Synthesis of Well-Defined Star-Branched Polymers by Coupling Reactions of Polymer Anions Consisting of Two Polymer Chains with Chain-End-Multifunctionalized Polystyrenes with Benzyl Bromide Moieties

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ABSTRACT: To synthesize star-branched polymers, we have developed a new methodology of using polymer anions (M_w = ca. 10 kg/mol) consisting of the same or different two polymer chains in the coupling reaction of chain-end-multifunctionalized polystyrenes with 4, 8, and 16 benzyl bromide moieties. The coupling reactions efficiently proceeded to afford 9-, 17-, and 33-arm regular star-branched polystyrenes as well as A_5B_4, A_9B_8, and $A_{17}B_{16}$ asymmetric stars consisting of polystyrene (A) and poly(4-trimethylsilylstyrene) (B) segments in greater than 85% isolated yields. However, the yields of the coupling reactions were high but not quantitative when either chain-end-functionalized polystyrene with 32 benzyl bromide moieties or a high molecular weight polymer anion (M_w = 20.0 kg/mol) was used.

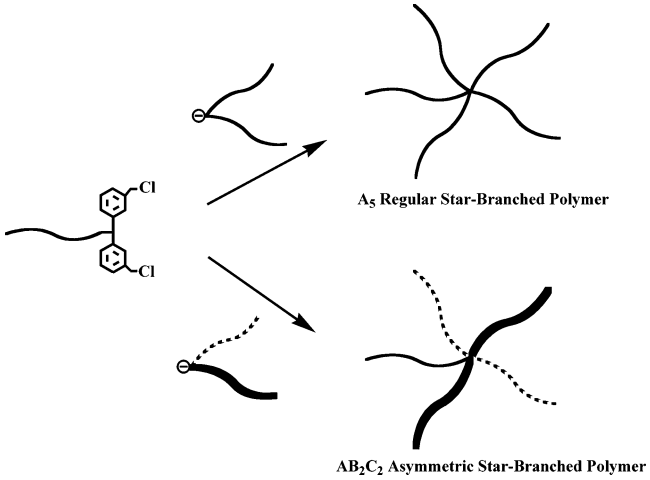
Introduction

Well-defined architectures of star-branched polymers are essential in order to understand fundamentally the relationship among chain-branched structure and several physical properties. For this purpose, many regular star-branched polymers having a definite number of arm segments with uniform chain lengths have so far been synthesized mainly by means of living anionic polymerization with use of multifunctional chlorosilane compounds as terminating agents.[1] Currently, great attention has been paid to asymmetric star-branched polymers in which arm segments differ in either molecular weight or composition, since such polymers are expected to show unique and interesting properties originating from their chain-branching as well as heterophase structures.[2−4] Although several synthetic methods for asymmetric star-branched polymers have been reported, structural variables such as arm number and composition to be controlled are still limited even at the present time.[2,3,5−22]

For the synthesis of star-branched polymers, we have recently been developing a new methodology using chain-end- and in-chain-multifunctionalized polymers with a definite number of benzyl halide moieties as polymeric coupling agents. A variety of well-defined star-branched polymers were successfully synthesized by coupling such benzyl halide-functionalized polymers with living anionic polymers of styrene, α-methylstyrene, isoprene, 2-vinylpyridine, and *tert*-butyl methacrylate.[23−27] The advantage of this methodology is that both regular and asymmetric star-branched polymers can be synthesized from the same functionalized polymer only by changing the living anionic polymer to be coupled. The availability of various benzyl halide-functionalized polymers is an additional advantage of this method.[27−31]

More recently, we have extended the methodology by employing specially designed polymer anions consisting of two same or different polymer chains. As shown in Scheme 1, regular and asymmetric star-branched polymers of the types A_5 and AB_2C_2 could be synthesized by the coupling reaction of such polymer anions with chain-end-functionalized polymer with two benzyl chloride moieties.[32] Thus, two same or different polymer chains could be simultaneously introduced via one benzyl chloride moiety.

Scheme 1. Synthesis of Regular and Asymmetric Star-Branched Polymers



Herein we report on the synthesis of many armed star-branched polymers by the extended methodology. The objective of the present study is to examine the synthetic potential of the methodology of using polymer anions and establish it as a general procedure for star-branched polymer syntheses.

Experimental Section

Materials. The reagents were purchased from Aldrich Japan, unless otherwise stated. Styrene (98%) and 1,1-diphenylethylene (DPE) (98%) were purified by washing NaOH solution, dried over $CaCl_2$, followed by distillation over CaH_2 under reduced pressures, and finally distilled over dibutylmagnesium (ca. 3 mol %) on a vacuum line. 4-Trimethylsilyl-

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styrene (98%) was twice distilled over CaH_2 under reduced pressure and finally distilled over dibutylmagnesium (ca. 3 mol %) on a vacuum line. Tetrahydrofuran (THF) (99%) was refluxed over a Na wire overnight and distilled over $LiAlH_4$ under nitrogen. It was finally distilled from its sodium naphthalenide solution on a vacuum line. Chloroform (98%), DMF (98%), acetonitrile (98%), and $(CH_3)_3SiCl$ (99%) were distilled over CaH_2 under nitrogen. LiBr (99.95%) was dried at 100 °C for 12 h under high-vacuum conditions (10^{-6} Torr). 1,1-Bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**) was synthesized according to our procedure previously reported.[28]

Measurements. Both ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX (300 MHz for ^1H and 75 MHz for ^{13}C) in $CDCl_3$. Chemical shifts were reported in ppm downfield relative to chloroform (δ 7.24 for ^1H, δ 77.1 for ^{13}C NMR spectra) as standard. Size exclusion chromatography (SEC) was measured at 40 °C with 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. Three polystyrene gel columns (TSK_{gel} $G5000H_{XL}$, $G4000H_{XL}$, $G3000H_{XL}$ or TSK_{gel} $G4000H_{XL}$, $G3000H_{XL}$, $G2000H_{XL}$) were used. Measurable molecular weight ranges in these columns are $10^3-4 \times 10^6$ g/mol. Fractionation by HPLC was performed at 40 °C using a Tosoh HLC 8020 type fully automatic instrument equipped with a TSK-$G4000H_{HR}$ column (600 nm in length and 21.5 mm in diameter). The measurable molecular weight range is $10^3-5 \times 10^5$ g/mol. All runs for fractionation were made with THF as an eluent. The concentration of the polymer solution for fractionation was adjusted to 10−20% w/v, depending on the molecular weight of the sample. For vapor pressure osmometry (VPO) measurement, a Corona 117 instrument with a highly sensitive thermoelectric couple and equipment of very exact temperature control was used for the determination of absolute M_n value in benzene solution at 40 °C. Number-avarage molecular weight up to 100 kg/mol could be determined within an analytical error of ±5%. The apparatus constant was obtained by measuring standard polystyrene samples (M_n values = 5.05, 10.2, 15.5, and 20.5 kg/mol) and calibrating to molecular weight, since the constant is somewhat dependent on molecular weight. Static light scattering (SLS) equipped with a He−Ne laser ($\lambda = 632.8$ nm) was perfomed with Ohotuka Electronics DSL-600R instrument in THF. All the solutions were clarified by filtration through 0.10 μm pore size Teflon filters before measurements. The refractive index increment (d*n*/d*c*) in THF at 25 °C was determined for each star-branched polymer with an Ootsuka Electronics DRM-1020 refractometer operating at 633 nm. The d*n*/d*c* values in THF were found to be among 0.175 and 0.185 mL/g for regular star-branched polystyrenes and from 0.163 to 0.173 mL/g for asymmetric A_nB_m star-branched polymers consisting of polystyrene and poly(4-trimethylsilylstyrene) segments. Zimm or Berry plots were used. No difference was observed between both plots. FT-IR spectra were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. Intrinsic viscosities of star-branched polymers were measured by Ubbelhobe viscometers in toluene at 35 °C. The concentrations were in the range from 0.4 to 1.0 g/dL, and flow times were around 2.5−3.5 min.

Anionic Polymerization of Styrene and 4-Trimethylsilylstyrene. All polymerizations were carried out under high-vacuum conditions (10^{-6} Torr) in sealed glass reactors equipped with break-seals. All reactors were prewashed with potassium naphthalenide solution in THF after being sealed off from a vacuum line. Either styrene or 4-trimethylsilylstyrene was added into *sec*-BuLi in THF at −78 °C with vigorous shaking, and the reaction mixture was allowed to stand for an additional 30 min. The concentrations of monomers and *sec*-BuLi were 0.5−0.8 and 0.01−0.02 M, respectively.

Synthesis of Chain-End-Functionalized Polystyrene with 2, 4, 8, 16, and 32 Benzyl Bromide Moieties. The title benzyl bromide-multifunctionalized polystyrenes were synthesized according to our procedure previously reported.[27]

Synthesis of Chain-End-Functionalized Polystyrenes with 1,1-Diphenylethylene (DPE) Moiety. The title DPE-chain-end-functionalized polystyrenes were synthesized according to our procedure previously reported.[32]

Preparation of Polymer Anions. Polymer anion was prepared by the reaction of either polystyryllithium or poly(4-trimethylsilylstyryllithium) with chain-end-functionalized polystyrene with DPE moiety in THF at −78 °C for 20 h. A 1.1-fold excess of DPE-chain-functionalized polymer is used for comopletely consuming the living anionic polymers.

Synthesis of Star-Branched Polymers by Coupling Reaction. Regular star-branched polystyrenes having 9, 17, 33, and 57 arms (average in this case) were synthesized by the coupling reaction of chain-end-functionalized polystyrene with 4, 8, 16, and 32 benzyl bromide moieties with the polymer anion consisting of two polystyrene chains in THF at −40 °C for 10 min−168 h. A 1.2-fold excess of polymer anion relative to the benzyl bromide moiety was always used. After quenching the reactions with degassed methanol, the reaction mixtures were poured into methanol to precipitate the polymers. The objective star-branched polystyrenes were then isolated in 85−95% yields by fractionational precipitation using cyclohexane and hexanes mixed solvents (4/1 to 1/1, v/v) at 5 °C. The isolated polymers were reprecipitated from THF to methanol twice and freeze-dried from their benzene solutions for 24 h under high-vacuum conditions. Similarly, asymmetric star-branched polymers were synthesized by the same benzyl bromide-multifunctionalized polystyrenes with the polymer anion consisting of polystyrene and poly(4-trimethylsilylstyrene) segments in THF at −40 °C for 24 h. The objective star-branched polymers were isolated by HPLC fractionation.

A representative reaction procedure of the 33-arm star-branched polystyrene is as follows: Polystyryllithium ($M_{n,SEC}$ = 5.33 kg/mol, 0.246 mmol) was reacted with chain-end-functionalized polystyrene with DPE moiety ($M_{n,NMR}$ = 5.10 kg/mol, 0.270 mmol) in THF at −78 °C for 20 h. A small amount of the polymer solution was taken to measure M_n and M_w/M_n values. The resulting polymer anion (0.205 mmol) was in-situ coupled with chain-end-functionalized polystyrene with 16 benzyl bromide moieties ($M_{n,NMR}$ = 9.23 kg/mol, 0.0106 mmol × 16 = 0.171 mmol per benzyl bromide moiety) dissolved in THF (3.53 mL) at −40 °C for 24 h. After terminating the reaction with degassed methanol, the reaction mixture was poured into a large amount of methanol to precipitate the polymer. The objective star-branched polystyrene was isolated in 90% yield by fractionational precipitation using a mixture of cyclohexane and hexanes (4/3, v/v) at 5 °C. The polymer was reprecipitated from THF to methanol twice and freeze-dried from its absolute benzene solution for 24 h. The M_w value determined by SLS of 184 kg/mol was in good agreement with that calculated (M_w = 180 kg/mol). The molecular weight distribution was very narrow, the M_w/M_n value measured by SEC being 1.03.

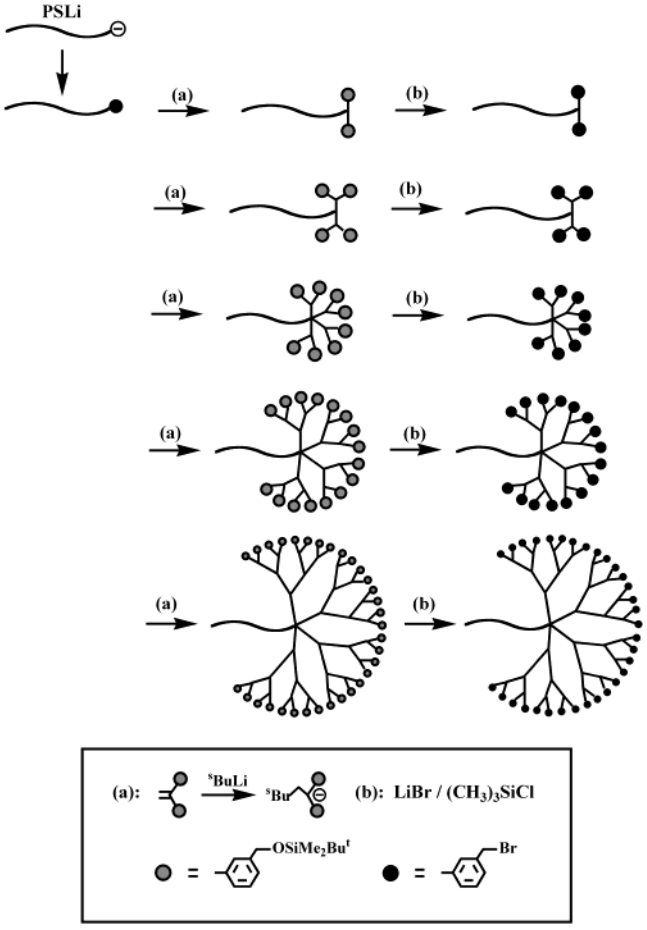
Results and Discussion

Chain-end-multifunctionalized polystyrenes with benzyl bromide moieties were synthesized by the recently developed methodology by us based on an iterative divergent approach.[27,31] As illustrated in Scheme 2, only two sets of reaction conditions are needed for the entire iterative reaction sequence which involves a coupling reaction of the terminal benzyl bromide moiety with a 1,1-diphenylalkyl anion prepared from **1** and *sec*-BuLi and a transformation reaction of the introduced *tert*-butyldimethylsilyloxymethylphenyl groups into benzyl bromide moieties by treatment with LiBr and $(CH_3)_3SiCl$. Since the resulting polymer had the same benzyl bromide moieties as the starting polymer, the same reaction sequence could be repeated five times to afford chain-end-multifunctionalized polystyrenes with 2, 4, 8, 16, and 32 benzyl bromide moieties in ca. 100% yields. These polymers have been designated by PS(BzBr)**,** and a subscript number corresponding to the benzyl bromide-end-functionalized polystyrene and the number of ter-

Table 1. Characterization Results of PS(BzBr)$_4$, PS(BzBr)$_8$, PS(BzBr)$_{16}$, and PS(BzBr)$_{32}$

	$M_n \times 10^{-3}$					functionality	
polymer	calcd	SEC	^{1}H NMR	VPO	M_w/M_n	calcd	^{1}H NMR
PS(BzBr)$_4$	4.96	4.52	5.12	4.91	1.03	4	4.0_0
PS(BzBr)$_8$	6.34	5.74	6.53	6.27	1.02	8	7.8_4
PS(BzBr)$_{16}$	9.18	6.75	9.50	9.23	1.02	16	$16._1$
PS(BzBr)$_{32}$	14.7	8.25	14.8	14.7	1.02	32	$32._0$
PS(BzBr)$_4$	7.33	6.56	7.42	7.28	1.09	4	3.9_4
PS(BzBr)$_8$	8.70	7.16	8.37	8.63	1.07	8	7.9_8

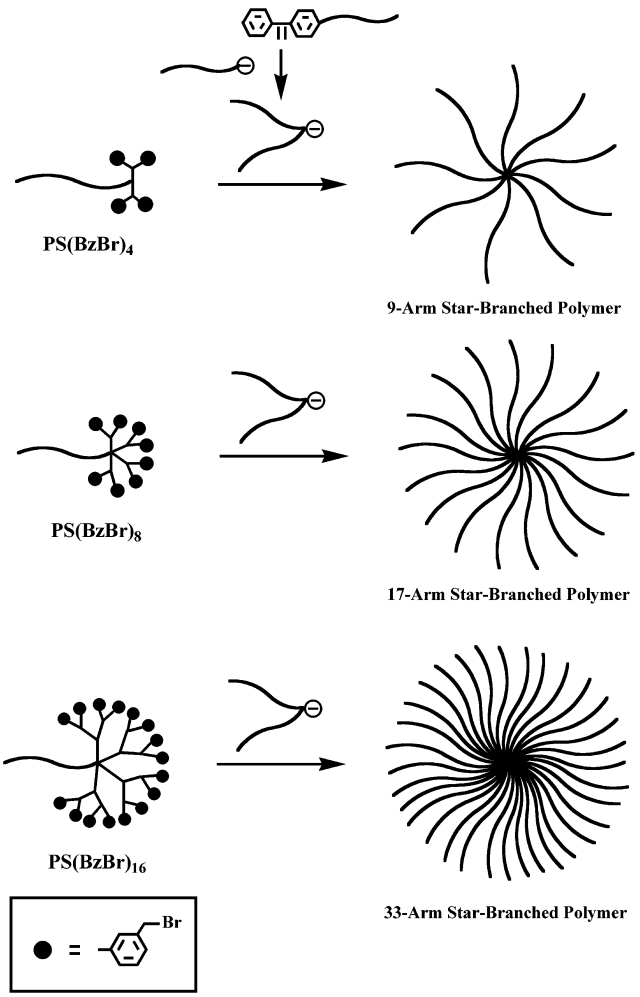
Scheme 2. Synthesis of Chain-End-Functionalized Polystyrenes with Benzyl Bromide Moieties by the Iterative Divergent Approach



minal benzyl bromide moieties and are therefore represented as PS(BzBr)$_2$, PS(BzBr)$_4$, PS(BzBr)$_8$, PS(BzBr)$_{16}$, and PS(BzBr)$_{32}$, respectively. Their characterization results are summarized in Table 1. The molecular weight of the polystyrene main chain always remained unchanged, while the dendritic branched end group increased in both size and molecular weight as the reaction sequence was repeated.

Synthesis of Regular Star-Branched Polystyrenes. As shown in Scheme 3, a series of star-branched polystyrenes were synthesized by the coupling reaction of polymer anions consisting of two polystyrene chains with benzyl bromide-functionalized polystyrenes. At first, the polymer anion was prepared by the reaction of polystyryllithium (PSLi) with chain-end-functionalized polystyrene with DPE moiety and was in-situ coupled with either PS(BzBr)$_4$, PS(BzBr)$_8$, PS(BzBr)$_{16}$, or PS(BzBr)$_{32}$. Since polystyrene segments of the polymer anions and the benzyl bromide-functionalized polystyrenes are ca. 5 kg/mol in molecular weight, the

Scheme 3. Synthesis of 9-, 17-, and 33-Arm Star-Branched Polystyrenes by Coupling Reaction of PS(BzBr)$_4$, PS(BzBr)$_8$, and PS(BzBr)$_{16}$ with Polymer Anions



resulting products can be virtually regarded as regular star-branched polystyrenes.

Figure 1A shows a SEC profile of the reaction mixture obtained by the coupling reaction with PS(BzBr)$_4$. There are a high molecular weight main peak presumable for the expected star-branched polymer and small low molecular weight peaks corresponding to the unreacted DPE-functionalized polystyrene and polymer anion used in excess in each of the reactions. The coupling reaction appeared virtually complete estimating from these peak areas. The high molecular weight polymer was isolated in 85% yield by fractional precipitation using hexanes−cyclohexane at 5 °C and characterized by SEC, VPO, and SLS. The results are summarized in Table 2.

The SEC exhibited a single peak with a narrow molecular weight distribution (see peak B in Figure 1). As expected, the observed M_n value of 41.3 kg/mol by

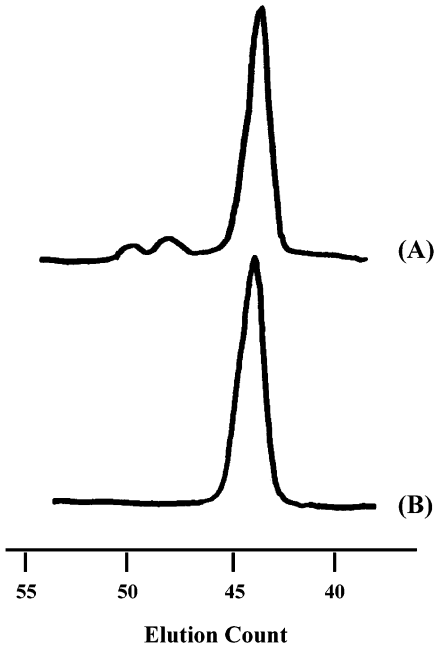


Figure 1. SEC profiles of reaction mixture (A) and 9-arm star-branched polystyrene isolated by fractional precipitation (B).

Table 2. Synthesis of 9-, 17-, and 33-Arm Star-Branched Polystyrenes by Coupling Reaction of Either $PS(BzBr)_4$, $PS(BzBr)_8$, or $PS(BzBr)_{16}$ with Polymer Anions in THF at −78 °C for 24 h

	$M_n \times 10^{-3}$			star polymer, $M_w \times 10^{-3}$		
arm no.	PS-D[a]	PSLi	$PS(BzBr)_n$ (n)	calcd	SLS	M_w/M_n
9[b]	5.70	5.88	7.28 (4)	55.2	57.8	1.03
17	5.70	6.20	8.63 (8)	109	112	1.02
33	5.10	5.33	9.23 (16)	180	184	1.03

[a] Chain-end-functionalized polystyrene. [b] $M_{n,calcd} = 53.6$ kg/mol, $M_{n,VPO} = 53.3$ kg/mol.

SEC was smaller than that predicted ($M_n = 53.6$ kg/mol). We have therefore determined the absolute M_n and M_w values by VPO and SLS. They were 53.3 and 57.8 kg/mol, respectively, and in fair agreement with those calculated ($M_n = 53.6$ kg/mol and $M_w = 55.2$ kg/mol) within analytical limits. These results are consistent with the formation of a 9-arm star-branched polystyrene. As mentioned later, the expected 9-arm architecture could also be supported by good agreement between g' values observed and calculated. Thus, the polymer anion was efficiently coupled with each of the four benzyl bromide moieties to introduce simultaneously eight polystyrene segments.

Since the coupling reaction has been shown to be effective for the synthesis of 9-arm star-branched polystyrene, the coupling reactions with $PS(BzBr)_8$ and $PS(BzBr)_{16}$ were carried out under similar conditions. The SEC profiles of the reaction mixtures showed figures similar to Figure 1A. The isolated polymers exhibited sharp monomodal SEC distributions. Their M_w values determined by SLS agreed quite well with those calculated (see Table 2). These results confirm the expectation that the coupling reactions efficiently proceed to form the corresponding 17- and 33-arm star-branched polystyrenes.

To examine the expected branched architectures of the star-branched polymers, their g' values defined as $[\eta]_{star}/[\eta]_{linear}$ were determined. Both $[\eta]_{star}$ and $[\eta]_{linear}$ are intrinsic viscosities of the star-branched polymer and the corresponding linear polymer with the same molecular weight under the same conditions. They were measured in toluene at 35 °C and calculated from the eq 1 previously reported.[33]

Table 3. Intrinsic Viscosities and g' Values for 9-, 17-, 33-, and 57-Arm Star-Branched Polystyrenes

				$g' = [\eta]_{star}/[\eta]_{linear}$		
arm no.	M_w, (kg/mol)	$[\eta]_{star}$[a] (dL/g)	$[\eta]_{linear}$[b] (dL/g)	exptl	calcd from eq 1[c]	calcd from eq 2[d]
9	57.8	0.11	0.28	0.39	0.42	0.40
17	112	0.11	0.44	0.25	0.24	0.24
33	186	0.11	0.70	0.16		0.14
57	313	0.093	1.05	0.089		0.090

[a] Measured in toluene at 35 °C. [b] Calculated from $[\eta] = 1.29 \times 10^{-4} M_w^{0.71}$. [c] Calculated from $g' = \{[(3f-2)/f^2]^{0.58}[0.724 - 0.015(f-1)]\}/0.724$ (f = arm number, $f \leq 17$). [d] $\log g' = 0.36 - 0.80 \log f$ ($f > 6$).

Table 4. Coupling Reactions of Either $PS(BzBr)_8$ or $PS(BzBr)_{16}$ with Polymer Anions in THF at −78 °C for 10 min ∼ 24 h

arm no.	$M_n \times 10^{-3}$ PS-D[a]	PSLi	$PS(BzBr)_n$(n)	time (h)	star polymer, $M_w \times 10^{-3}$ calcd	SLS	M_w/M_n
17	5.31	5.80	6.27 (8)	24	97.2	97.3	1.03
17	5.31	5.27	6.27 (8)	10	94.0	93.4	1.04
17	5.31	5.13	6.27 (8)	1	92.0	95.2	1.03
17	5.31	4.42	6.27 (8)	10 min	84.9	84.4	1.02
33	5.10	5.33	9.23 (16)	24	180	184	1.03
33	5.31	5.24	9.23 (16)	10 min	182	186	1.03

[a] Chain-end-functionalized polystyrene with DPE moiety.

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

The results are listed in Table 3. The g' values were calculated by the well-established two equations proposed by Douglas, Roovers, Freed (arm number < 17) (eq 2),[34] and Roovers (arm number > 6) (eq 3)[35] and listed in this table.

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

$$\log g' = 0.36 - 0.80 \log f \quad (3)$$

where f is the arm number. As can be seen, agreement between g' values observed and calculated is always very satisfactory in each sample synthesized here. This is actually surprising by considering that the calculated values are obtained from equations generated using stars having high molecular weight arms, and on the other hand, short arm segments near the core of many armed star-branched polymers synthesized here are forced to take on more expanded conformations. We believe that dendritic large cores of the resulting stars may be responsible for this.

To follow the progress of the coupling reaction, the reaction of either $PS(BzBr)_8$ or $PS(BzBr)_{16}$ with the polymer anion was monitored in THF at −40 °C for 24 h, 10 h, 1 h, or 10 min (see Table 4). The reaction was unexpectedly rapid and complete within 10 min even with the use of $PS(BzBr)_{16}$. Although it has recently been known that this kind of coupling reaction rapidly proceeds,[26,27,36−39] these results are remarkable considering the fact that the polymer anion seems more sterically hindered than PSLi and the functionalized polystyrenes have many reaction sites, up to 16.

Table 5. Synthesis of 9-Arm A_5B_4, 17-Arm A_9B_8, and 33-Arm $A_{17}B_{16}$ Asymmetric Star-Branched Polymers Whose A and B Segments Are Polystyrene and Poly(4-trimethylsilylstyrene) Chains

arm no.	$M_n \times 10^{-3}$ PS-D[a]	$M_n \times 10^{-3}$ PSiSLi[b]	$M_n \times 10^{-3}$ $PS(BzBr)_n$ (n)	star polymer, $M_w \times 10^{-3}$ calcd	star polymer, $M_w \times 10^{-3}$ SLS	M_w/M_n
9[c]	5.31	5.21	7.28 (4)	50.5	51.2	1.03
17	5.31	5.08	8.63 (16)	93.9	96.8	1.03
33	5.31	5.68	9.23 (32)	188	190	1.02

[a] Chain-end-functionalized polystyrene. [b] Poly(4-trimethylsilylstyryllithium). [c] $M_{n,calcd} = 49.0$ kg/mol, $M_{n,VPO} = 50.0$ kg/mol.

Table 6. Synthesis of Regular and Asymmetric Star-Branched Polymers by Coupling Reaction of $PS(BzBr)_{32}$ with Polymer Anions in THF at −40 °C for 168 h

$M_n \times 10^{-3}$ PS-D[a]	$M_n \times 10^{-3}$ PSLi	$M_n \times 10^{-3}$ $PS(BzBr)_{32}$	star polymer, $M_w \times 10^{-3}$ calcd	star polymer, $M_w \times 10^{-3}$ SLS	M_w/M_n	coupling efficiency	introduced arm number
5.10	5.06	14.7	350	311	1.03	88	56
5.31	5.28[b]	14.7	358	270	1.02	75	48
5.31	14.0	9.23[c]	327	232	1.05	70	23

[a] Chain-end-functionalized polystyrene with DPE moiety. [b] Poly(4-trimethylsilylstyryllithium). [c] $PS(BzBr)_{16}$.

Synthesis of Asymmetric Star-Branched Polymers. The most advantageous feature of the present method of using polymer anion is that two different polymer segments can be simultaneously introduced by one-step coupling reaction via one benzyl bromide moiety, as shown in Scheme 1. We first carried out the coupling reaction of either $PS(BzBr)_4$ or $PS(BzBr)_8$ with a polymer anion from PSLi and DPE-end-functionalized polyisoprene. Although the results on molecular weight characterization were satisfactory, their polyisoprene compositions observed by ^{1}H NMR were always smaller than those calculated from the feed ratios.[40] Further characterizations are required for both samples.

We have therefore chosen poly(4-trimethylsilylstyrene) instead of polyisoprene. A new polymer anion was prepared from DPE-chain-end-functionalized polystyrene and poly(4-trimethylsilylstyryl)lithium and in situ coupled with $PS(BzBr)_4$. The SEC profile of the reaction mixture is very similar to Figure 1A. The objective polymer was isolated in 85% yield by HPLC fractionation and characterized by SEC, ^{1}H NMR, VPO, and SLS measurements. The results are summarized in Table 5.

The polymer possessed a sharp monomodal SEC distribution. The M_n and M_w values measured by VPO and SLS were very close to the calculated ones. The [polystyrene] to [poly(4-trimethylsilylstyrene)] ratio of 67/33 observed by ^{1}H NMR agreed well with the calculated one (68/32). Thus, all of the analytical results indicate the 9-arm A_5B_4 star architecture of the resulting polymer.

Similarly, the coupling reaction of either $PS(BzBr)_8$ or $PS(BzBr)_{16}$ with the new polymer anion efficiently proceeded. As was seen in Table 5, all of the observed values of molecular weights and compositions were in fair agreement with those calculated. Thus, asymmetric 17-arm A_9B_8 and 33-arm $A_{17}B_{16}$ stars have been successfully synthesized. Again, it appears that there is no steric limitation in the coupling reaction of either $PS(BzBr)_4$, $PS(BzBr)_8$, or $PS(BzBr)_{16}$ with the polymer anion consisting of polystyrene and poly(4-trimethylsilylstyrene) segments.

Synthetic Limitation of the Methodology of Using Polymer Anions. Difficulty arose in the coupling reaction of either polymer anion with $PS(BzBr)_{32}$. Incomplete conversions were observed even for a longer reaction time to 168 h. The SEC profiles of the reaction mixtures showed sharp monomodal high molecular weight peaks and low molecular weight peaks corresponding to the starting polymers used in excess.

The higher molecular weight fractions were isolated and characterized by ^{1}H NMR, SEC, and SLS (Table 6). Although the isolated polymers exhibited narrow molecular distributions, their M_w values determined by SLS were somewhat lower than those calculated. The coupling efficiencies of these coupling reactions were not quantitative, but corresponded to 88% and 75%, respectively, indicating that average polymer segments of 56 and 48 in number were introduced. Thus, the polymer anion consisting of two same or different polymer segments was unable to undergo complete coupling reaction with $PS(BzBr)_{32}$ presumably because of steric hindrance arising from the polymer anions and intermediate branched polymers. There must be a maximum number of the benzyl bromide moiety between 16 and 32 in number, which is required to achieve complete coupling reaction under the conditions employed here.

Next, a higher molecular weight polymer anion ($M_w = 20.0$ kg/mol) was newly prepared by the reaction of PSLi ($M_w = 14.5$ kg/mol) with DPE-chain-end-functionalized polystyrene ($M_w = 5.50$ kg/mol) and in situ reacted with $PS(BzBr)_{16}$ in THF at −40 °C for 24 h. The SEC profile of the reaction mixture showed a sharp high molecular weight peak and small low molecular weight peaks, very similar to Figure 1A. The M_w value of the isolated polymer by SLS was 232 kg/mol. The coupling efficiency was 70% based on this M_w value, indicating that the 11 benzyl bromide moieties were coupled with the polymer anion. Thus, the effect of the molecular weight of polymer anion is also critical in the present coupling reaction. We are now investigating such limited factors in the coupling reaction in more detail in order to utilize the methodology of using polymer anions as a general procedure for the synthesis of both regular and asymmetric star-branched polymers.

Conclusions

For the development of a new general procedure for the synthesis of star-branched polymer, we have extended the methodology of using polymer anions. The in-situ coupling reactions of the polymer anions with either of $PS(BzBr)_4$, $PS(BzBr)_8$, or $PS(BzBr)_{16}$ proceeded efficiently to afford well-defined 9-, 17-, and 33-arm regular star-branched polystyrenes as well as 9-arm A_5B_4, 17-arm A_9B_8, and 33-arm $A_{17}B_{16}$ asymmetric star-branched polymers. It was however found that the coupling reaction could not completely proceed by increasing the number of benzyl bromide moiety up to 32 and the molecular weight of polymer anion up to 20 kg/mol.

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