. This is in contrast to the result of the reaction of polystyryllithium with **2** in THF mentioned above. The fast rate of the reaction in the second iteration may possibly be due to the fact that the three DPE moieties introduced at the polymer chain end are not conjugated and do not interact with each other as with the DPE moieties of **2**. Figure 2A shows the SEC profile of the reaction mixture obtained after the second iteration. There are only two peaks, presumably for the expected 6-arm star-branched polystyrene and the unreacted polystyrene used in excess in the reaction. The desired polymer was isolated by fractional precipitation (Figure 2B). The results are also listed in Table 2.

Again in this isolated polymer sample, the M_n value observed by SEC was smaller than that calculated as expected. The absolute M_n and M_w values determined by VPO and SLS agreed well with those calculated. The degree of DPE functionalization determined by ^{1}H NMR was 3.0_3. Thus, a 6-arm star-branched polystyrene was successfully synthesized by repeating the two reactions in the second iteration.[32]

In the iterative synthesis previously reported, the 6-arm star-branched polystyrene was obtained after the third iterative reaction sequence. On the other hand, the same 6-arm star-branched polymer could be synthesized only after the second iteration in this synthesis using **2**. In the further synthesis of 9-, 12-, and 15-arm star-branched polymers, however, the steric hindrance around the core parts of the resulting star-branched polymers may increase as the iteration proceeds. The iteration involving the living linking reaction with polystyryllithium and the in-situ reaction with **1** was therefore repeated three more times under the same conditions. In each of the iterations, the resulting polymer was always used as a starting polymer in the next iteration.

Surprisingly, all of the living linking reactions were very fast and complete within 10 min. It thus appears that no steric limitation is practically encountered in the living linking reaction even at the fifth iteration in THF at −78 °C. The results are also summarized in Table 2.

The SEC profiles of all of the reaction mixtures were similar to these in Figure 2A, and the peak for the desired polymer shifted to higher molecular weight side as the iteration proceeded. SEC profiles of the isolated polymers all showed sharp monomodal distributions. The degree of DPE functionalization of the polymers obtained by the third, fourth, and fifth iterations were

Scheme 2. Synthesis of A_3, A_6, A_9, A_{12}, and A_{15} Star-Branched Polystyrenes by an Iterative Methodology Using 2

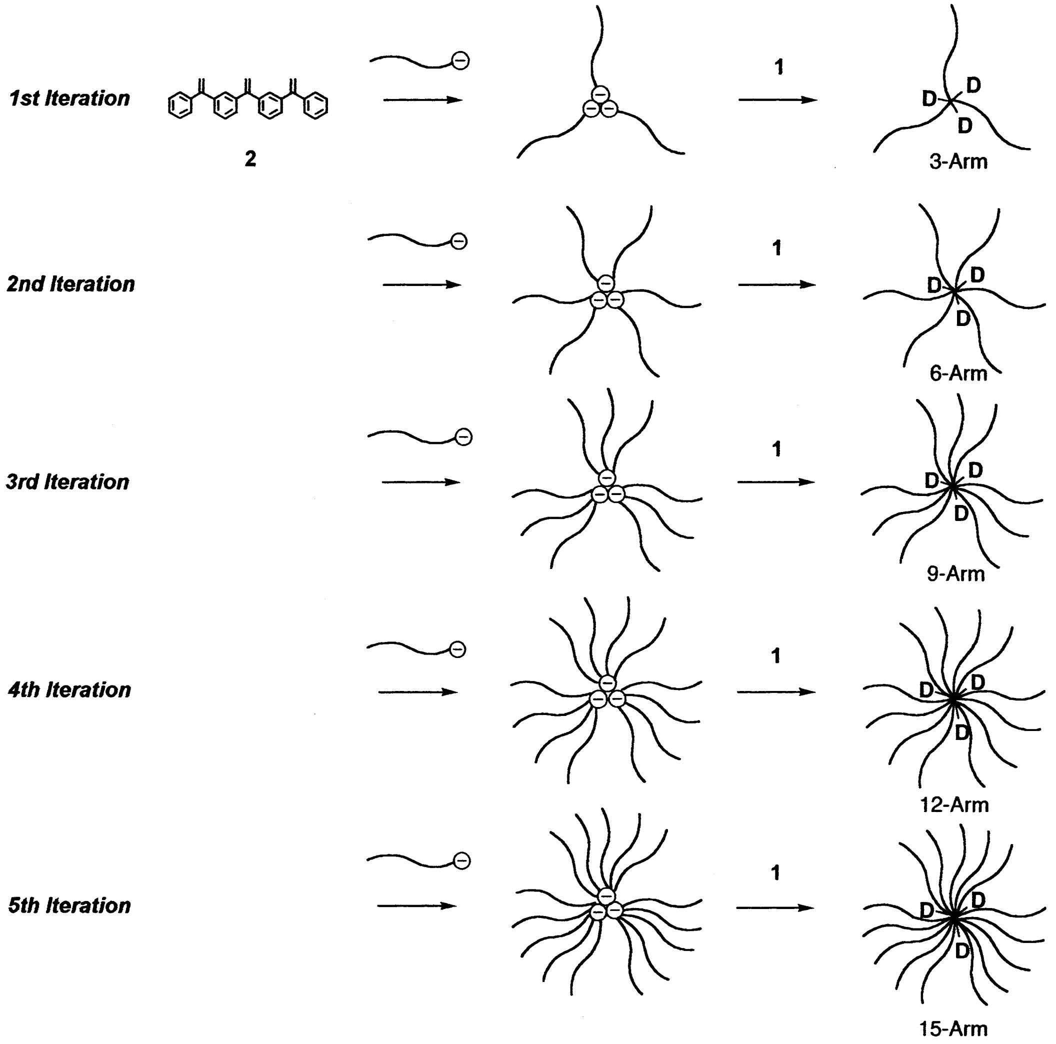


Table 2. Synthesis of 3-, 6-, 9-, 12-, and 15-Arm Star-Branched Polystyrenes[a]

	M_n (kg/mol)			M_w (kg/mol)			M_w/M_n	f[d]
type	calcd	SEC	VPO	calcd[b]	SLS[c]	dn/dc	SEC	^{1}H NMR
A_3	32.9	27.5	31.8	33.6	32.2	0.186	1.02	3.0_1
A_6	66.9	43.8	66.2	68.9	69.7	0.185	1.03	3.0_3
A_9	99.4	42.3	98.2	103	102	0.183	1.04	~3
A_{12}	134	74.2		141	142 (143)[e]	0.179 (0.105)[e]	1.05	~3
A_{15}	166	82.3		173	175 (174)[e]	0.178 (0.104)[e]	1.04	~3

[a] M_n values of polystyryllithiums were around 10 kg/mol in all cases. [b] Calculated from M_n(calcd) and M_w/M_n(SEC). [c] In THF at 25 °C. [d] Functionality of DPE moieties. [e] In benzene at 25 °C.

ca. 3.0 according to ^{1}H NMR analysis. These values were not very accurate due to the broadening of resonances at around 5.4 ppm assigned to vinylene protons of the DPE moieties.

The molecular weights of the resulting three polymers observed by SEC were always smaller than those calculated as expected from their branched structures. Their M_w values determined by SLS agreed quite well with the calculated values of 9-, 12-, and 15-arm star-branched polystyrenes. The M_n value of the 9-arm star polymer determined by VPO also agreed well with that calculated. Reliable M_n values of the 12- and 15-arm star-branched polystyrenes could not be obtained by VPO because their molecular weights were greater than the limit of measurable molecular weight by VPO. Therefore, the M_w values of both polymers were measured by SLS in both benzene and THF. These values also agreed with those calculated. All of the analytical results indicate that the syntheses of the 3-, 6-, 9-, 12-, and 15-arm star-branched polystyrenes by the iterative methodology were successful. At each stage in the iteration, the number of arms of the star-branched polystyrene triples.

The star-branched polymers synthesized in this study are not strict regular types except for the 3-arm star-branched polystyrene obtained by the first iteration. However, these polymers are essentially regular star-branched polymers because their arm segments are around 10 kg/mol in molecular weight. Therefore, the branched architecture of the resulting polymers can be characterized by g', defined as $[\eta]_{\text{star}}/[\eta]_{\text{linear}}$ where $[\eta]_{\text{star}}$ and $[\eta]_{\text{linear}}$ are the intrinsic viscosities of star-branched

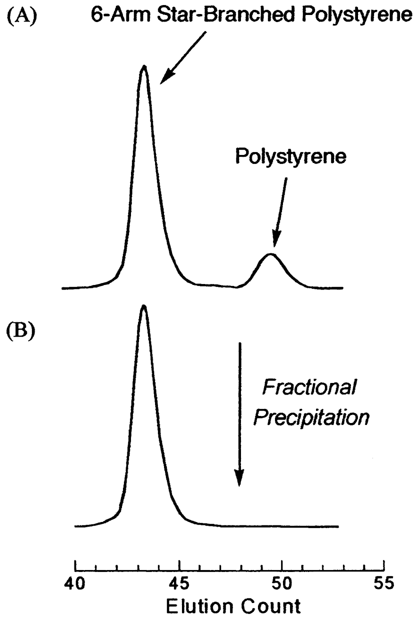


Figure 2. SEC RI traces of the polymers obtained by the living linking reaction of the 3-arm star-branched polystyrene having three DPE moieties with polystyryllithium, followed by in-situ treatment with **1**: (A) before fractionation; (B) after fractionation.

Table 3. Viscosities and g' Values for 3-, 6-, 9-, 12-, and 15-Arm Star-Branched Polystyrenes

type (arm)	M_w,[a] kg/mol	$[\eta]_{star}$,[b] dL/g	$[\eta]_{linear}$,[c] dL/g	g' exptl	g' calcd[d]
A_3 (3)	32.2	0.174	0.205	0.85	0.83
A_6 (6)	69.7	0.194	0.354	0.55	0.56
A_9 (9)	102	0.198	0.464	0.43	0.42
A_{12} (12)	142	0.201	0.587	0.34	0.33
A_{15} (15)	175	0.199	0.681	0.29	0.27

[a] Determined by SLS. [b] In toluene at 35 °C. [c] Calculated from eq 1. [d] Calculated from eq 2.

polymer and linear polymer with the same molecular weight under the same conditions. The intrinsic viscosities of the star-branched polymers were measured in toluene at 35 °C. The $[\eta]_{linear}$ values were calculated from the eq 1 previously established.[33]

$$[\eta] = 1.29 \times 10^{-4} M_w^{\ 0.71} \tag{1}$$

The results are listed in Table 3. Several research groups previously reported the relationship between g' value and arm number of star-branched polymer based on theoretical models and experimental results.[34-39] Accordingly, the g' values for 3-, 6-, 9-, 12-, and 15-arm star-branched polymers were calculated from the eq 2 proposed by Douglas, Roovers, and Freed[38] as also listed in Table 3.

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

The overall experimental g' values agree satisfactorily with those calculated in all of the polymer samples. This supports the branched structures of the 3-, 6-, 9-, 12-, and 15-arm star-branched polymers synthesized herein.

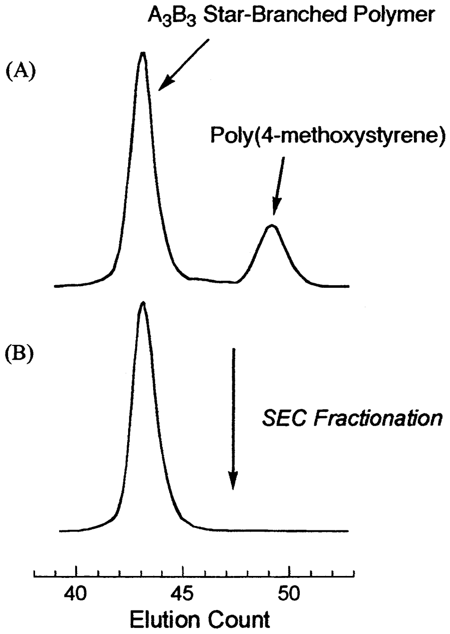


Figure 3. SEC RI traces of the polymers obtained by the living linking reaction of the 3-arm star-branched polystyrene having three DPE moieties with poly(4-methoxystyryl)lithium, followed by in-situ treatment with **1**: (A) before fractionation; (B) after fractionation.

Synthesis of 6-Arm A_3B_3 and 9-Arm $A_3B_3C_3$ Asymmetric Star-Branched Polymers. Asymmetric star-branched polymers should be acceptable simply by reacting a different kind of living anionic polymer in each living linking reaction. As our first attempt, we synthesized new 6-arm A_3B_3 and 9-arm $A_3B_3C_3$ asymmetric star-branched polymers whose A, B, and C segments are polystyrene, poly(4-methoxystyrene), and poly(4-*tert*-butyldimethylsilyloxystyrene), respectively. Every arm segment in the asymmetric star-branched polymers was around 10 kg/mol in molecular weight. The same 3-arm A_3 star-branched polystyrene with three DPE moieties mentioned before was used as the starting polymer. In the second iteration, a 6-arm A_3B_3 star-branched polymer with three DPE moieties was synthesized by the living inking reaction of the 3-arm star-branched polystyrene with a 4.2-fold excess of poly(4-methoxystyryl)lithium in THF at −78 °C, followed by treatment with **1** under the same conditions. As shown in Figure 3A, the SEC profile of the reaction mixture exhibits only two sharp single peaks for the expected A_3B_3 star-branched polymer and the unreacted poly(4-methoxystyrene) used in excess. The higher molecular weight fraction was isolated by fractionation with SEC. The results are summarized in Table 4.

The isolated polymer exhibited a sharp monomodal SEC distribution as shown in Figure 3B. The M_n value was measured by VPO. In addition, the M_n value was also determined from the composition ratio observed by ^{1}H NMR and the M_n value of polystyrene segment. Both values were very close to those calculated. Moreover, the M_w value determined by SLS also agreed with that calculated. Agreement between the compositions calculated and observed by ^{1}H NMR was excellent within the analytical limit. The degree of DPE functionalization of this polymer sample was 3.0_2 based on ^{1}H NMR analysis. Thus, the expected 6-arm A_3B_3 star-branched polymer with three DPE moieties at the core were synthesized.

In the third iteration, the same two reactions were repeated under the same conditions using the resulting 6-arm star-branched polymer obtained in the second iteration. In this synthesis, poly(4-*tert*-butyldimethyl-

Table 4. Synthesis of 6-Arm A_3B_3 and 9-Arm $A_3B_3C_3$ Star-Branched Polymers

		M_n (kg/mol)				M_w (kg/mol)			M_w/M_n	f^d
type[a]	C	calcd	SEC	VPO	^{1}H NMR	calcd[b]	SLS[c]	d*n*/d*c*	SEC	^{1}H NMR
A_3B_3[e]		65.8	44.2	64.2	62.6	67.8	66.7	0.180	1.03	3.0_2
$A_3B_3C_3$[f]	PSOS[g]	95.4	49.2	93.9	92.6	98.3	97.2	0.163	1.03	~3
$A_3B_3C_3$[h]	PSS[i]	95.1	51.6	94.4	96.6	97.0	97.1	0.172	1.02	~3
$A_3B_3C_3$	PI[j]	96.7	59.2			101	103	0.163	1.04	~3

[a] A and B were polystyrene and poly(4-methoxystyrene), respectively. Their M_n values were 10.6 and 10.7 kg/mol, respectively, in all cases. [b] Calculated from M_n(calcd) and M_w/M_n(SEC). [c] In THF at 25 °C. [d] Functionality of DPE moieties. [e] A:B = 52:48 (^{1}H NMR), 50:50 (calcd). [f] A:B:C = 33:35:32 (^{1}H NMR), 34:35:31 (calcd). [g] Poly(4-*tert*-butyldimethylsilyloxystyrene) (M_n = 9.86 kg/mol). [h] A:B:C = 35:34:31 (^{1}H NMR), 34:35:31 (calcd). [i] Poly(4-trimethylsilylstyrene) (M_n = 9.75 kg/mol). [j] Polyisoprene (M_n = 10.3 kg/mol).

silyloxystyryl)lithium was used in the living linking reaction. The results are also summarized in Table 4.

All of the observed molecular weights by VPO, ^{1}H NMR, and SLS agreed well with those calculated. The compositions calculated and measured by ^{1}H NMR also agreed well. These results confirm that the iteration proceeds successively three times without problem to afford the expected 9-arm $A_3B_3C_3$ star-branched polymer with well-defined architecture. The possible deprotection of C segment in the resulting polymer would permit the synthesis of an interesting star-branched polymer having poly(4-vinylphenol) segments with hydrophilic and ionic character.

Two more 9-arm $A_3B_3C_3$ star-branched polymers were synthesized in a similar fashion by using the above-mentioned 6-arm A_3B_3 star-branched polymer. The C segments of these asymmetric star-branched polymers were poly(4-trimethylsilylstyrene) and polyisoprene. Their well-defined architectures and precisely controlled chain lengths were demonstrated by SEC, SLS, VPO, and ^{1}H NMR as was seen in Table 4. The $A_3B_3C_3$ star-branched polymer with polyisoprene segments was obtained in 100% yield. The two observed M_w values by SLS in THF and benzene agreed well with that calculated. However, the composition of polyisoprene segment observed by ^{1}H NMR analysis was smaller than expected. The observed compositions in $CDCl_3$, C_6D_6, and THF-d_8 were around 75% of the expected value. Although the reason is not clear at the present time, we tentatively consider that the molecular motion of polyisoprene segment may be somehow restricted in the star-branched polymer. Thus, the iterative methodology developed in this study is also very effective for the synthesis of 6-arm A_3B_3 and 9-arm $A_3B_3C_3$ asymmetric star-branched polymers.

Conclusions

For the synthesis of both regular and asymmetric star-branched polymers, we have developed an iterative methodology that involves only two sets of reactions: a living linking reaction and an in-situ reaction. By repeating the two reactions in the iteration five times, well-defined 3-, 6-, 9-, 12- and 15-arm star-branched polystyrenes were synthesized successively in virtually quantitative yields. Similarly, 6-arm A_3B_3 and 9-arm $A_3B_3C_3$ asymmetric star-branched polymers were synthesized successfully simply by changing the living anionic polymers used in the living linking reactions at the second and third iterations. Since each of the iterations proceeded cleanly and quantitatively as desired, the resulting star-branched polymers possessed well-defined architectures with high degrees of compositional homogeneity.

The iterative methodology using **2** developed in this study can thus be extended to the synthesis of various star-branched polymers. Therefore, the generality and versatility of the iterative methodology have been demonstrated to a certain extent. Importantly, there does not seem to be a steric limitation even in the fifth iteration in this synthesis. It may therefore be possible to further continue the iterative reaction sequence, thus forming star-branched polymers with more arms and with different compositions. Moreover, both $(A_x)_n$ and $(A_xB_xC_x...)$ star-branched polymers may possibly be synthesized if a specially designed DPE derivative with x DPE moieties is used as the starting core material. We are now investigating the possible synthesis of D_x with x DPE moieties ($x = 4-6$) and the practical limit of the iterative sequence for star-branched polymer synthesis.

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