Successive Synthesis of Well-Defined Asymmetric Star-Branched Polymers up to Seven-Arm, Seven-Component ABCDEFG Type by an Iterative Methodology Based on Living Anionic Polymerization

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ABSTRACT: The successive synthesis of asymmetric star-branched polymers with chemically different arms by the iterative methodology in which a 1,3-butadiene (Bd) functionality is utilized as a reaction site at each stage of the iteration, is described. The methodology involves only two sets of the following reaction conditions for the entire iterative synthetic sequence: (a) linking reaction of a living anionic polymer with the Bd functionality preintroduced into polymer and (b) reintroduction of the Bd functionality by reacting 4-methylene-5-hexenyl bromide with the Bd-derived anion *in situ* generated by the linking reaction. By repeating the two reaction sequence five times, a series of two-arm AB diblock, three-arm ABC, four-arm ABCD, five-arm ABCDE, followed by six-arm ABCDEF star-branched polymers were successively synthesized. In these polymers, the A, B, C, D, E, and F segments correspond to polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), poly(4-methoxystyrene), poly(4-trimethylsilylstyrene), and poly(4-*tert*-butyldimethylsilyloxystyrene) convertible to poly(4-vinylphenol), respectively. The resulting polymers all were well-defined in star-branched architecture and precisely controlled in chain length as confirmed by the characterization results with SEC, ^{1}H NMR, and RALLS. A seven-arm ABCDEFG asymmetric star-branched polymer was synthesized by using the intermediate six-arm ABCDEF star-branched polymer anion as a macroinitiator to anionically polymerize 2-vinylpyridine to make the seventh arm. The resulting asymmetric star-branched polymer is quite new and composed of chemically different seven arms including acidic poly(4-vinylphenol) and basic poly(2-vinylpyridine) segments.

Introduction

Asymmetric star-branched polymers, whose arms differ in chemical structure, so-called miktoarm star-branched polymers, have recently attracted much attention due to their abilities to either change the morphological map of the linear counterparts[1–21] or to create novel morphological nano-objects with many potential applications in the field of nanotechnology. It has been, however, recognized that asymmetric star-branched polymers are much more difficult to synthesize than regular star-branched polymers because of experimental difficulties which require multistep synthetic routes accompanied with isolation of intermediate polymers. The well-defined asymmetric star-branched polymers reported are generally composed of less than three different arms. Several synthetic examples of three-arm ABC star-branched polymers have so far been reported.[22–42] On four-arm ABCD star-branched polymers, however, only a few examples have been synthesized even at the present time, since the first successful synthesis reported in 1993 by Hadjichristidis and his co-workers.[43–48] For such situations, the development of general and effective methodologies for multicomponent asymmetric star-branched polymers have long been strongly desired.

In order to synthesize such multicomponent asymmetric star-branched polymers, we have been recently developing a novel iterative methodology based on living anionic polymerization with use of specially designed 1,1-diphenylethylene (DPE) derivatives.[49,50] The methodology basically involves only two sets of the reaction conditions for the entire iterative synthetic sequence. As illustrated in Scheme 1, a typical synthetic procedure is as follows: (a) linking reaction of a living anionic polymer with the DPE functionality preintroduced into polymer(s) and (b) reintroduction of the same DPE functionality by reacting a DPE-functionalized agent with the DPE-derived anion *in situ* generated by the linking reaction. As the DPE-functionalized agent, 1-(4-(3-bromopropyl)phenyl)-1-phenylethylene (**1**) is employed in this scheme. Thus, the DPE functionality is utilized as a linking reaction site at each stage of the iteration and then reintroduced for the next linking reaction. If the two reactions proceed with excellent efficiencies close to 100%, they can be repeated, in principle, many times to afford a series of asymmetric star-branched polymers having chemically different multiple arms.

As illustrated in Scheme 1, we have indeed successfully synthesized two-arm AB diblock copolymer, three-arm ABC, four-arm ABCD, and even five-arm ABCDE asymmetric star-branched polymers by repeating the two reaction sequence four times using a different living anionic polymer at each stage of the iteration.[51,52] Because of the very efficient two reactions and the use of premade living anionic polymers, the star-branched polymers synthesized by this procedure were well-defined in star-branched architecture and precisely controlled in chain length.

The iterative methodology has been further extended to the synthesis of various well-defined asymmetric star-branched polymers. For example, four-arm A_2B_2 and six-arm $A_2B_2C_2$ star-branched polymers were synthesized by the iterative methodology using 1,3-bis(1-phenylethenyl)benzene composed of two DPE skeletons as a core agent.[53] Similarly, the synthesis of three-arm A_3, six-arm A_3B_3, and nine-arm $A_3B_3C_3$ stars were possible by the methodology using 1,1-bis(3-(1-phenylethenyl)phenyl)ethylene composed of three DPE skeletons as a core agent.[54] Recently, carrying out the above two reaction sequence with 3,5-bis(3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl bromide having two DPE moieties as a DPE-functionalized agent instead of **1**, the synthesis of three-arm AB_2, seven-arm AB_2C_4, 15-arm $AB_2C_4D_8$, followed by 31-arm $AB_2C_4D_8E_{16}$ star-branched polymers has been successfully achieved.[55] Complex

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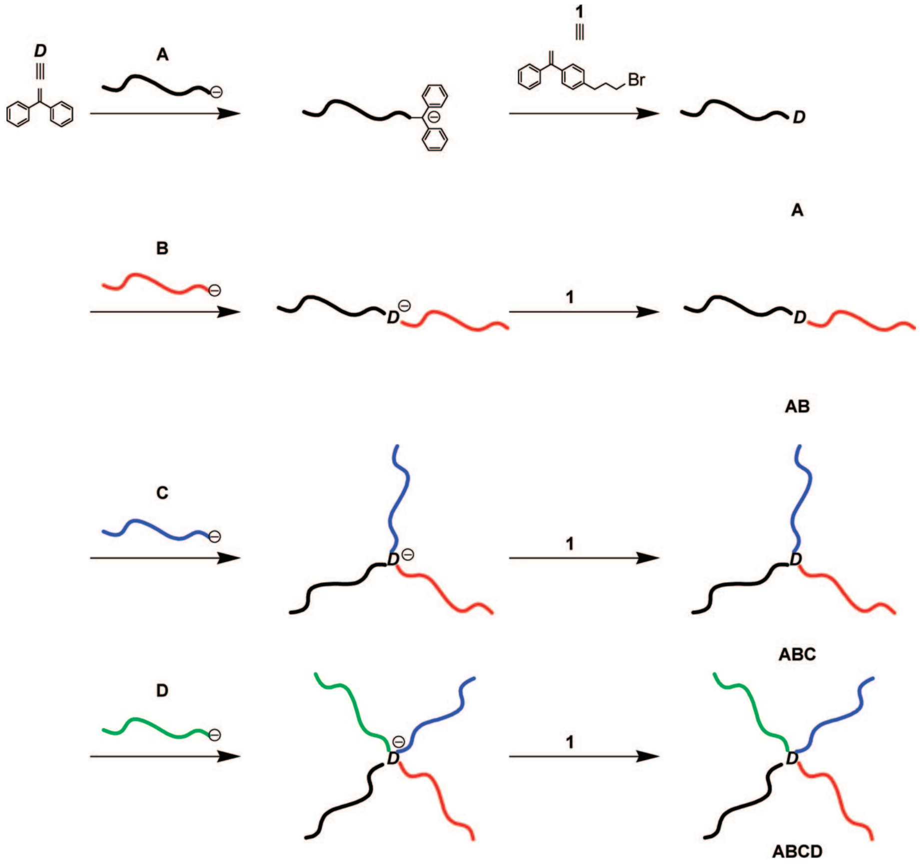
Scheme 1



architectural asymmetric stars such as five-arm A_2B_2C, seven-arm $A_2B_2C_2D$, and 13-arm $A_4B_4C_4D$ as well as six-arm ABC_2D_2 and seven-arm $ABCD_2E_2$ types were also synthesized by using the intermediate polymer anions *in situ* generated by the linking reactions as either macro-coupling agents[56–59] or macroinitiators.[60]

Recently, we have found that a 1,3-butadiene- (Bd-) functionalized polystyrene (PS) macromonomer adds stoichiometrically to polystyryllithium (PSLi) to link the two PS chains and no more addition occurs under the specific conditions at −78 °C even after 24 h.[61] A new Bd-derived anion was *in situ* generated at the linking point by the addition reaction. This reactivity of the Bd terminus is a good indication for the possible utility of Bd functionality as an alternative reaction site in the iterative methodology. An additional interest is that the Bd functionality undergoes either Diels−Alder or oxidation reaction to quantitatively transform into reactive anhydride or diepoxy function.[61] For such reasons, we report herein on the possible utility of the Bd functionality as a new alternative reaction site in the iterative methodology throughout the synthesis of multicomponent asymmetric star-branched polymers.

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). 2-Chloro-1,3-butadiene (chloroprene) in toluene (20 wt %) (kindly supplied from Denki Chemical Co. Ltd., Japan) was distilled over CaH_2 under reduced pressure. DPE, styrene, α-methylstyrene, 4-methylstyrene, 4-methoxystyrene, and 2-vinylpyridine were washed with 10% NaOH(aq), dried over $MgSO_4$, and distilled over CaH_2 under reduced pressure. 4-Trimethylsilylstyrene,[62] 4-*tert*-butyldimethylsilyoxystyrene,[63a,b] and 6-bromo-3-methylene-1-hexane (**2**)[64] were synthesized according to the methods previously reported. All styrene derivatives and **2** were finally distilled in the presence of 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 an eluent 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. All runs for fractionation were made with THF as an eluent. Right angle laser light scatterings (RALLS) were measured on an Asahi Techneion Viscotek model 302 TDA with triple detector software. Three polystyrene gel columns, one TSK_{gel} $G2000H_{HR}$ and two TSK_{gel} $GMH_{HR\text{-}H}$, were used. THF was used as an eluent at a flow rate 1.0 mL/min. The refractive index increment (dn/dc) was also determined for each polymer sample with an Ohotsuka Electronics DRM-1020 refractometer operating at 633 nm (a He−Ne laser). Intrinsic viscosities were measured with an Ubbelohde viscometer in toluene at 35 °C.

Preparation of Living Anionic Polymers. All the polymerizations and reactions were carried out under high vacuum conditions (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) was prepared by the *sec*-BuLi-initiated polymerization of styrene in THF at −78 °C for 20 min. Poly(α-methylstyryl) lithium (PαMSLi), poly(4-methylstyryl)lithium (PMSLi), poly(4-methoxystyryl)lithium (PMOSLi), poly(4-trimethylsilylstyryl)-lithium (PMSiSLi), and poly(4-*tert*-butyldimethylsilyloxystyryl)lithium (PBMSiOSLi) were prepared by the *sec*-BuLi-

Scheme 2

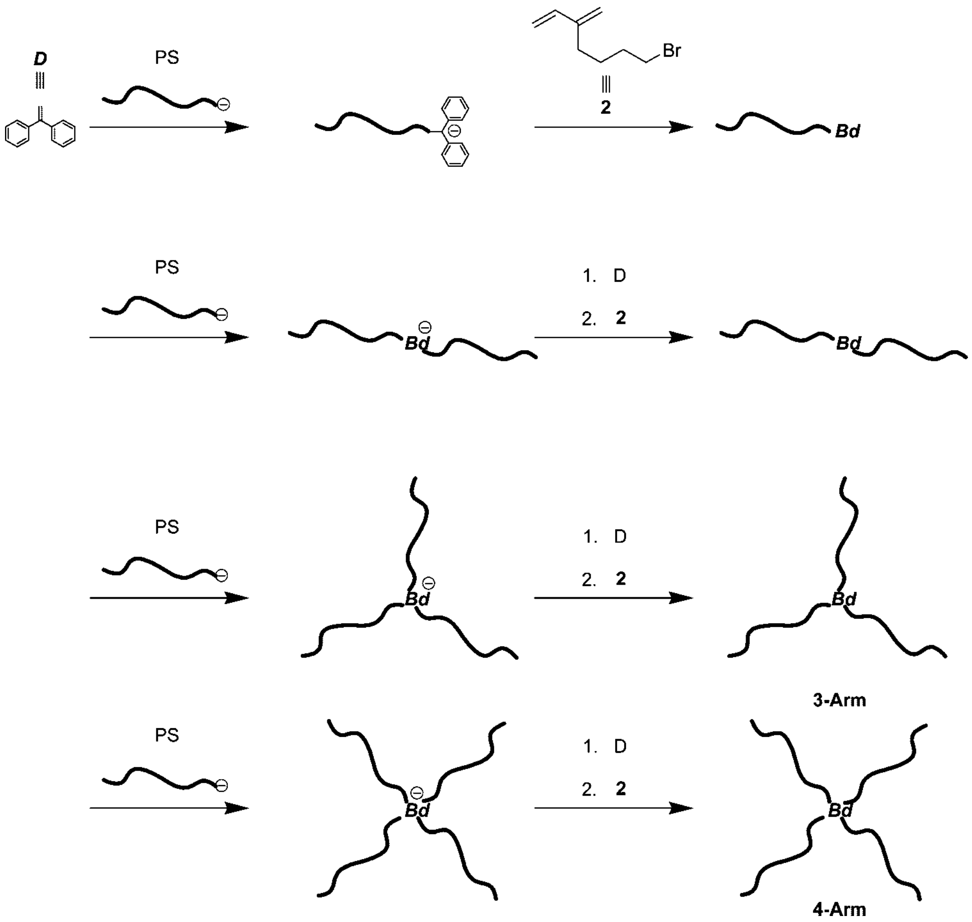


Table 1. Successive Synthesis of Bd-Chain-End- and Bd-in-Chain-Functionalized Polystyrenes, and Bd-Core-Functionalized 3- and 4-Arm Star-Branched Polystyrenes by an Iterative Methodology with 2

	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	functionality[a]	
type	calcd	SEC	RALLS[b]	calcd[c]	RALLS	SEC	calcd	^{1}H NMR
chain-end	10.6	10.4	10.8	10.7	11.0	1.02	1	1.0_3
in-chain	22.0	24.3	24.3	22.4	24.8	1.02	1	1.0_8
three-arm	35.0	26.3	37.6	36.1	38.7	1.03	1	1.0_2
four-arm	48.2	36.6	47.6	49.6	48.6	1.02	1	1.0_0

[a] Bd functionality. [b] In THF at 30 °C. The d*n*/d*c* values were in between 0.181−0.184 mL/g. [c] Calculated from M_n(calcd) and M_w/M_n(SEC) values.

initiated polymerization of the corresponding monomers in THF at −78 °C for 3, 1, 1, 0.5, and 0.5 h, respectively.

Successive Synthesis of Star-Branched Polystyrenes by Iterative Methodology with 2. Synthesis of Chain-End-Functionalized Polystyrene with the Bd Moiety. To avoid the unwanted attack of PSLi on the Bd moiety, PSLi (3.27 g, 0.323 mmol) in THF (32.3 mL) was first end-capped with DPE (0.437 mmol) in THF (4.70 mL) at −78 °C for 30 min and then **2** (0.679 mmol) in THF (2.89 mL) was *in situ* added to the resultant living polymer solution at −78 °C for 15 min. The mixture was poured into a large amount of methanol to precipitate the polymers. It was reprecipitated two times from THF to methanol and freeze-dried from its benzene solution for 24 h (2.81 g, 0.278 mmol, M_n(SEC) = 10.4 kg/mol, M_w/M_n(SEC) = 1.02).

First Iterative Process. PSLi (0.132 mmol, M_n(SEC) = 11.6 kg/mol) in THF (13.0 mL) was added to the Bd-chain-end-functionalized PS synthesized above (0.991 g, 0.0953 mmol) in THF (13.8 mL) at −78 °C and the mixture was allowed to stand for at −78 °C for additional 24 h. Then, DPE (0.0630mmol) in THF (2.07 mL) was *in situ* added to end-cap the excess PSLi, and subsequently, **2** (0.266 mmol) in THF (2.36 mL) was added at −78 °C for 15 min. The mixture was poured into a large amount of methanol to precipitate the polymers. The linked product was isolated by fractional precipitation using a mixture of cyclohexane and hexane (1/1, *v/v*) at 5 °C, reprecipitated from its THF solution to methanol twice, and freeze-dried from its benzene solution for 24 h (2.18 g, 0.0899 mmol, M_n(RALLS) = 24.3 kg/mol, M_w/M_n(SEC) = 1.02).

Second and Third Iterative Processes. Similarly, the second and third iterative processes were carried out to successively synthesize three-, followed by four-arm star-branched polystyrenes, respectively. A 1.2-fold excess of PSLi end-capped with DPE toward Bd moiety was used in each linking reaction under the same conditions. After the addition of DPE to end-cap the excess PSLi, a 2.0-fold excess of **2** was *in situ* added in THF at −78 °C for 20 min. The resulting star-branched polystyrenes were isolated by fractional precipitation, reprecipitated twice, and freeze-dried from their benzene solutions for 24 h.

Successive Synthesis of Asymmetric Star-Branched Polymers by Iterative Methodology with 2. First Iterative Process. PαMSLi (0.543 mmol, M_n = 11.9 kg/mol) in THF (50.9 mL) was added to a Bd-chain-end-functionalized PS (4.84 g, 0.425 mmol, M_n(SEC) = 11.4 kg/mol) in THF (49.5 mL) at −78 °C and the mixture was allowed to stand for at −78 °C for additional 24 h. To avoid the unwanted attack of PαMSLi toward the Bd moiety, DPE (0.352 mmol) in THF (3.8 mL) was added to end-cap the excess PαMSLi and subsequently **2** (0.860 mmol) in THF (3.43 mL) was added to the reaction mixture at −78 °C for 15 min. The mixture was poured into a large amount of methanol to precipitate the polymers. The linked product was isolated by fractional precipitation using a mixture of cyclohexane and hexane (1/1, v/v) at 5 °C, reprecipitated twice from THF to methanol, and freeze-dried from its benzene solution for 24 h (8.49 g, 0.351 mmol, M_n(RALLS) = 24.4 kg/mol, M_w/M_n(SEC) = 1.04).

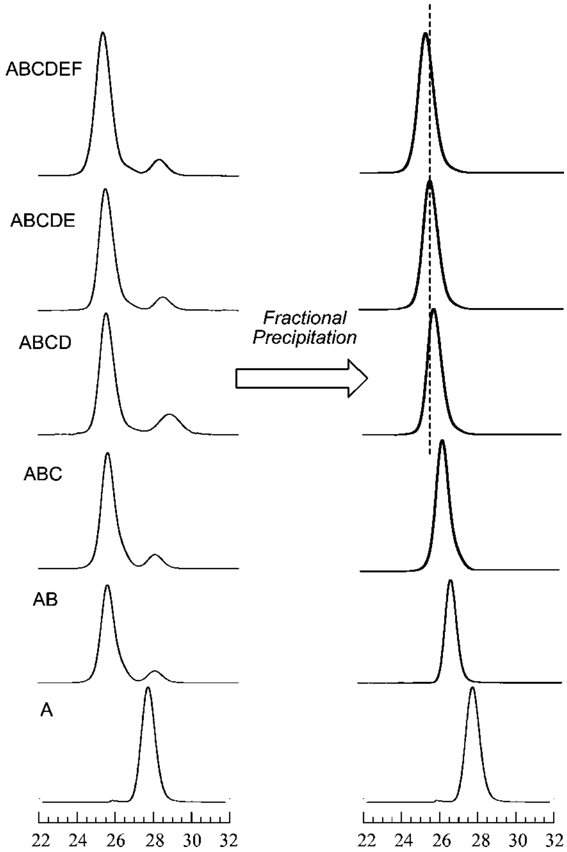


Figure 1. SEC profiles of the reaction mixtures and the isolated polymers for the synthesis of Bd-chain-end-functionalized PS (A), AB diblock copolymer, three-arm ABC, four-arm ABCD, five-arm ABCDE, and six-arm ABCDEF asymmetric star-branched polymers.

Second Iterative Process. PMSLi (0.298 mmol, $M_n = 10.1$ kg/mol) in THF (31.1 mL) was added to the Bd-in-chain-functionalized AB block copolymer synthesized above (5.44 g, 0.223 mmol, M_n(RALLS) = 24.4 kg/mol) dissolved in THF (49.5 mL) at −78 °C and the mixture was allowed to stand for at −78 °C for additional 24 h. After the addition of DPE (0.192 mmol) in THF (3.12 mL) to the reaction mixture to end-cap the excess PMSLi, **2** (0.386 mmol) in THF (2.68 mL) was *in situ* added at −78 °C for 15 min. The mixture was poured into a large amount of methanol to precipitate the polymers. The linked product was isolated by fractional precipitation using cyclohexane and hexane at 5 °C similar to the procedure used for the isolation of regular star polystyrene. The resulting polymer was reprecipitated two times from THF to methanol and freeze-dried from its benzene solution for 24 h (6.48 g, 0.182 mmol, M_n(RALLS) = 35.6 kg/mol, M_w/M_n(SEC) = 1.01).

Third Iterative Process. PMOSLi (0.248 mmol, $M_n = 11.1$ kg/mol) in THF (28.9 mL) was added to the Bd-core-functionalized ABC star-branched polymer obtained by the second iteration (5.44 g, 0.178 mmol, M_n(RALLS) = 35.6 kg/mol) at −78 °C and the reaction mixture was allowed to stand for at −78 °C for additional 24 h. Then, DPE (0.199 mmol) in THF (3.33 mL) was added to end-cap the excess PMOSLi, followed by *in situ* addition of **2** (0.367 mmol) in THF (3.28 mL) at −78 °C for 15 min. The reaction mixture was poured into a large amount of methanol to precipitate the polymers. The linked product was isolated by fractional precipitation using cyclohexane and hexane at 5 °C, reprecipitated twice from THF to methanol, and freeze-dried from its benzene solution for 24 h (7.30 g, 0.156 mmol, M_n(RALLS) = 46.8 kg/mol, M_w/M_n(SEC) = 1.01).

Fourth and Fifth Iterative Processes. Similarly, the fourth and fifth iterative processes were carried out to successively synthesize five-arm ABCDE and six-arm ABCDEF star-branched polymers, respectively. A 1.2-fold excess of living anionic polymer toward each of the Bd-functionality was always used in the linking reaction in THF at −78 °C for 24 h. After the linking reaction, a small excess of DPE was *in situ* added to end-cap the excess living polymer and subsequently a 2.0-fold excess of **2** was added to the intermediate star-branched polymer anion in THF at −78 °C for 20 min. The resulting five-arm ABCDE and six-arm ABCDEF asymmetric star-branched polymers were isolated by fractional precipitation using a mixture of toluene and methanol. Here, the A, B, C, D, E, and F segments were polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), poly(4-methoxystyrene), poly(4-trimethylsilylstyrene), and poly(4-*tert*-butyldimethylsilyloxystyrene), respectively.

Synthesis of Seven-Arm ABCDEFG Asymmetric Star-Branched Polymer. PBMSiOSLi (0.0226 mmol, M_n(^{1}H NMR) = 9.80 kg/mol) in THF (4.04 mL) was added to a Bd-core-functionalized five-arm ABCDE asymmetric star-branched polymer (0.686 g, 0.0120 mmol, M_n(RALLS) = 57.2 kg/mol) dissolved in THF (7.50 mL) at −78 °C and the mixture was allowed to stand for at −78 °C for additional 24 h. To the reaction mixture was then added 2VP (2.03 mmol) in THF (3.98 mL) to polymerize at −78 °C for 3 h. The reaction was quenched with degassed methanol. The polymers were precipitated by pouring into a large amount of methanol. The resulting polymer was isolated by fractional precipitation using toluene and methanol, reprecipitated two times from THF to methanol, and freeze-dried from its benzene solution for 24 h (0.360 g, 0.00485 mmol, M_n(RALLS) = 74.2 kg/mol, M_w/M_n(SEC) = 1.03).

Results and Discussion

Synthesis of Regular Star-Branched (PS)s by Iterative Methodology with 2. In order to investigate the reliability and effectiveness of this new iterative methodology using **2** as a Bd-functionalized agent, a series of regular star-branched (PS)s has been synthesized by the procedure outlined in Scheme 2. Except for the use of **2**, the synthetic procedure is exactly the same as that illustrated in Scheme 1. Thus, the two reaction sequence was employed at each stage of the iterative process, i.e., (a) the linking reaction of PSLi with the Bd functionality preintroduced into PS(s) and (b) the reintroduction of the Bd functionality by the reaction of **2** with the anion *in situ* generated by the linking reaction. The PS used in the synthesis was adjusted to be *ca.* 10 kg/mol in M_n value to compare the previous results. Throughout the synthesis, a 1.2-fold excess of PSLi reacted with Bd-chain-functionalized PS under the conditions in THF at −78 °C for 24 h and then a 2.0-fold excess of **2** was reacted with the generated anion to reintroduce Bd group at −78 °C for 20 min. Since the crude product always contained the excess PS used in the linking reaction, the objective product was isolated in more than 80% by fractional precipitation and characterized by SEC, ^{1}H NMR, and RALLS, respectively.

At the first stage of the iteration, PSLi reacted with a Bd-chain-end-functionalized PS (PS−Bd), and subsequently, **2** reacted with the anion *in situ* generated. The SEC profile of the resulting reaction mixture showed only two distinct sharp peaks. The higher molecular weight peak corresponded to the linked product, while the lower peak was the excess PS used in the linking reaction. No higher molecular weight fraction was formed, strongly indicating no more addition of PS−Bd to the 1:1 adduct anion. The linking efficiency was virtually quantitative by comparing the two peak areas. The linked product isolated by fractional precipitation exhibited a narrow molecular weight distribution ($M_w/M_n = 1.02$) and a M_n value comparable to that calculated as summarized in Table 1. The ^{1}H NMR of the resulting polymer showed resonances at 5.00−5.20 ppm that were assigned to the 1,3-butadienyl vinyl protons. All of the analytical results clearly indicate that the two reactions proceed efficiently to afford the objective Bd-in-chain-functionalized PS.

Since the resulting polymer had the same Bd functionality, the iterative process involving the two reaction sequence was repeated

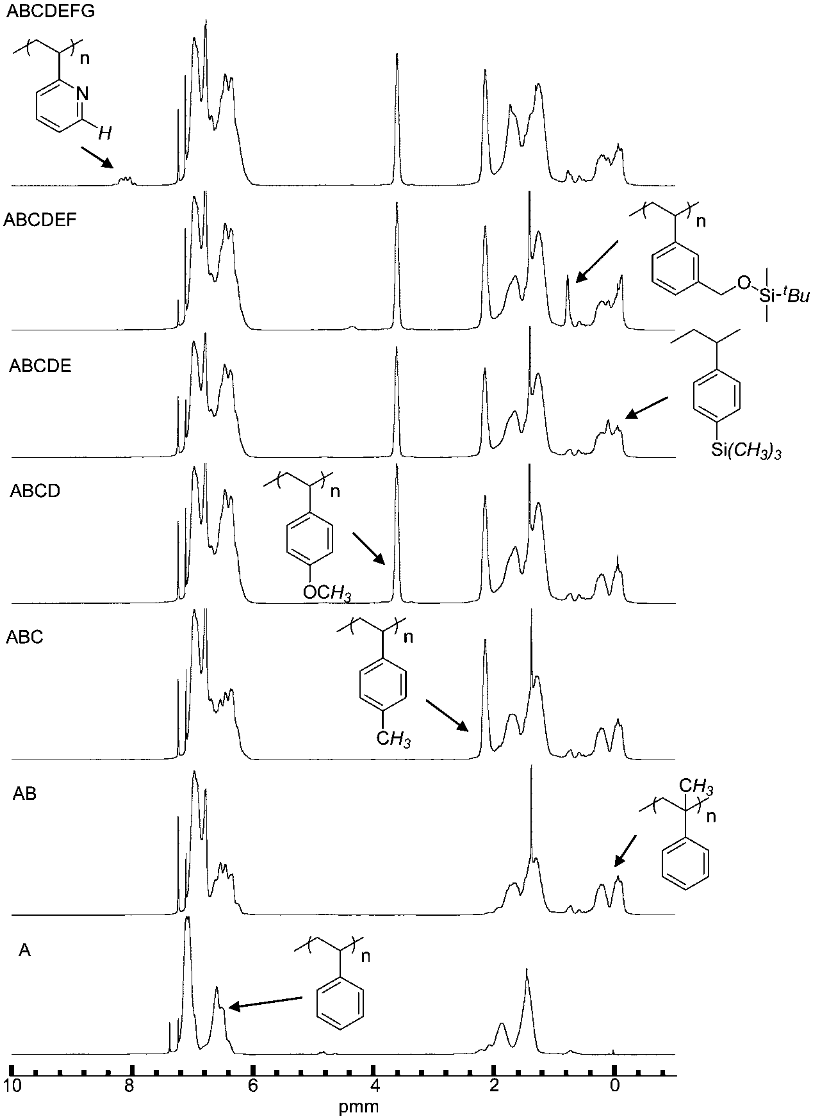


Figure 2. ^{1}H NMR spectra of poly(A), diblock copolymer (AB), three-arm ABC, four-arm ABCD, five-arm ABCDE, six-arm ABCDEF, and seven-arm ABCDEFG asymmetric star-branched polymers.

Table 2. Synthesis of Bd-Chain-End-Functionalized Polystyrene (A), AB Diblock Copolymer, Three-Arm ABC, Four-Arm ABCD, Five-Arm ABCDE, and Six-Arm ABCDEF Asymmetric Star-Branched Polymers by an Iterative Methodology with 2

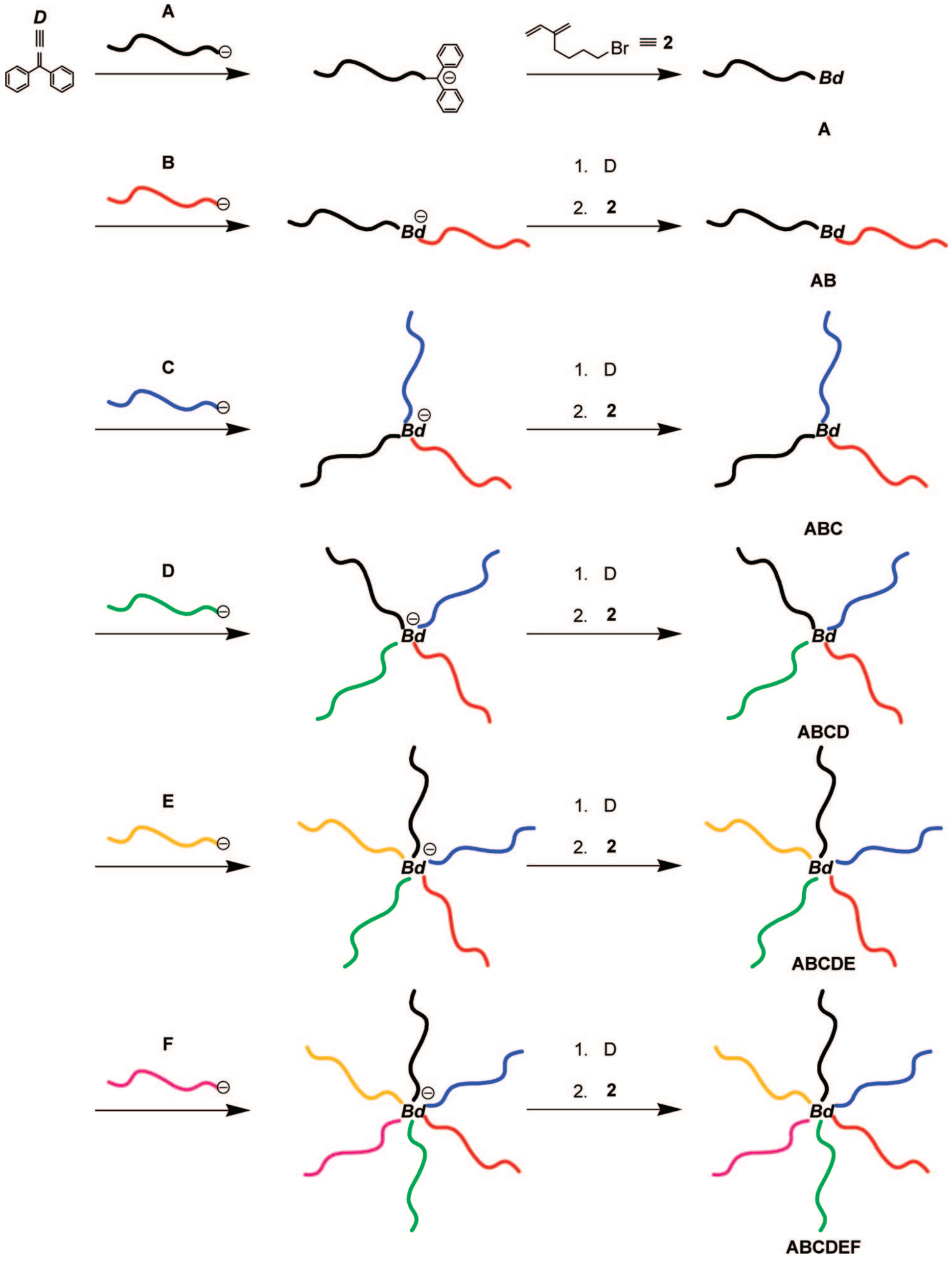
	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	composition (wt %)[a]	
type	calcd	SEC	RALLS[b]	calcd[c]	RALLS	SEC	calcd	^{1}H NMR
A	10.9	11.4	11.2	11.2	11.5	1.03	100	100
AB	23.3	24.5	24.4	24.2	25.3	1.04	47/53	49/51
ABC	34.5	31.9	35.6	34.8	35.9	1.01	32/36/32	33/34/33
ABCD	46.7	33.1	46.8	47.1	47.2	1.01	24/26/24/26	25/27/25/23
ABCDE	57.6	36.4	57.2	58.8	58.5	1.02	19/22/19/21/19	20/21/20/21/18
ABCDEF	69.7	40.7	69.3	71.8	71.5	1.03	16/18/16/17/16/17	17/18/17/17/15/16

[a] A/B, A/B/C, A/B/C/D, A/B/C/D/E, and A/B/C/D/E/F, respectively. [b] In THF at 30 °C. The d*n*/d*c* values were 0.184, 0.189, 0.186, 0.183, 0.180, and 0.180 mL/g for A, AB, ABC, ABCD, ABCDE, and ABCDEF polymers. The d*n*/d*c* values of A, B, C, D, E, and F segments were 0.184, 0.190, 0.185, 0.185, 0.176, and 0.181 mL/g. [c] Calculated from M_n(calcd) and M_w/M_n(SEC) values.

two more times in order to synthesize three-arm followed by four-arm star-branched (PS)s. The resulting two polymers, after the isolation, exhibited narrow molecular weight distributions and good agreement between calculated and observed molecular weights (also see Table 1). Accordingly, the three-arm and four-arm star-branched (PS)s could be synthesized by repeating the same process two times in the iterative methodology using **2**. The repeatability of the same process is the most important point of the iterative methodology. The repetition of at least three times was indeed guaranteed by the above results. Thus, the Bd functionality works very satisfactorily as a linking reaction site in the iterative methodology. Therefore, the methodology with **2** has been applied to the synthesis of asymmetric star-branched polymers in the next section.

Synthesis of Three-Arm ABC, Four-Arm ABCD, Five-Arm ABCDE, and Six-Arm ABCDEF Asymmetric Star-Branched Polymers by Iterative Methodology with 2. In order to synthesize a series of asymmetric star-branched polymers having chemically different arms, the following five

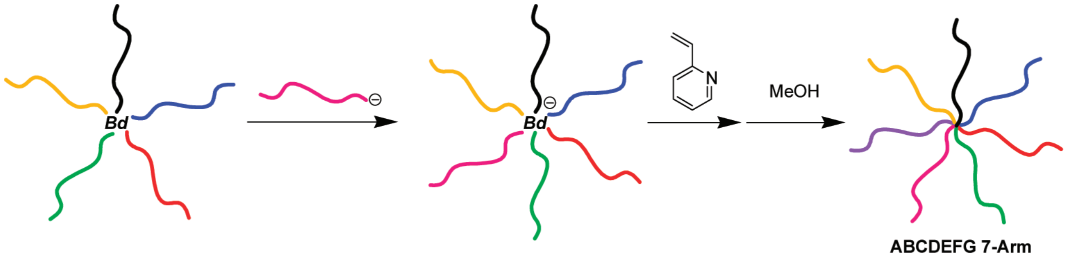
Scheme 3



different living anionic polymers of substituted styrene derivatives ($M_n = ca.$ 10 kg/mol) in addition to PSLi were employed: poly(α-methylstyryl)lithium (PαMSLi), poly(4-methylstyryl)lithium (PMSLi), poly(4-methoxystyryl)lithium (PMOSLi), poly(4-trimethylsilylstyryl)lithium (PMSiSLi), and poly(4-*tert*-butyldimethylsilyloxystyryl)lithium (PBMSiOSLi), respectively. The choice of such living polymers is based on the facts that they have precisely controlled molecular weights, extremely narrow molecular weight distributions, and highly reactive chain-end carbanions capable of reacting with Bd group. As an additional advantage, each of these polymers has characteristic ^{1}H NMR resonances as follows: PS (6.2−7.2 ppm for the phenyl protons), P(αMS) (−0.7 ppm for the α-CH_3 protons), PMS (2.35 ppm for the CH_3 protons), PMOS (3.73 ppm for the OCH_3 protons), PMSiS (0.22 ppm for the Si−CH_3 protons), and PBMSiOS (0.94 ppm for Si−C−CH_3 protons and 0.06 ppm for Si−CH_3 protons). Thus, the composition can be readily determined by using such resonances. Throughout the synthesis, a 1.2-fold excess of living anionic polymer toward the Bd functionality preintroduced was used in the linking reaction in THF at −78 °C for 24 h and a 2.0-fold excess of **2** was added to react with the anion *in situ* generated at −78 °C for 20 min. As the two reactions actually proceeded with efficiencies close to 100% at each stage of the iteration, the same process was repeated five times. The objective linked products were isolated in 80% or higher yields by fractional precipitation. The SEC profiles of the reaction mixtures and isolated polymers obtained at all the stages are shown in Figure 1. Figure 2 shows the ^{1}H NMR spectra of the resulting polymers. The characterization results of the resulting polymers are summarized in Table 2.

As illustrated in Scheme 3, the synthetic procedure completely followed the pattern developed for the synthesis of regular star (PS)s mentioned above. At the first stage of the iteration, PαMSLi reacted with PS−Bd and subsequently **2** reacted with the *in situ* generated anion to reintroduce Bd group. As can be seen in Figure 1, the SEC chromatogram of the reaction mixture exhibits only two sharp monomodal peaks corresponding to the linked product and the excess PαMS used in the reaction. No

Scheme 4



higher molecular weight fraction was formed at all, clearly indicating that PαMSLi reacted with PS−Bd only in a 1:1 addition manner and no more addition occurred. The linked product isolated by fractional precipitation exhibited a sharp monomodal SEC distribution and good agreement between calculated and observed molecular weights (see Figure 1 and Table 2). The composition determined by ^{1}H NMR was 47/53 which is very close to 49/51 of the calculated value.

At the second iteration stage, PMSLi was used in the linking reaction with the Bd-in-chain-functionalized AB diblock copolymer synthesized by the first stage. The resulting polymer, after the isolation by fractional precipitation, showed a narrow monomodal SEC distribution and possessed the M_n and M_w values and the composition which were in good agreement with both observed and calculated values. Thus, the expected Bd-core-functionalized three-arm ABC star-branched polymer was successfully synthesized. As the two reaction sequence proceeded very efficiently, the same iterative process was repeated two more times in order to synthesize four-arm ABCD followed by five-arm ABCDE star-branched polymers.

As D and E segments, PMOSLi and PMSiSLi, were employed, respectively. The reactions were carried out under the same conditions and the resulting two polymers were isolated by fractional precipitation. Their SEC profiles exhibited sharp monomodal distributions. As can be seen in Table 2, the good agreement of the determined molecular weights and compositions with those calculated indicate that the resulting polymers are the targeted four-arm ABCD and five-arm ABCDE star-branched polymers. The successful synthesis of these two polymers in addition to two-arm AB block copolymer and three-arm ABC star is also supported by the agreement between the overall d*n*/d*c* values experimentally determined and those calculated from each sample. Accordingly, the Bd function has been found very effective as a reaction site in the iterative methodology.

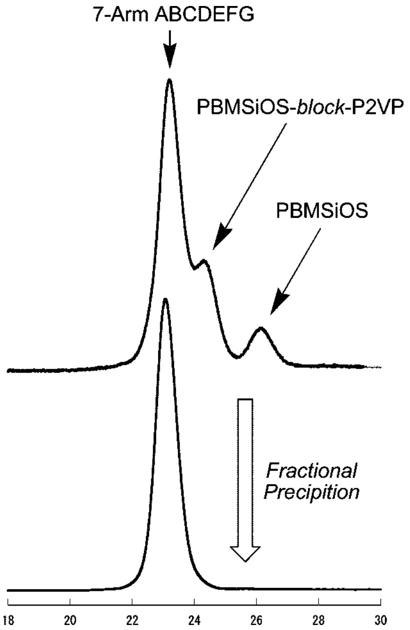


Figure 3. SEC profiles of the reaction mixture and the isolated polymer in the synthesis of seven-arm ABCDEFG asymmetric star-branched polymer.

The synthesis of six-arm ABCDEF star-branched polymer was performed by repeating the two reaction sequence one more time. In this synthesis, PBMSiOSLi readily convertible to poly(4-vinylphenol) was selected as the F segment.[63] The two reactions were carried out under the same conditions and the resulting polymer was isolated by fractional precipitation. The molecular weights (M_n and M_w) were in agreement with those calculated and a narrow monomodal SEC peak was observed. The composition determined by ^{1}H NMR was close to that calculated from the feed ratio within the analytical error. Furthermore, the measured d*n*/d*c* value comparable to that estimated from each d*n*/d*c* value of all arms and the composition. These results clearly demonstrate that the two reaction sequence proceeds efficiently even at the fifth iteration stage to afford the expected six-arm ABCDEF star-branched polymer with well-defined structures. To the best of our knowledge, this is the first successful asymmetric star-branched polymer having chemically different six arms. A new functional six-arm ABCDEF′ star-branched polymer having one poly(4-vinylphenol) arm could be obtained by quantitative deprotection of the F segment with $(C_4H_9)_4NF$.

Synthesis of Seven-Arm ABCDEFG Asymmetric Star-Branched Polymer. Since the six-arm ABCDEF asymmetric star-branched polymer possesses the Bd functionality at the core, the synthesis of the next seven-arm ABCDEFG star-branched polymer would be expected by repeating the same reaction sequence. However, we have adopted a different procedure in order to explore another possibility of the present methodology. In this procedure, the intermediate six-arm star-branched polymer anion is used as a macroinitiator to polymerize 2-vinylpyridine (2VP) to make the seventh arm as shown in Scheme 4.

Similar to that outlined in Scheme 3, a six-arm ABCDEF asymmetric star-branched polymer anion was prepared by linking a 2.0-fold excess of PBMSiOSLi with the Bd-core-functionalized five-arm ABCDE star and then 2VP was added to the reaction mixture to *in situ* polymerize in THF at −78 °C for 3 h. A polymer yield was quantitative. As shown in Figure 3, the SEC profile exhibits three peaks which correspond to the objective star-branched polymer, an AB diblock copolymer, PBMSiOS-*block*-P2VP, and PBMSiOS, respectively. They were actually isolated by fractional precipitation and identified as above. Since a 2.0-fold excess of PBMSiSOSLi was used in the linking reaction, the formation of the diblock copolymer by the anionic polymerization of 2VP with the excess PBMSiSOSLi was not avoidable. The homopolymer of BMSiOS may be produced by the unwanted termination of PBMSiSOSLi with impurities in the starting five-arm star polymer prior to the linking reaction.

Table 3. Synthesis of Seven-Arm ABCDEFG Asymmetric Star-Branched Polymer

	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	composition (wt %)[a]	
type	calcd	SEC	RALLS[b]	calcd[c]	RALLS	SEC	calcd	^{1}H NMR
ABCDEFG	77.0 (75.4)[d]	39.8	74.2	79.3 (77.6)[d]	76.5	1.03	15/15/14/15/15/13/13	16/16/14/15/15/14/10

[a] A/B/C/D/E/F/G. [b] In THF at 30 °C. The d*n*/d*c* values of ABCDEFG star and P(2VP) were 0.181 mL/g and 0.195 mL/g, respectively. [c] Calculated from M_n(calcd) and M_w/M_n(SEC) values. [d] Calculated value based on the molecular weight of P2VP (M_n = 7.9 kg/mol) in the star.

The results are summarized in Table 3. The molecular weight of P(2VP) in the resulting star-branched polymer was estimated to be 7.2 kg/mol by subtracting from the M_n value (74.2 kg/mol) of the 7 arm star-branched polymer to that (57.2 + 9.80 = 67.0 kg/mol) of the intermediate six-arm star. More reliable M_n values of the P2VP segment were determined to be 8.0 and 7.5 kg/mol by the elemental analysis (N %) and ^{1}H NMR of the resulting polymer. These values were relatively lower than the value of 9.50 kg/mol calculated by the feed ratio. On the other hand, the molecular weight of P2VP segment in the recovered PBMSiOS-*block*-P2VP was determined to be 11.1 kg/mol ($M_{n\ block}$ (20.9 kg/mol) − $M_{n\ PBMSiOS}$ (9.80 kg/mol)). By taking into consideration on the molar ratio of the star-branched polymer anion, PBMSiOSLi, and the deactivated PBMSiOS, the molecular weight of P2VP segment in the star can be calculated to be 7.9 kg/mol, which is close to the observed values of 8.0 and 7.5 kg/mol. The d*n*/d*c* value of the seven-arm ABCDEFG thus synthesized is also comparable to that estimated by that of each polymer segment and the composition.

Thus, a quite new seven-arm and seven-component ABCDEFG asymmetric star-branched polymer has been synthesized by using the intermediate six-arm star-branched polymer anion as a macroinitiator to *in situ* polymerize 2VP. Interestingly, the resulting star-branched polymer includes both acidic poly(4-vinylphenol) and basic poly(2-vinylpyridine) segments in addition to other five segments. The advantage of this procedure is that in essence any monomer that undergoes living anionic polymerization can be used. However, the successive synthesis of star-branched polymer can no longer be continued, since the Bd reactive site at the core disappears after the polymerization.

Conclusions

We have successfully developed the iterative methodology with **2** for the synthesis of a series of asymmetric star-branched polymers. The methodology involves only two sets of the reaction conditions for the entire iterative synthetic sequence, *i.e.*, (a) linking reaction of a living anionic polymer with a Bd-chain-functionalized polymer and (b) reintroduction of the Bd functionality by reacting **2** with the anion *in situ* generated by the linking reaction. By repeating the two reaction sequence five times, two-arm AB diblock copolymer, three-arm ABC, four-arm ABCD, and five-arm ABCDE, followed by six-arm ABCDEF asymmetric star-branched polymers were successively synthesized. Here, the A, B, C, D, E, and F segments in such polymers correspond to polystyrene, poly(α-methylstyrene), poly(4-methylstyrene), poly(4-methoxystyrene), poly(4-trimethylsilylstyrene), and poly(4-*tert*-butyldimethylsilyloxystyrene) convertible to poly(4-vinylphenol), respectively. A high degree of structural and compositional homogeneity in each of all the star-branched polymers is confirmed by the characterization results with ^{1}H NMR, SEC, and RALLS. Thus, we have successfully demonstrated the utility of the Bd functionality as a new alternative reaction site at each stage of the iteration in the iterative methodology. Since the six-arm ABCDEF star still possesses the Bd group in the core, the synthesis of seven-arm or more arm stars would be expected by repeating the two reaction sequence.

A seven-arm ABCDEFG asymmetric star-branched polymer was synthesized by using the intermediate six-arm ABCDEF star polymer anion as a macroinitiator to anionically polymerize 2-vinylpyridine to make the seventh arm. The resulting asymmetric star-branched polymer is quite new and composed of chemically different seven arms including acidic poly(4-vinylphenol) and basic poly(2-vinylpyridine) segments.

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