Synthesis of Well-Defined Star-Branched Polymers by Using Chain-End-Functionalized Polystyrenes with a Definite Number of 1,3-Butadienyl Groups and Its Derivatized Functions

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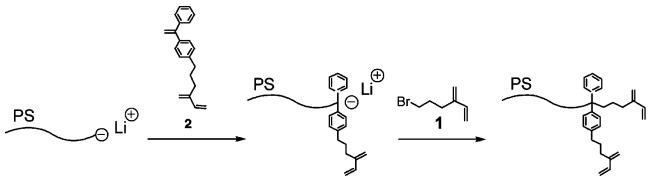
ABSTRACT: A series of new chain-end-functionalized polystyrenes with two, four, and eight 1,3-butadienyl groups ($PS(Bd)_n$, $n = 2$, 4, and 8) were synthesized by the reaction of chain-end-functionalized polystyrenes with the same numbers of benzyl bromide moieties with the 1,1-diphenylalkyl anion prepared from oligo(α-methylstyryl)lithium and 1-[4-(4-methylene-5-hexenyl)phenyl]-1-phenylethylene. These 1,3-butadiene-functionalized polymers reacted efficiently with polystyryllithium (PSLi) to afford well-defined 3-, 5-, and 9-arm star-branched polystyrenes. A successive synthesis from $(PS(Bd)_4$ to 5-arm followed by 9-arm star-branched polystyrenes was demonstrated by twice repeating the reaction sequence involving the reaction of PSLi with $(PS(Bd)_4$ and subsequent in-situ introduction of 1,3-butadienyl groups via the generated anions. The terminal 1,3-butadienyl groups were quantitatively converted into highly reactive anhydride and epoxy functions by the Diels−Alder and epoxidation reactions, respectively. The resulting anhydride- and epoxy-functionalized polymers were successfully used as new polymeric coupling agents to synthesize well-defined star-branched polystyrenes.

Introduction

1,3-Butadiene and its derivatives are readily polymerized with ionic initiators and Ziegler−Natta and related catalytic systems to produce industrially important synthetic elastomers.[1−4] In addition to their high polymerizabilities, the conjugated diene functions are highly reactive groups that undergo a wide variety of reactions.[5] Therefore, we are interested in introducing 1,3-butadienyl groups at polymer chain-ends because the resulting polymers may function as macromonomers and chain-end-functionalized polymers. Recently, we successfully introduced 1,3-butadienyl groups at chain-ends or in-chains by reacting either 6-bromo-3-methylene-1-hexene (**1**)[6] or 1-[4-(4-methylene-5-hexenyl)phenyl]-1-phenylethylene (**2**)[7] with living anionic polymers of styrene and isoprene. Two 1,3-butadienyl groups could also be introduced at the chain-end by the reaction of **2** with polystyryllithium (PSLi), followed by treatment with **1** as shown in Scheme 1. Furthermore, the 1,3-butadienyl groups thus introduced could be quantitatively converted into anhydride and epoxy functions by the Diels−Alder and epoxidation reactions, respectively. Thus, we were successful in preparing novel chain-end-functionalized polymers with anhydride and epoxy functions via 1,3-butadienyl groups that were difficult to be introduced by any other methods.[7]

In the course of our research works, we intended to exploit the anionic polymerizability of the chain-end-functionalized polymers with 1,3-butadienyl groups for the synthesis of well-defined densely comblike polymers. Although the terminal 1,3-butadienyl group

Scheme 1. Synthesis of a Chain-End-Functionalized Polystyrene with Two 1,3-Butadienyl Groups



was anionically polymerized to some extent, high conversions were not realized under usual conditions.[8] On the other hand, it was found that the reaction of a 1.5-fold excess of polystyryllithium ($M_n = 5.00$ kg/mol) with 1,3-butadiene-terminated polystyrene macromonomer ($M_n = 5.05$ kg/mol) proceeded quantitatively in a monoaddition manner in THF at −78 °C for 24 h. Only the coupled product ($M_n = 10$ kg/mol) was obtained in the reaction. Accordingly, polymers functionalized with 1,3-butadienyl chain-ends do not seem to be suitable macromonomers, but potentially usable as nonpolymerizable prepolymers, similar to known examples of chain-end-functionalized polymers with 1,1-diphenylethylene (DPE) moieties often used for the synthesis of star-branched polymers[9−12] and graft copolymers.[13]

Herein we report the synthesis of new well-defined chain-end-functionalized polystyrenes with two or more 1,3-butadienyl groups. Furthermore, we describe the successful synthesis of star-branched polymers by using chain-end-functionalized polystyrenes with anhydride and epoxy functions derived from 1,3-butadienyl groups.

Experimental Section

Materials. Unless stated otherwise, all chemicals (>98% purities) were purchased from Tokyo Kasei Kogyo Co., Ltd.

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(Japan) and used as received. Dibutylmagnesium (1.0 M solution in heptane, Aldrich, Japan) and *sec*-BuLi (1.3 M solution in cyclohexane, Aldrich, Japan) were used without purification. Oligo(α-methylstyryl)lithium was prepared by the reaction of a 2−3-fold excess of α-methylstyrene with *sec*-BuLi in THF at 25 °C for 0.5 min and then at −78 °C for an additional 30 min. Both styrene and α-methylstyrene, after washing with 10% NaOH and water, 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. Isoprene, after washing with 10% NaOH and distilling twice from CaH_2 under nitrogen, was distilled after addition of *n*-BuLi at 0 °C on the vacuum line. Tetrahydrofuran (THF) (99%, Mitubishi Chemical Co., Ltd.) was refluxed over a Na wire for 12 h and distilled from $LiAlH_4$ under nitrogen. It was finally distilled from its sodium naphthalenide solution on a vacuum line. Benzene, after washing with concentrated H_2SO_4 and water, drying over P_2O_5, and distilling from CaH_2, was distilled from its *n*-BuLi solution under nitrogen. Dichloromethane (99%, Wako Pure Chemical Industries Co., Ltd.), chloroform (99%, Nakarai Tesque Co., Ltd.), acetonitrile (99%, Nakarai Tesque Co., Ltd.), and trimethylsilyl chloride were distilled from CaH_2 under nitrogen. LiBr (99%, Koso Chemical Co., Ltd., Japan) was dried under high vacuum (10^{-6} Torr) at 100 °C for 12 h. Diethylaluminum chloride (1.0 M solution in heptane), maleic anhydride (99%, Wako Pure Chemical Industries Co., Ltd., Japan), and 3-chloroperoxybenzoic acid (70% purity) were used as received. 6-Bromo-3-methylene-1-hexene (**1**),[6] 1-[4-(4-methylene-5-hexenyl)phenyl]-1-phenylethylene (**2**),[7] 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)-ethylene (**3**),[14] and 1-(3-bromopropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane (**4**)[15] were synthesized and purified according to our previously reported procedures.

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 (pore size (bead size): 650 Å (9 μm), 200 Å (5 μm), and 75 Å (5 μm)) were used; the measurable molecular weight range is $10^4-4 \times 10^6$. The other set is consist of the following three column: pore size (bead size): 200 Å (5 μm), 75 Å (5 μm), and 20 Å (5 μm). The measurable molecular weight range is $10^3-1.5 \times 10^4$. Calibration curves were made with standard polystyrene, poly(α-methylstyrene), and polyisoprene samples for determining both M_n and M_w/M_n values. Static light scattering (SLS) measurements were performed with an Ootsuka Electronics SLS-600R instrument equipped with a He−Ne laser (633 nm) in THF at 25 °C. 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. 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 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 Ubbelohde viscometer in toluene at 35 °C.

Preparation of Anionic Living Polymers. All polymerizations 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. Styrene and α-methylstyrene were polymerized with *sec*-BuLi in THF at −78 °C for 10 min and 3 h, respectively. Isoprene was polymerized with *sec*-BuLi in heptane at 40 °C for 2 h. Heptane was then removed under vacuum, and THF (10 mL/1 g) chilled at −78 °C was added to the residual mixture at −78 °C prior to the following reactions. Monomers and initiators were used in the concentration ranges of ca. 0.5−1.0 M and ca. 0.02−0.4 M, respectively. In typical experiments, styrene (12.7 mmol) in THF solution (12.0 mL) was added to a heptane solution (4.70 mL) of *sec*-BuLi (0.142 mmol) at −78 °C with shaking. Similarly, α-methylstyrene (11.8 mmol) in THF solution (12.3 mL) was polymerized with *sec*-BuLi (0.133 mmol) in heptane solution at −78 °C for 1 h. Isoprene (23.0 mmol) in heptane solution was polymerized with *sec*-BuLi (0.135 mmol) in heptane (18.0 mL) at 40 °C for 2 h.

Coupling Reaction of Living Anionic Polymers with Chain-End-Functionalized Polystyrene with one 1,3-Butadienyl Group (PS(Bd)). The starting PS(Bd) ($M_{n,SEC}$ = 9.60 kg/mol, M_w/M_n = 1.02) was synthesized by our previous procedure[6] and used in the reactions with living anionic polymers of styrene, α-methylstyrene, and isoprene. A typical procedure for the reaction of PSLi with PS(Bd) is as follows: PSLi ($M_{n,SEC}$ = 9.40 kg/mol, 1.33 g, 0.142 mmol) in THF (15.0 mL) was added to a THF solution (10.2 mL) of PS(Bd) (0.935 g, 0.0974 mmol) at −78 °C, and the reaction mixture was stirred at −78 °C for 24 h. After the reaction was terminated with degassed methanol, the reaction mixture was poured into a large amount of methanol to precipitate the polymers. The polymers (2.26 g) were quantitatively recovered and analyzed by SEC.

Similarly, the coupling reactions of poly(α-methylstyryl)-lithium or polyisoprenyllithium with PS(Bd) were carried out on a similar scale.

Synthesis of Chain-End-Functionalized Polystyrenes with a Definite Number of 1,3-Butadienyl Groups (PS-(Bd)$_n$: n = 2, 4, and 8). A series of PS(Bd)$_n$ (n = 2, 4, and 8) were synthesized from the chain-end-functionalized polystyrenes with two, four, and eight benzyl bromide moieties (PS(BzBr)$_n$: n = 2, 4, and 8), the synthesis of which was described in detail elsewhere.[16]

The objective PS(Bd)$_n$ (n = 2, 4, and 8) were synthesized by the reaction of PS(BzBr)$_n$ (n = 2, 4, and 8) with the functionalized 1,1-diphenylalkyl anion prepared from **2** and oligo(α-methylstyryl)lithium.[17] In a typical experiment, PS(Bd)$_8$ was synthesized according to the following procedure: The 1,1-diphenylalkyl anion prepared from **2** (0.928 mmol) and oligo(α-methylstyryl)lithium (0.803 mmol) in THF (15.0 mL) was added to a THF (11.0 mL) solution containing PS(BzBr)$_8$ (M_n = 15.0 kg/mol (M_n of the polystyrene main chain = 11.2 kg/mol), 1.03 g, 0.551 mmol for eight benzyl bromide moieties) at −78 °C. The reaction mixture was allowed to stand at −78 °C for an additional 1 h and poured into a large amount of methanol to precipitate the polymer. The resulting polymer (PS(Bd)$_8$) was purified by the reprecipitation twice from THF into methanol and then freeze-drying from its benzene solution for 24 h (1.15 g, 94%). The polymer was analyzed by ^1H and ^{13}C NMR, SEC, and VPO.

Determination of Functionality. Functionality of the benzyl bromide moiety introduced at chain-end was determined by comparing the signal intensities at 4.2−4.4 ppm assigned to bromomethylene protons with those at 0.2−0.8 ppm of methyl protons of initiator fragments of the polymer. Similarly, functionality of the 1,3-butadienyl moiety was determined from the signal ratio of 1,3-butadienyl vinyl protons at 5.0−5.2 ppm to the methyl protons of the initiator fragments. Since the signals of the initiator fragments of the polymer and those of *sec*-Bu group used for preparing the 1,1-diphenylalkyl anions crossover to some extent, the analytical error was usually in the range between 5 and 10%. To determine the functionality more accurately, methoxybenzene was added as an internal standard.

Synthesis of Star-Branched Polystyrenes by Reaction of PSLi with PS(Bd)$_n$ (n = 2, 4, and 8). To synthesize 3-, 5-, and 9-arm star-branched polystyrenes, the reaction of PSLi with each PS(Bd)$_n$ was carried out in THF at −78 °C for 24 h. A 1.5-fold excess of PSLi relative to 1,3-butadienyl group was usually used. A typical experiment for synthesizing a 9-arm star-branched polystyrene is as follows: PSLi ($M_{n,SEC}$ = 9.50 kg/mol, M_w/M_n = 1.02, 1.63 g, 0.172 mmol) in THF (16.8 mL) was added to a THF solution (2.52 mL) of PS(Bd)$_8$ (M_n = 18.1 kg/mol (M_n of the polystyrene main chain = 11.2 kg/mol), M_w/M_n = 1.02, 0.262 g, 0.116 mmol for eight 1,3-butadienyl groups) at −78 °C. The reaction mixture was stirred at −78 °C for 24 h and quenched with degassed methanol. The resulting polymer was precipitated in methanol and isolated by frac-

Table 1. Reaction of Living Anionic Polymers with PS(Bd) (M_n = 9.60 kg/mol) in THF

living anionic polymers					monoadduct			
					M_n		M_w/M_n	yield[b]
entry	type	M_n (SEC)	temp (°C)	time (h)	calcd	SEC[a]	(SEC)	(%)
PSLi	polystyryllithium	10.7	−78	1	20.3	16.7	1.04	22[c]
PSLi	polystyryllithium	9.40	−78	24	19.0	19.3	1.03	100
PSLi	polystyryllithium	10.0	−40	24	19.3	20.4	1.02	100
PαMSLi	poly(α-methylstyryl)lithium	10.5	−78	24	20.1	22.5	1.01	100
PILi	polyisoprenyllithium	11.7	−78	24	21.3	19.0	1.02	14[c]

[a] Calculated based on SEC peak using polystyrene calibration curve. [b] Calculated based on SEC calibration curve (molar ratio vs area ratio) of the addition product with two precursors by using UV detector. The yields of monoadducts were almost the same after the fractionation. [c] Although the yields of resulting polymers were quantitative, the monoadducts were obtained in 22 and 14% yields.

tional precipitation with cyclohexane/hexanes (4/1, v/v) at 5 °C. After collecting the polymer by filtration, it was reprecipitated from THF into methanol three times and freeze-dried from its absolute benzene solution. The 9-arm star-branched polystyrene (1.27 g) was obtained in 90% yield.

Successive Synthesis of Star-Branched Polymer. The synthetic procedures from $PS(Bd)_4$ to 5-arm followed by 9-arm star branched polystyrenes are as follows:

First Iteration: The PSLi ($M_{n,SEC}$ = 11.5 kg/mol, M_w/M_n = 1.03, 0.835 g, 0.0726 mmol) in THF (7.50 mL) was added to a THF solution (2.10 mL) of $PS(Bd)_4$ (M_n = 14.4 kg/mol (M_n of the polystyrene main chain = 11.2 kg/mol), M_w/M_n = 1.02, 0.183 g, 0.0508 mmol for four 1,3-butadienyl groups) at −78 °C, and the mixture was stirred at −78 °C for 24 h. A THF solution (3.80 mL) of **1** (0.0925 mmol) was added and stirred at −78 °C for an additional 1 h. After fractional precipitation with cyclohexane/hexanes (4/1, v/v) at 5 °C followed by reprecipitation from THF into methanol three times, the 5-arm star-branched polystyrene (0.669 g) was obtained in 90% yield. The polymer was freeze-dried three times from its absolute benzene solution and used for the second iteration.

Second Iteration: The PSLi ($M_{n,SEC}$ = 11.2 kg/mol, M_w/M_n = 1.03, 0.678 g, 0.0605 mmol) in THF (5.50 mL) was added to a THF solution (2.10 mL) of the 5-arm star-branched polystyrene (0.583 g, 0.0398 mmol for four 1,3-butadienyl groups) at −78 °C. The reaction mixture was stirred at −78 °C for an additional 24 h. A THF solution (3.32 mL) of **1** (0.0802 mmol) was then added, and the mixture was stirred at −78 °C for 1 h. After fractional precipitation, the 9-arm star-branched polystyrene (0.973 g) was obtained in 95% yield.

Synthesis of Star-Branched Polymers by Using Chain-End-Functionalized Polystyrenes with Anhydride and Epoxy Functions. *Synthesis of PS−NH_2 and Chain-End-Functionalized Polystyrene (PS(Anh)$_n$)*: The PS−NH_2 (M_n = 10.2 kg/mol, M_w/M_n = 1.04, and degree of NH_2 functionality (TLC−FID) = 98%) was synthesized by the reaction of PSLi with **4** according to our procedure previously reported.[15] The polymer was purified by reprecipitation three times, and a trace amount of water was removed completely by azeotropic distillation from its absolute benzene solution three times.

The terminal 1,3-butadienyl groups were transformed into anhydride functions by the Diels−Alder reaction of $PS(Bd)_n$ with maleic anhydride according to the our previously reported procedure.[6,7] A typical experiment for the synthesis of $PS(Anh)_4$ is as follows: Under a nitrogen atmosphere, a mixture of $PS(Bd)_4$ (M_n = 14.4 kg/mol (M_n of the polystyrene main chain = 11.2 kg/mol), M_w/M_n = 1.02, 0.207 g, 0.0575 mmol for four 1,3-butadienyl groups) and maleic anhydride (0.425 g, 4.33 mmol) was dissolved in CH_2Cl_2 (3.0 mL), and Et_2AlCl in hexane (0.95 M, 0.10 mL, 0.0950 mmol) was added at once. The reaction mixture was stirred at 15 °C for 24 h. After evaporation, the residues were dissolved in THF and poured into methanol to precipitate the polymer. The resulting polymer was reprecipitated three times from THF to methanol and purified by azeotropic distillation from its absolute benzene solution three times. After freeze-drying, $PS(Anh)_4$ (0.475 g) was obtained in 96% yield.

Synthesis of 5-Arm Star-Branched Polystyrene by Reaction of PS−NH_2 with PS(Anh)$_4$: The $PS(Anh)_4$ (0.251 g, 0.0738 mmol for four anhydride functions) dissolved in dry benzene (2.5 mL) was added to a dry benzene solution (3.0 mL) of PS−NH_2 (1.13 g, 0.111 mmol) at 25 °C under an atmosphere of nitrogen. The reaction mixture was allowed to stand at 25 °C for an additional 1 h. The 5-arm star-branched polystyrene (0.880 g) was isolated in 88% yield by SEC fractionation.

Synthesis of 9-Arm Star-Branched Polystyrene by Reaction of PSLi with Chain-End-Functionalized Polystyrene with Eight Epoxy Functions: Chain-end-functionalized polystyrenes with epoxy functions ($PS(EO)_n$) were synthesized by the procedure previously reported by us.[7] A typical experiment for the synthesis of $PS(EO)_8$ is as follows: 3-Chloroperoxybenzoic acid (1.11 g, 4.52 mmol) in CH_2Cl_2 (14.0 mL) was added to a solution of $PS(Bd)_4$ (M_n = 14.4 kg/mol (M_n of the polystyrene main chain = 11.2 kg/mol), M_w/M_n = 1.02, 0.407 g, 0.113 mmol for four 1,3-butadienyl groups) dissolved in CH_2Cl_2 (6.0 mL) at 15 °C, and the reaction mixture was stirred at 15 °C for 24 h. The polymer was precipitated in methanol. After reprecipitation and freeze-drying of the resulting polymer, the $PS(EO)_8$ (0.422 g) was obtained in 97% yield.

The PSLi ($M_{n,SEC}$ = 10.0 kg/mol, M_w/M_n = 1.03, 1.52 g, 0.152 mmol) in THF (15.0 mL) was added to a THF solution (2.32 mL) of $PS(EO)_8$ (M_n = 18.2 kg/mol (M_n of the polystyrene main chain = 11.2 kg/mol), M_w/M_n = 1.02, 0.234 g, 0.103 mmol for eight epoxy functions) at −78 °C, and the reaction mixture was stirred at −78 °C for 168 h. The polymer was precipitated in methanol. After SEC fractionation, the 9-arm star-branched polystyrene (1.10 g) was obtained in 90% yield.

Results and Discussion

Reaction of Living Anionic Polymers with Chain-End-Functionalized Polystyrene with 1,3-Butadienyl Group. PSLi reacted stoichiometrically with chain-end-functionalized polymer with 1,3-butadienyl group (PS(Bd)) in THF at −78 °C to afford the corresponding monoaddition product. Under such conditions, the terminal 1,3-butadienyl group did not polymerize or even oligomerize. We therefore attempted to synthesize star-branched polymers by monoaddition. We studied this addition reaction in more detail, since monoaddition is essential for the synthesis.

To follow the progress of the reaction, PS(Bd) (M_n = 9.60 kg/mol) was reacted with a 1.5-fold excess of PSLi (M_n = 10.7 kg/mol) in THF at −78 °C for 1 h. Since the reaction proceeded slowly, the coupling efficiency was only 22%. The expected monoaddition product ($M_{n,calcd}$ = 19.0 kg/mol, $M_{n,SEC}$ = 19.3 kg/mol) was quantitatively formed after 24 h, and no higher molecular weight products were produced. Below −40 °C, the reaction always afforded only the monoaddition product in 100% yield after 24 h. The results are summarized in Table 1. Poly(α-methylstyryl)lithium also quantitatively underwent monoaddition with PS(Bd) in THF at −78 °C. As expected, poly(2-methyl-1,3-butadienyl)lithium reacted very slowly with the 1,3-butadienyl group of PS(Bd) forming only in 14% of the monoaddition product at −78 °C after 24 h. Both PSLi and poly(α-methylstyryl)-lithium are therefore potentially usable for our purpose.

Scheme 2. Synthesis of Chain-End-Functionalized Polystyrenes with Benzyl Bromide Moieties Based on an Iterative Approach

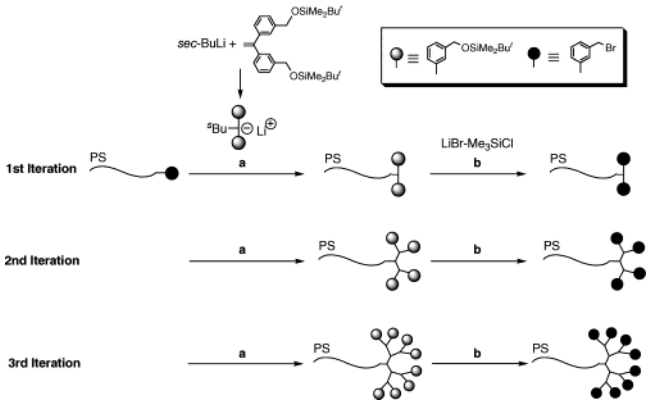


Table 2. Synthesis of PS(BzBr)$_n$[a]

	M_n (kg/mol)					f[b]	
type	calcd	SEC	^{1}H NMR	VPO	M_w/M_n (SEC)	calcd	^{1}H NMR
PS(BzBr)$_2$	10.6	11.5	11.5	12.1	1.02	2	2.0_8
PS(BzBr)$_4$	12.3[c]	11.9	12.3	12.5	1.02	4	3.9_4
PS(BzBr)$_8$	13.6[c]	12.8	15.0	15.0	1.03	8	8.0_0

[a] Yields of PS(BzBr)$_n$ were 100% in all cases. [b] Functionality of benzyl bromide moieties. [c] The M_n value was calculated by using the average value of the three observed M_n values (11.7 kg/mol) of PS(BzBr)$_2$.

Synthesis of Chain-End-Functionalized Polystyrenes with Two, Four, and Eight 1,3-Butadienyl Groups. For the synthesis of a series of star-branched polymers, chain-end-functionalized polymers with two or more 1,3-butadienyl groups are needed. As shown in Scheme 1, chain-end-functionalized polystyrene with two 1,3-butadienyl groups (PS(Bd)$_2$) could be synthesized by the addition reaction of PSLi to **2**, followed by treatment with **1**.[7] Unfortunately, further functionalization with more than three 1,3-butadienyl groups at the polymer chain-end is impossible by this method. We recently developed a new general, versatile, and convenient method for the synthesis of chain-end-multifunctionalized polystyrenes with benzyl bromide moieties (PS(BzBr)$_n$) based on an iterative divergent approach, which involves two reactions in each iterative reaction sequence as illustrated in Scheme 2.[16] The first reaction is a coupling reaction of the terminal benzyl bromide moiety with 1,1-diphenylalkyl anion prepared from *sec*-BuLi and 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**3**) to introduce two 3-*tert*-butyldimethylsilyloxymethylphenyl groups at the chain-end. In the second reaction, the two 3-*tert*-butyldimethylsilyloxymethylphenyl groups are transformed into two benzyl bromide moieties by treatment with a 1:1 mixture of LiBr and trimethylsilyl chloride. Fortunately, these two reactions proceed quantitatively. Thus, the number of benzyl bromide moieties doubles. Since the resulting polystyrene has the same benzyl bromide moieties as the starting polymer, this reaction sequence can be repeated. Both PS(BzBr)$_4$ and PS(BzBr)$_8$ were readily obtained by repeating the reaction sequence two more times. The results are summarized in Table 2.

If the functionalized 1,1-diphenylalkyl anion prepared from *sec*-BuLi (see ref 16) and **2** instead of **3** reacts with PS(BzBr)$_n$, the same number of 1,3-butadienyl groups as benzyl bromide moieties should be introduced as shown in Scheme 3. Indeed, reaction of the 1,1-diphenylalkyl anion prepared from **2** and oligo(α-methylstyryl)lithium with PS(BzBr)$_2$ proceeded virtually quantitatively in THF at −78 °C for 1 h. The results are summarized in Table 3. The resulting polymer shown in Figure 1 exhibits a sharp monomodal SEC distribution, which is almost identical to that of the original benzyl bromide-functionalized polymer. Neither shoulder nor tailing was observed. The molecular weight distribution was very narrow, with $M_w/M_n = 1.02$. The M_n values observed by SEC, VPO, and ^{1}H NMR agreed well with that calculated. The ^{1}H NMR spectrum of the polymer showed new resonances at 5.00−5.20 ppm assigned to the 1,3-butadienyl vinyl protons, while the resonance at 4.35 ppm for methylene protons of the benzyl bromide completely disappeared. The degree of 1,3-butadienyl functionality was determined to be 2.00 by comparing the above-mentioned resonances with those corresponding to methyl protons of the initiator fragments. Thus, the end-functionalization was quantitative within analytical limits.

Scheme 3. Synthesis of Chain-End-Functionalized Polystyrenes with Two, Four, and Eight 1,3-Butadienyl Groups

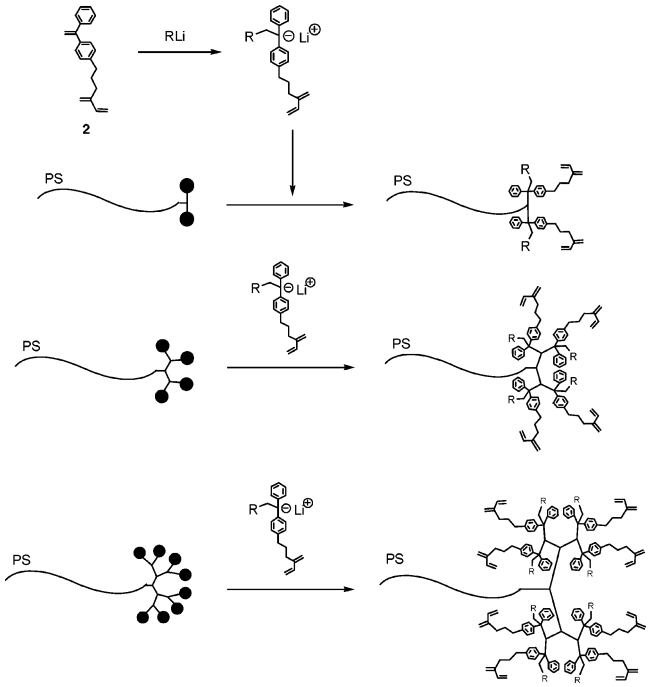


Table 3. Synthesis of PS(Bd)$_n$[a]

	M_n (kg/mol)					f[b]	
type	calcd	SEC	^{1}H NMR	VPO	M_w/M_n (SEC)	calcd	^{1}H NMR
PS(Bd)$_2$	12.5[c]	12.3	12.5	12.9	1.02	2	2.0_0
PS(Bd)$_4$	14.2[c]	13.4	14.4	14.0	1.02	4	4.0_0
PS(Bd)$_8$	18.0[c]	19.3	18.1	17.9	1.02	8	8.0_7

[a] Yields of PS(Bd)$_n$ were 100% in all cases. M_n of the polystyrene main chain = 11.2 kg/mol. [b] Functionality of 1,3-butadienyl groups. [c] The molecular weights of oligo(α-methylstyrylene) were 291, 295, and 352 g/mol, respectively.

Similarly, 1,1-diphenylalkyl anion prepared from **2** was reacted with either PS(BzBr)$_4$ or PS(BzBr)$_8$ under identical conditions. The results are also summarized in Table 3. The resulting polymers possessed sharp monomodal SEC distributions. The M_n values determined by VPO and ^{1}H NMR agreed quite well with those calculated. The ^{1}H NMR analyses showed evidence for quantitative degrees of end-functionalization

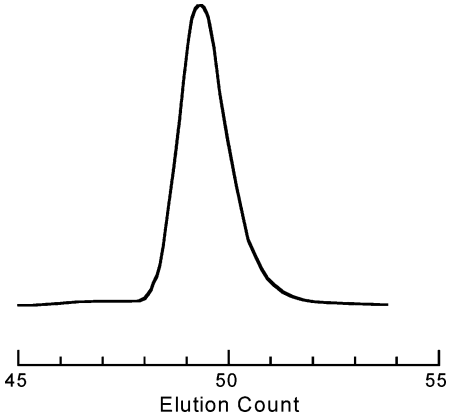
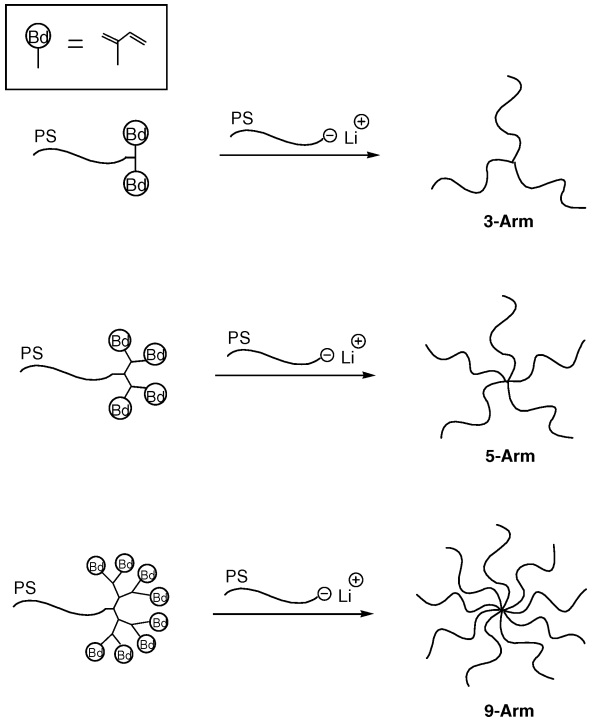


Figure 1. SEC RI trace of $PS(Bd)_2$.

Scheme 4. Synthesis of Star-Branched Polystyrenes by Using Chain-End-Functionalized Polystyrenes with 1,3-Butadienyl Groups



in both samples. Thus, the coupling reactions also proceed satisfactorily to afford well-defined $PS(Bd)_4$ and $PS(Bd)_8$. In this polymer series, the molecular weight of the polystyrene main chain remained unchanged (M_n = 11.2 kg/mol), while the dendritic end groups increased in size and molecular weight going from $PS(Bd)_2$ to $PS(Bd)_8$.

Synthesis of Star-Branched Polystyrenes by Coupling of PSLi with $PS(Bd)_2$, $PS(Bd)_4$, and $PS(Bd)_8$. The reaction of PSLi with either $PS(Bd)_2$, $PS(Bd)_4$, or $PS(Bd)_8$ was attempted for the synthesis of star-branched polymers as illustrated in Scheme 4. All of the reactions were carried out in THF at −78 °C for 24 h. A 1.5-fold excess of PSLi to each 1,3-butadienyl group was used to force the reaction to completion. The M_n value of PSLi was designed to be around 10 kg/mol. The resulting star-branched polystyrenes are therefore regular type star-branched polymers.

Figure 2A shows a representative SEC profile of the reaction mixture from the reaction of PSLi with $PS(Bd)_8$. There are two distinct peaks presumably for the expected star-branched polymer and the unreacted polystyrene used in excess. No higher molecular weight polymer was produced under these conditions. In addition, a very small peak eluted at 47 mL was observed in Figure 2. This is often observed when PSLi is allowed to stand in THF at −78 °C for 24 h or longer reaction times and may be the dimeric linked product by the reaction of PSLi with polystyrene with a terminal phenylvinylene group produced by eliminating LiH from PSLi.[18,19] The coupling efficiency of the reaction was estimated to be virtually quantitative based on these peak areas by UV detection and isolated in 90% yield by fractional precipitation using hexanes and cyclohexane (v/v, 1/4) at 5 °C. As shown in Figure 2B, the isolated polymer showed a sharp monomodal SEC distribution without any shoulders and tailings, indicating that the polymer was pure and free of both $PS(Bd)_8$ and polystyrene used as an arm segment. Similarly, other star-branched polystyrenes were synthesized and isolated in 85−95% yields by fractional precipitation. The results are summarized in Table 4. As expected from the star-branched structures, the M_n values estimated from SEC relative to polystyrene were smaller than those predicted in all samples. However, the absolute molecular weights determined by SLS agreed quite well with those predicted. ^{1}H NMR analysis indicates that all of the 1,3-butadienyl groups had reacted in each product. Thus, the reactions proceeded quantitatively to afford the 3-, 5-, and 9-arm star-branched polystyrenes with well-defined structures.

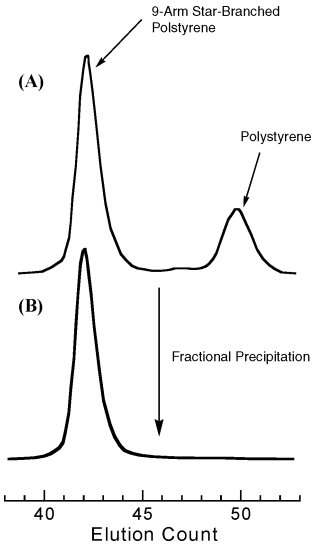


Figure 2. SEC RI trace of polymers obtained by the reaction of PSLi with $PS(Bd)_8$: (A) before fractionation; (B) after fractionation.

To obtain further evidence for star-branched architectures of the resulting polymers, the parameter g' defined as $[\eta]_{star}/[\eta]_{linear}$ was calculated in each sample. The values of intrinsic viscosity, $[\eta]_{star}$, of the star-branched polymers were measured in toluene at 35 °C. The $[\eta]_{linear}$ values were calculated from eq 1 previously reported.[20]

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

Since the correlation between g' and arm number of star-branched polymer has been well-established on the basis of theoretical models and experimental results,[21−26] the g' values for 3-, 5-, and 9-arm star-branched

Table 4. Synthesis of 3-, 5-, and 9-Arm Star-Branched Polystyrenes by Reaction of PSLi with PS(Bd)$_n$[a]

	PSLi			star-branched polystyrene[b]					
	M_n (kg/mol)		M_w/M_n	M_n (kg/mol)		M_w(kg/mol)			M_w/M_n
type	calcd	SEC	(SEC)	calcd	SEC	calcd[c]	SLS[d]	dn/dc	(SEC)
3-arm	10.1	10.8	1.02	34.4	30.6	35.4	36.6	0.191	1.03
5-arm	10.5	10.2	1.03	55.0	44.3	57.2	57.0	0.188	1.04
9-arm	10.0	9.50	1.02	94.1	52.6	99.1	96.2	0.185	1.03

[a] M_n of the polystyrene main chain = 11.2 kg/mol. [b] Yields of star-branched polystyrenes after fractionation were more than 85% in all cases. [c] Calculated from M_n (calcd) and M_w/M_n (SEC). [d] In THF at 25 °C.

Table 5. Viscosities and g' Values for 3-, 5-, and 9-Arm Star-Branched Polystyrenes

	M_w,[a]	$[\eta]_{star}$,[b]	$[\eta]_{linear}$,[c]	g'	
type	kg/mol	dL/g	dL/g	exptl	calcd[d]
3-arm	36.6	0.183	0.224	0.82	0.83
5-arm	57.0	0.196	0.307	0.64	0.63
9-arm	96.2	0.197	0.445	0.44	0.42

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

polymers were calculated from eq 2 proposed by Douglas, Roovers, and Freed.[25]

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

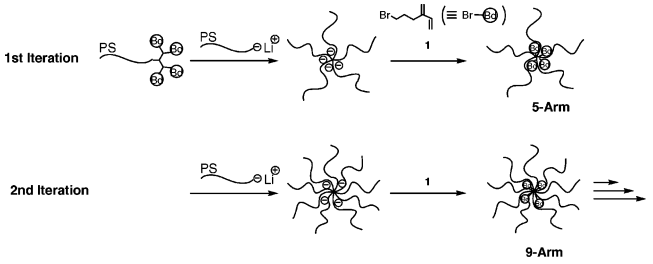
The results are summarized in Table 5. Agreement between g' values experimentally determined and calculated from eq 2 is quite satisfactory in each sample. Thus, the results are consistent with the formation of the expected 3-, 5-, and 9-arm star-branched polystyrenes.

We conclude that the reaction of PSLi with either of PS(Bd)$_n$ (n = 2, 4, and 8) proceeds quantitatively to afford the corresponding star-branched polystyrenes. In each case, the 1,3-butadienyl group reacted stoichiometrically with PSLi. Neither polymerization nor oligomerization occurred. Thus, we have demonstrated that a series of PS(Bd)$_n$ are successfully employed as precursor polymers or polymeric coupling agents in conjunction with living anionic polymers for star-branched polymer synthesis. The key point for this success is to find the suitable reaction conditions under which the terminal 1,3-butadienyl groups of PS(Bd)$_n$ undergo stoichiometric monoaddition reaction with PSLi. If poly(α-methylstyryl)lithium is used instead of PSLi in the reaction with PS(Bd)$_n$, the syntheses of well-defined asymmetric star-branched polymers are expected.

Successive Synthesis of Star-Branched Polymer. The addition reaction of PSLi to PS(Bd)$_n$ is not a termination reaction. In this reaction, a number of polystyrene chains are linked around the core, and the same numbers of 1,3-butadienyl anions are generated simultaneously at the linking points, which permits further functionalization reactions and polymerizations. Therefore, reactions of this type, named "living functionalization reaction" by Quirk,[27] have synthetic advantages over general termination reactions. Herein, if 1,3-butadienyl groups can be introduced via the generated anions, PSLi can again be added to the 1,3-butadienyl groups thus introduced to afford a new star-branched polymer with increasing polystyrene segments as illustrated in Scheme 5.

To realize such a successive star-branched polymer synthesis, PS(Bd)$_4$ was reacted with a 1.5-fold excess

Scheme 5. Successive Synthesis of Star-Branched Polystyrenes



of PSLi toward each 1,3-butadienyl function in THF at −78 °C for 24 h, followed by treatment with a 1.2-fold excess of **1** toward PSLi for 1 h under the same conditions. The SEC profiles of the polymers obtained before and after the reaction with **1** were almost identical. The resulting polymer was isolated in 90% yield by fractional precipitation and characterized by ^{1}H NMR, SEC, SLS, and viscosity measurement. The results are summarized in Table 6. These analytical results are consistent with the formation of the expected 5-arm star-branched polystyrene. More importantly, four 1,3-butadienyl groups were introduced quantitatively in the resulting polymer. This also provides a direct evidence for generating four 1,3-butadienyl anions by the reaction of PS(Bd)$_4$ with PSLi.

With the 5-arm star-branched polystyrene having four 1,3-butadienyl groups, the reaction with PSLi followed by treatment with **1** was carried out under the same conditions. Similar to the 5-arm star-branched polystyrene mentioned before, the SEC profile of the reaction mixture shown in Figure 3A exhibits only two peaks corresponding to the desired star-branched polymer and unreacted polystyrene used in excess in the reaction. As can be seen in Figure 3, the peak of the starting 5-arm star-branched polystyrene overlaps to some extent with that of the 9-arm star-branched polystyrene. It is therefore difficult to detect a small amount of the 5-arm star-branched polystyrene, if any, from Figure 3. The higher molecular weight polymer was isolated in 95% yield by fractional precipitation (see Figure 3C) and characterized by ^{1}H NMR, SEC, and SLS. The results are also listed in Table 6. The M_w value determined by SLS agreed well with that predicted assuming that the resulting polymer was the expected 9-arm star-branched polystyrene. The introduction of four 1,3-butadienyl groups in this polymer was clearly observed by ^{1}H NMR. Thus, we have successfully synthesized 5-arm followed by 9-arm star-branched polystyrenes with PS(Bd)$_4$ as a starting material by repeating two times the reaction sequence involving the reaction with PSLi followed by treatment with **1**. More iterations are still needed to establish the procedure as a general methodology and are therefore under investigation.

Table 6. Successive Synthesis of 5- and 9-Arm Star-Branched Polystyrenes with PS(Bd)$_4$[a] Used as a Starting Polymer

	PSLi			star-branched polystyrene[b]							
	M_n (kg/mol)		M_w/M_n	M_n (kg/mol)		M_w (kg/mol)			M_w/M_n	f[e]	
type	calcd	SEC	(SEC)	calcd	SEC	calcd[c]	SLS[d]	dn/dc	(SEC)	calcd	^{1}H NMR
5-arm	11.0	11.5	1.02	58.6	45.3	60.9	59.6	0.188	1.04	4	4.2_1
9-arm	11.1	11.2	1.02	103	64.9	106	105	0.188	1.03	4	4.0_0

[a] M_n of the polystyrene main chain = 11.2 kg/mol. [b] Yields of star-branched polystyrenes after fractionation were more than 90% in both cases. [c] Calculated from M_n (calcd) and M_w/M_n (SEC). [d] In THF at 25 °C. [e] Functionality of 1,3-butadienyl groups.

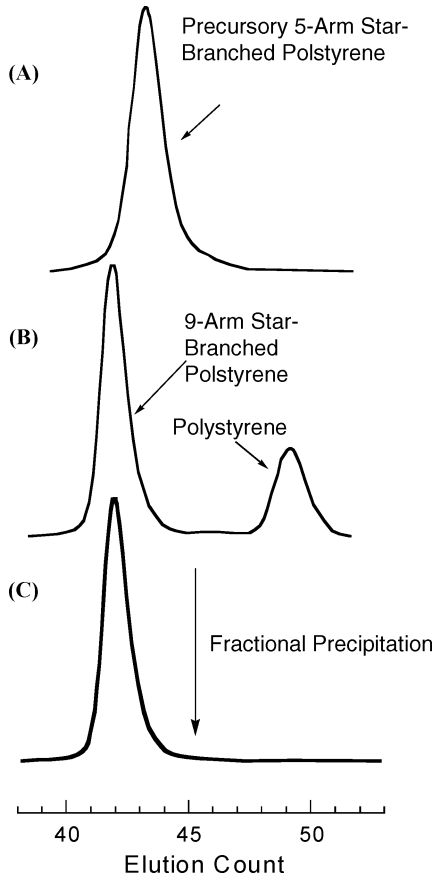


Figure 3. SEC RI trace of polymers obtained by reaction of PSLi with a 5-arm star-branched polystyrene with four 1,3-butadienyl groups at the core: (A) before fractionation; (B) after fractionation.

Synthesis of Star-Branched Polystyrenes by Using Chain-End-Functionalized Polystyrenes with Anhydride and Epoxy Functions. Previously, we were successful in converting the terminal 1,3-butadienyl groups into anhydride[6,7] and epoxy[7] functions by the Diels−Alder and epoxidation reactions. We anticipated that such highly reactive anhydride- and epoxy-functionalized polymers could also be utilized as new polymeric coupling agents for the synthesis of star-branched polymers. For this purpose, two or more terminal anhydride and epoxy functions are needed. Therefore, the Diels−Alder and epoxidation reactions of PS(Bd)$_2$, PS(Bd)$_4$, and PS(Bd)$_8$ were performed carefully, and the resulting anhydride- and epoxy-multifunctionalized polymers were used for the synthesis of star-branched polymers.

At first, the Diels−Alder reactions of each PS(Bd)$_n$ with maleic anhydride in the presence of a catalytic amount of Et_2AlCl were carried out in CH_2Cl_2 at 15 °C for 24 h. All of the samples exhibited sharp monomodal SEC distributions. Little change was observed in the SEC profiles before and after the reaction. The ^{13}C NMR spectra showed a new resonance at 174.5 ppm assigned to the anhydride carbonyl carbons, while two resonances at 113.3 and 115.5 ppm for the 1,3-butadienyl vinyl carbons disappeared completely in each spectrum. The ^{1}H NMR spectra also revealed the complete disappearance of the 1,3-butadienyl groups and the quantitative formation of anhydrides. A new multiplet at 5.4 ppm assigned to the cyclohexene olefinic protons was clearly observed after the reaction. The degrees of anhydride functionalization were determined to be quantitative (>98%) in all polymer samples. Thus, two, four, and even eight anhydrides were successfully introduced at polymer chain-ends.

Table 7. Synthesis of 5- and 9-Arm Star-Branched Polystyrenes by Using PS(Anh)$_4$ and PS(EO)$_8$[a]

	M_n (kg/mol)		M_w (kg/mol)			M_w/M_n
type	calcd	SEC	calcd[b]	SLS[c]	dn/dc	(SEC)
5-arm	54.2	44.6	56.4	55.6	0.188	1.04
9-arm	94.7	53.8	100	99.6	0.180	1.06

[a] Yields of star-branched polystyrenes after fractionation were more than 88% in both cases. [b] Calculated from M_n (calcd) and M_w/M_n (SEC). [c] In THF at 25 °C.

The chain-end-functionalized polystyrene with four anhydride functions thus synthesized (PS(Anh)$_4$) was reacted with a 6-fold excess of polystyrene functionalized with NH_2 at the chain-end (PS−NH_2, a 1.5-fold excess of NH_2 group to each anhydride) in dry benzene at 25 °C under an atmosphere of nitrogen. The reaction was rapid and complete within 1 h. The SEC profile of the reaction mixture showed only two sharp monomodal peaks corresponding to the coupled product and unreacted PS−NH_2 used in excess (see Figure 4). The peaks of the PS(Anh)$_4$ precursor and PS−NH_2 completely overlapped. However, the peak area ratio of the coupled product with such low molecular weight polymers by UV detection was very close to that calculated assuming that the PS(Anh)$_4$ precursor was consumed and the excess PS−NH_2 remained. Thus, the yield of the coupled product was estimated to be virtually quantitative. The coupled product was isolated in 88% yield by SEC fractionation and was characterized by SEC and SLS. The results are summarized in Table 7. The SEC profile of the isolated polymer showed a narrow molecular weight distribution. The M_w value determined by SLS agreed quite well with that predicted. Accordingly, PS(Anh)$_4$ works effectively as a polymeric coupling agent toward PS−NH_2 to afford a 5-arm star-branched polystyrene. The star-branched polymer obtained by this reaction possesses four polar amide bonds and carboxylic acids in its core and therefore may have interesting solution behavior.

As another possible polymeric coupling agent, a series of chain-end-functionalized polymers with epoxy functions were synthesized by the reaction of PS(Bd)$_n$ with 3-chloroperoxybenzoic acid and used for the synthesis of star-branched polymers. The SEC profiles of polymers before and after the reaction were almost identical. The

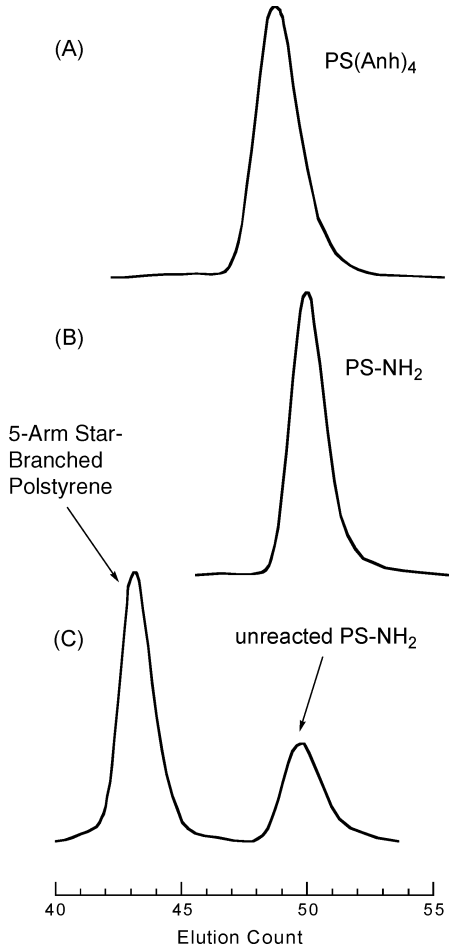


Figure 4. SEC RI trace of polymer mixture obtained by reaction of $PS(Anh)_4$ with $PS-NH_2$.

^{13}C NMR spectra of the resulting polymers showed new resonances at 44.0 and 44.4 ppm assigned to the epoxy primary carbons and complete disappearance of two resonances at 113.3 and 115.5 ppm for the 1,3-butadienyl vinyl carbons. The ^1H NMR spectra also indicated that the conversion from 1,3-butadienyl group to diepoxide was quantitative by the observation that all of the 1,3-butadienyl vinyl protons had disappeared and new resonances at 2.43 and 2.65−2.90 ppm assigned to the epoxy protons appeared. The degrees of functionalization of epoxy groups by ^1H NMR spectra are quantitative in all cases by comparing peak area ratio of epoxy protons with those methyl protons of initiator fragments. Thus, a series of novel well-defined chain-end-functionalized polystyrenes with 4, 8, and 16 epoxy functions, $PS(EO)_4$, $PS(EO)_8$, and $PS(EO)_{16}$, were obtained. The number of the epoxy group doubles by the epoxidation of the 1,3-butadienyl group.

The synthesis of 9-arm star-branched polymer was attempted by reacting a 1.5-fold excess of PSLi toward each epoxy function of the $PS(EO)_8$ in THF at −78 °C for 168 h. The coupling efficiency of this reaction was also nearly quantitative estimated from the two peak areas by UV detection. The coupled product was isolated in 90% yield and characterized by ^1H NMR, SEC, and SLS. The results are also summarized in Table 7. The resulting polymer possessed a narrow molecular weight distribution and a molecular weight close to that predicted. The ^1H NMR analysis revealed that all of the epoxy groups had reacted completely. All of the analytical results are consistent with the formation of the expected 9-arm star-branched polystyrene. Thus, $PS-(EO)_8$ is also an effective polymeric coupling agent.

The principal advantage of using both $PS(Anh)_n$ and $PS(EO)_n$ is that these terminal functions have much higher reactivities toward electrophiles than the 1,3-butadienyl group and thereby permit use of less reactive living anionic polymers and several chain-end-functionalized polymers with electrophilic functional groups such as NH_2 and OH. Moreover, the star-branched polymers obtained by the reactions herein possess a number of carboxylic acids and alkoxides (or hydroxy groups) produced at the linking points that can be used for further functionalizations. The synthetic utility of $PS(Bd)_n$, $PS(Anh)_n$, and $PS(EO)_n$ is thus obvious for the synthesis of star-branched polymers.

Conclusions

A series of chain-end-functionalized polystyrenes with 1,3-butadienyl groups, $PS(Bd)_2$, $PS(Bd)_4$, and $PS(Bd)_8$, were readily and quantitatively synthesized by the reaction of $PS(BzBr)_2$, $PS(BzBr)_4$, and $PS(BzBr)_8$ with the functionalized 1,1-diphenylalkyl anion prepared from **2**. By using either of these polymers as a polymeric coupling agent in the reaction of PSLi, well-defined 3-, 5-, and 9-arm star-branched polystyrenes were synthesized successfully. The possibility of successive star-branched polymer synthesis was demonstrated by repeating the reaction sequence involving the reaction of $PS(Bd)_4$ with PSLi followed by **1**. The terminal 1,3-butadienyl groups of $PS(Bd)_n$ were converted quantitatively into anhydrides and epoxy functions by the Diels−Alder and epoxidation reactions, respectively. Thus, novel well-defined chain-end-functionalized polystyrenes with 2, 4, and 8 anhydrides and 4, 8, and 16 epoxy functions were successfully synthesized. Among them, the $PS(Anh)_4$ and the $PS(EO)_8$ were effective polymeric coupling agents with $PS-NH_2$ and PSLi respectively for synthesizing the corresponding 5- and 9-arm star-branched polystyrenes. Accordingly, other anhydride- and epoxy-multifunctionalized polystyrenes are expected to be used as polymeric coupling agents or functionalized precursor polymers.

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