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Synthesis of Well-Defined High-Density Branched Polymers Carrying Two Branch Chains in Each Repeating Unit by Coupling Reaction of Benzyl Bromide-Functionalized Polystyrenes with Polymer Anions Comprised of Two Polymer Segments

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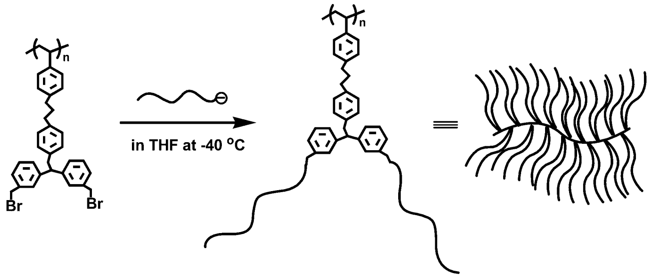
ABSTRACT: A series of high-density branched polymers have been synthesized by the coupling reaction of poly(4-(3-(4-bromomethylphenyl)propyl)styrene with polymer anion comprised of two same or different polymer chains, prepared from polystyryllithium and either polystyrene or polyisoprene with 1,1-diphenylethylene chain-end functionalization. Under certain conditions, the reaction proceeded essentially quantitatively to afford the requisite extremely high-density branched polymers carrying two branch chains in each repeating unit and having M_w values of up to 3×10^6. Furthermore, quite new graft-block copolymers with similar high-density branched architectures could also be successfully synthesized. The resulting polymers are well-defined in branched architecture and precisely controlled in chain lengths of both backbone and branch segments. It was however observed that the reaction efficiency was significantly affected by several variables such as degrees of polymerization of the backbone polymer and polymer anion and branched and chemical structures of the polymer anion. The structures of the resulting high-density branched polymers were investigated by intrinsic viscosity measurement. These polymers may possibly adopt starlike structures in toluene as evidenced by their g' values.

Introduction

High-density branched polymers carrying one branch chain in each repeating unit are usually synthesized by the polymerization of macromonomers.[1−6] Recently, the controlled synthesis of such high-density branched polymers has been undertaken by means of living anionic, ring-opening methathesis, and atom transfer radical polymerizations of macromonomers.[7−21] The poly(macromonomer)s thus synthesized are well-defined in densely branched architecture and precisely controlled in chain lengths of both backbone and branch segments. However, it has been difficult to synthesize high molecular weight poly(macromonomer)s and, in most cases, degrees of polymerization (DP)s of backbone and branch segments are limited to less than hundred.

It has been long believed that such densely branched polymers cannot be synthesized by means of "grafting-onto" method because of serious steric limitation.[22] In 1997, Deffieux and Schappacher first demonstrated that densely branched polymers structurally analogous to the aforementioned poly(macromonomer)s are successfully synthesized by the living cationic polymerization of 2-chloroethyl vinyl ether, followed by the coupling reaction of the resulting poly(2-chloroethyl vinyl ether) with polystyryllithium based on grafting-onto methodology.[23−25] In fact, the reaction proceeded essentially quantitatively to introduce one polystyrene chain into each repeating unit of the poly(2-chloroethyl vinyl ether) used as a backbone polymer. Soon after, we and Hadjichristidis and co-workers also successfully synthesized similar well-defined high-density branched polymers by the coupling reactions of poly(3-chloro(or bromo)methylstyrene),[26−28] poly(4-chloromethylstyrene),[30] or poly(4-(3,4-epoxybutyl)styrene)[29] with a wide variety of living anionic polymers of styrene, isoprene, 2-vinylpyridine, *tert*-butyl methacrylate, or ethylene oxide. High molecular weight densely branched polymers with M_w values of up to 3×10^6 could be synthesized.[27] Furthermore, the possible introduction of high molecular weight branch segments ($M_w \sim 7 \times 10^5$) is an additional advantage of the above-mentioned coupling reactions.[27]

Scheme 1. Synthesis of High-Density Branched Polymer Carrying Two Polymer Chains in Each Repeating Unit



More recently, we have further demonstrated that it is possible to introduce even two branch chains into each repeating unit of the backbone polymer by the reaction of a specially designed polystyrene derivative bearing two benzyl bromide functionalities in each monomer unit with various living anionic polymers as illustrated in Scheme 1.[31,32] Thus, quite surprisingly, no steric limitation as predicted is practically present in these coupling systems under appropriate conditions. Accordingly, the grafting-onto methodology using specified coupling reactions allows a promising procedure for the synthesis of well-defined high-density branched polymers carrying one and even two branch chains in each repeating unit.

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Herein, we report on an alternative methodology based on grafting-onto method for the synthesis of high-density branched polymers carrying two same or different branch segments in each repeating unit. The methodology involves a precise synthesis of poly(4-(3-(4-bromomethylphenyl)propyl)styrene) via living anionic polymerization and a coupling reaction of the resulting poly(4-(3-(4-bromomethylphenyl)propyl)styrene) with polymer anion comprised of two polymer chains, prepared from polystyryllithium and either polystyrene or polyisoprene with 1,1-diphenylethylene chain-end functionalization. The objective of the present study is to examine the synthetic potential as well as limitation of the methodology, which may allow access to extremely high-density branched polymers carrying two branch segments in each repeating unit.

Experimental Section

Materials. All reagents were purchased from Aldrich Japan, unless otherwise stated. Styrene (98%) and isoprene (99%) were washed with NaOH (10%) aqueous solution and dried over $MgSO_4$. After filtration of $MgSO_4$, styrene was distilled twice over CaH_2 under reduced pressure and finally distilled over dibutylmagnesium (ca. 3 mol-%) on the vacuum line into ampules equipped with break seals that were prewashed with potassium naphthalenide in THF. Isoprene was distilled over CaH_2 under nitrogen and finally distilled over *n*-BuLi (ca. 2 mol-%) at 0 °C on the vacuum line into ampules with break seals that were prewashed with *sec*-BuLi in heptane. Tetrahydrofuran (THF) (99%) was refluxed over Na wire for overnight and distilled over $LiAlH_4$ under nitrogen. It was distilled from its sodium naphthalenide solution on the vacuum line. Chloroform (98%), *N*,*N*-dimethylformamide (98%), acetonitrile (98%), and trimethylsilyl chloride (99%) were distilled over CaH_2 under nitrogen or reduced pressure. Dibutylmagnesium, *tert*-butyldimethylsilyl chloride (98%, Shinetsu Chemical Co., Ltd. Japan), imidazole, and *sec*-BuLi (1.3 M, in cyclohexane) were used as received. LiBr (99.95%) was dried at 120 °C for 12 h under high vacuum conditions (10^{-6} Torr).

Measurements. Both ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to tetramethylsilane (δ 0.00) for ^{1}H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR, respectively. Size-exclusion chromatograms (SEC) were measured with a TOSOH HLC-8020 at 40 °C with UV (254 nm) or refractive index detection. THF was used as carrier solvent at a flow rate of 1.0 mL/min at 40 °C. Three polystyrene gel columns of bead size 5 μm and pore size of 200, 75, and 20 Å or bead size 9 μm and pore size of 650, 200, and 75 Å were used. These sets of the column covered molecular weight range from $10^3 \sim 4 \times 10^5$ g/mol and $10^4 \sim 4 \times 10^6$ g/mol, respectively. Fractionation by HPLC was performed at 40 °C using TOSOH HLC-8020 type fully automatic instrument equipped with a TSK-G4000H_{HR} column (600 nm in length and 21.5 mm in diameter). Measurable molecular weight range is $10^3 \sim 5 \times 10^5$ 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. Calibration curves were made with standard polystyrene and polyisoprene samples to determine M_n and M_w/M_n values. Static light scattering (SLS) equipped with a He−Ne laser (λ = 632.8 nm) was perfomed with an Ohotsuka Electronics DSL-600R instrument in THF or benzene at 25 °C. Berry plot was used to determine the M_w value of each star-branched polymer. The refractive index increment (d*n*/d*c*) in THF or benzene at 25 °C was determined with an Ohotsuka Electronics DRM-1020 refractometer operating 632.8 nm. Vapor pressure osmometry (VPO) measurements were made with a Corona 117 instrument in benzene at 40 °C with a highly sensitive thermoelectric couple (TM-32K: sensitivity 35 000 μV ± 10%/1 M) and with equipment of very exact temperature control. Therefore, the molecular weight can be measured up to 100 kg/mol with an error of about 5%. The apparatus constant was obtained by measuring standard polystyrene samples (M_n = 5.05, 10.2, 20.5, and 45.0 kg/mol) and calibrating their values against M_n values. FT-IR spectra were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. Intrinsic viscosities of branched polymers were measured by Ubbelhode viscometers in toluene at 35 °C.

Poly(3-bromomethylstyrene). It was synthesized according to our procedure previously reported.[33]

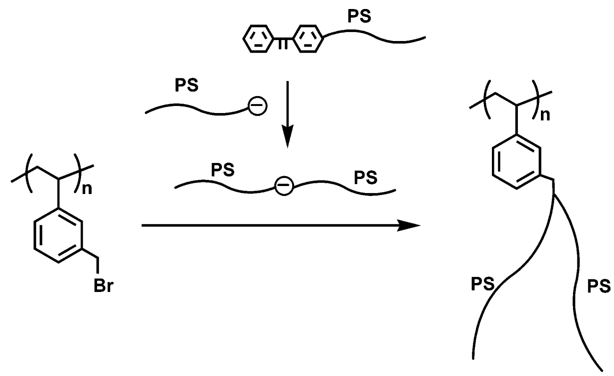
Poly(4-(3-(4-bromomethylphenyl)propyl)styrene) (3). It was synthesized according to our procedure previously reported.[32]

Anionic Polymerization of Styrene and Isoprene. 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 or with *sec*-BuLi in heptane after being sealed off from a vacuum line. Styrene was polymerized by adding styrene precooled at −78 °C into *sec*-BuLi in THF at −78 °C with vigorous shaking, and the reaction mixture was allowed to stand for additional 30 min. Isoprene was polymerized with *sec*-BuLi in heptane at 40 °C for 2 h. The concentrations of monomers and *sec*-BuLi were 0.3~0.8 M and 0.01~0.02 M, respectively.

Synthesis of Chain-End-Functionalized Polystyrene and Polyisoprene with 1,1-Diphenylethylene (DPE) Moiety. The title DPE-chain-end-functionalized polymers were prepared from either of DPE-end-capped polystyryllithium (PSLi) or polyisoprenyllithium (PILi) with 1-(4-(4-bromobutyl)phenyl)-1-phenylethylene according to our procedure previously reported.[34,35] The resulting polymers were characterized by ^{1}H NMR, FT-IR, SEC, and VPO measurements.

Preparation of Polymer Anions. The polymer anion was prepared in THF at −78 °C for 20 h by the addition reaction of PSLi to a 1.1-fold excess of DPE-chain-end-functionalized polystyrene or polyisoprene. The use of a 1.1-fold excess of DPE-chain-functionalized polymer is esstential for completely consuming PSLi. The reactions appeared to go to completion within 1 h in the model reaction, but the reaction mixtures were usually allowed to stir for an additional 20 h at −78 °C by way of precaution. A typical reaction is as follows: Polystyryllithium ($M_{w\,SEC}$ = 5.54 kg/mol, 0.240 mmol) in THF (12.2 mL) was added to chain-end-functionalized polystyrene with DPE moiety ($M_{w\,SEC}$ = 5.70 kg/mol, 0.266 mmol) in THF (14.4 mL) at −78 °C, and the reaction mixture was allowed to stir at −78 °C for additional 20 h. The resulting polymer anion was used in situ in the next coupling reaction. Prior to the reaction, a small amount of the polymer solution was taken to determine the M_n and M_w/M_n values of the polymer anion.

Scheme 2. Reaction of Poly(3-bromomethylstyrene) with Polymer Anion Comprised of Two Polystyrene Chains



Synthesis of High-Density Branched Polymers. A series of high-density branched polymers were synthesized by the coupling reaction of either poly(3-bromomethylstyrene) or **3** with the polymer anions comprised of two polystyrene chains in THF at −40 °C for 1~168 h. A 1.2-fold excess of polymer anion relative to the benzyl bromide functionality was always used. After quenching, the reactions with degassed methanol, the reaction mixtures were poured into methanol to precipitate the polymers. The objective high-density branched polystyrenes were isolated in more than 90% yields by fractionational precipitation using cyclohexane and hexane mixed solvents (4/1 ~ 1/1, *v*/*v*) at 5 °C. The isolated polymers were reprecipitated twice from THF to methanol and freeze-dried from their benzene solutions for 24 h under high vacuum. Similarly, high-density branched copolymers were synthesized by reacting **3** with the block polymer anion comprised of polystyrene and polyisoprene chains in THF at −40 °C for 168 h. The objective branched copolymers were isolated by HPLC fractionation.

A typical synthetic procedure is as follows: PSLi ($M_{\mathrm{w\,SEC}}$ = 5.54 kg/mol, 0.380 mmol) in THF (19.0 mL) was reacted with DPE chain-end-functionalized polystyrene ($M_{\mathrm{w\,SEC}}$ = 5.70 kg/mol, 0.417 mmol) in THF (21.6 mL) 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 (0.245 mmol) was in situ coupled with **3** (M_w = 6.08 kg/mol, 0.201 mmol per benzyl bromide functionality) dissolved in THF (1.13 mL) at −40 °C for 168 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 high-density branched polystyrene was isolated in 92% yield by fractionational precipitation using a mixture of cyclohexane and hexane (4/1, 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 216 kg/mol was in good agreement with that calculated (M_w = 217 kg/mol). The molecular weight distribution was very narrow, the M_w/M_n value measured by SEC being 1.02.

Results and Discussion

Reaction of Poly(3-bromomethylstyrene) with Polymer Anion. The synthesis of extremely high-density branched polymers carrying two branch chains in each repeating unit was first attempted by the coupling reaction of poly(3-bromomethylstyrene)s with polymer anions comprised of two polystyrene chains. The synthetic outline is illustrated in Scheme 2.

Table 1. Synthesis of Poly(3-bromomethylstyrene) and 3

	$M_n \times 10^{-3}$			$M_w \times 10^{-3}$	$\mathrm{DP_w}$	M_w/M_n
polymer	calcd	SEC	^{1}H NMR	SLS	SLS	SEC
PBMS[a]	4.50	3.79	4.46	4.59[b]	23.3	1.03
PBMS	16.5	14.3	17.0	17.5	88.7	1.03
3a	6.05	4.23	5.96	6.08[b]	19.3	1.02
3b	16.7	10.6	16.7	17.0	53.9	1.02
3c	30.5	21.1	32.9	33.7	107	1.02

[a] Poly(3-bromomethylstyrene). [b] M_w was calculated from M_n by ^{1}H NMR and M_w/M_n by SEC.

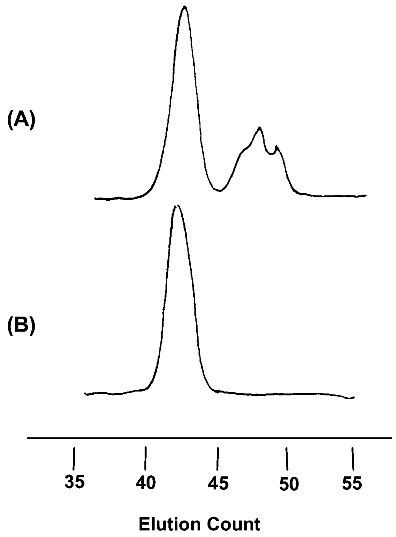


Figure 1. SEC profiles of reaction mixture (**A**) and branched polymer isolated by fractional precipitation (**B**).

Two poly(3-bromomethylstyrene)s different in molecular weights used as backbone polymers were prepared by the living anionic polymerization of 3-(*tert*-butyldimethylsilyloxymethyl)styrene, followed by treatment with LiBr−$(CH_3)_3SiCl$ to transform the silyl group into the benzyl bromide moiety. Since the transformation reaction proceeded cleanly and quantitatively, the resulting polymers possessed predictable molecular weights and narrow molecular weight distributions. The results are summarized in Table 1. The polymer anion comprised of two polystyrene chains was prepared by the addition reaction of PSLi to a 1.1-fold excess of DPE chain-end-functionalized polystyrene and then used in situ in the next coupling reaction.

The reaction of poly(3-bromomethylstyrene) with a 1.2-fold excess of the polymer anion was carried out in THF at −40 °C for 168 h. Figure 1A shows the SEC profile of the reaction mixture obtained by coupling poly(3-bromomethylstyrene) (M_w = 4.59 kg/mol, $\mathrm{DP_w}$ = 23.3) with the polymer anion comprised of two polystyrene chains (M_w = 5.71 kg/mol + 5.29 kg/mol = 11.0 kg/mol). There are a high molecular weight main peak for the objective branched polymer and three additional small low molecular weight peaks. Based on their molecular weights, two small low molecular weight peaks were corresponding to the deactivated polymer anion and DPE-chain-end-functionalized polystyrene used in excesses in the reactions. A residual small peak among the main and two small peaks was not significant after 24 h of the reaction, but increases gradually with time as was seen in Figure 1A.[36] The coupled polymer was isolated in 93% yield by fractional precipitation using cyclohexane−hexane at 5 °C and characterized by SEC and SLS, respectively. The results are summarized in Table 2.

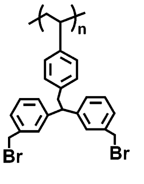
Table 2. Synthesis of High-Density Branched Polymers by Coupling Reaction of Poly(3-bromomethylstyrene)s with Polymer Anions Comprised of Two Polystyrene Chains in THF at −40 °C for 168 h

PBMS[a]		PSLi	PS-D[b]	polymer anion	branched polymer[c] $M_w \times 10^{-3}$			
$M_w \times 10^{-3}$	DP_w	$M_w \times 10^{-3}$	$M_w \times 10^{-3}$	$M_w \times 10^{-3}$	calcd	SEC	SLS	CE[d] (%)
4.59	23.3	5.71	5.29	11.0	256	60	202	79
4.59	23.3	26.0	5.29	31.3	730	197	545	75
17.5	88.7	5.04	5.76	10.8	959	150	441	46
17.5	88.7	20.3	5.76	26.1	2314	355	810	35

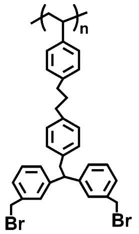
[a] Poly(3-bromomethylstyrene). [b] Chain-end-functionalized polystyrene with DPE moiety. [c] $M_w/M_n = 1.02{\sim}1.03$. [d] Coupling efficiency.

The isolated polymer, shown in Figure 1B, exhibits a sharp monomodal distribution. The M_w/M_n value estimated by SEC was 1.03. However, the absolute M_w value of 202 kg/mol measured by SLS was smaller than the expected value of 256 kg/mol. Based on these values, the coupling efficiency was calculated to be 79%. Increasing the molecular weight of the polymer anion (M_w = 26.0 kg/mol + 5.29 kg/mol = 31.3 kg/mol) slightly decreased the efficiency to 75% in the reaction. Furthermore, the efficiencies considerably dropped to 46% and 35%, respectively, in the reaction of the higher molecular weight poly(3-bromomethylstyrene) (M_w = 17.5 kg/mol, DP_w = 88.7) with the corresponding polymer anions. Thus, the molecular weight of poly(3-bromomethylstyrene) used as a backbone polymer significantly affected the efficiency of the reaction with polymer anion. Unfortunately, the reaction was not quantitative under the conditions employed here, and the requisite high-density branched polymer carrying two branch segments in each repeating unit could not be obtained.

Reaction of Poly(4-(3-(4-bromomethylphenyl)-propyl)styrene) with Polymer Anion. We previously observed that the introduction of the spacer between backbone chain and reaction site was essential for synthesizing densely branched polymers carrying two branch segments in each repeating unit by the similar coupling reaction (see Scheme 1). The functionalized polystyrene bearing two benzyl bromide functionalities, **1**, shown below, did not completely undergo coupling reaction with PSLi-end capped with DPE. On the other hand, the polystyrene derivative, **2**, in which the two benzyl bromide functionalities were separated from the backbone polystyrene chain by three methylene units, readily and quantitatively reacted with DPE-end-capped PSLi under the same conditions.[32]



1



2

With the success of the reaction by using the spacer in mind, we have employed poly(4-(3-(4-bromomethylphenyl)propyl)styrene) (**3**) as an alternative backbone polymer. The backbone polymer, **3**, is designed in such a way that the benzyl bromide functionality is separated from the backbone polystyrene chain by three methylene units. The preparation of **3** was carried out by the living anionic polymerization of 4-(3-(4-*tert*-butyldimethylsilyloxymethylphenyl)propyl)styrene, followed by treatment with LiBr−$(CH_3)_3SiCl$. The expected chemical and chain structures of the resulting polymers were confirmed by ^1H and ^{13}C NMR, SEC, VPO, and SLS. As was seen, three polymers different in molecular weights, **3a** (M_w = 6.08 kg/mol), **3b** (M_w = 17.0 kg/mol), **3c** (M_w = 33.7 kg/mol) were prepared as backbone polymers used in the coupling reaction. The results are also summarized in Table 1. As illustrated in Scheme 3, the reaction of **3** with polymer anion was performed under the conditions in THF at −40 °C identical to those used in the coupling reaction of poly(3-bromomethylstyrene)s with polymer anions. We always set the reaction time of 168 h by way of precaution, although the reaction was usually complete within 24 h as described later. The results are summarized in Table 3.

Scheme 3. Reaction of 3 with Polymer Anion Comprised of Two Polystyrene Chains

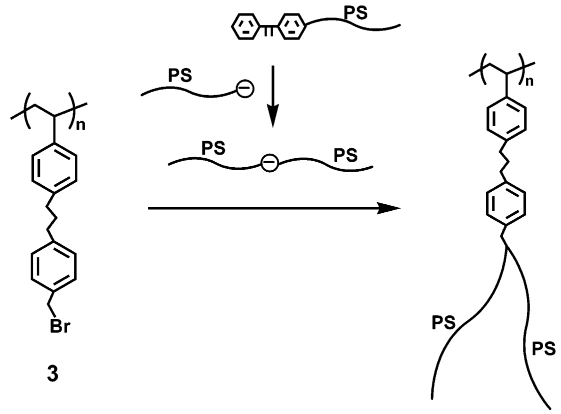


Figure 2A gives the SEC profile of the reaction mixture obtained by the reaction of **3a** (M_w = 6.08 kg/mol, DP_w = 19.3) with the polymer anion comprised of two polystyrene chains (M_w = 5.54 kg/mol + 5.70 kg/mol = 11.2 kg/mol). As can be seen, there are a high molecular weight main peak for the coupled product and small additional three peaks eluted at low molecular weight sides corresponding to its prepolymers and unknown polymers similar to those produced in the reaction of poly(3-bromomethylstyrene) with polymer anion mentioned in the preceding section. This reaction appeared virtually complete estimating from these peak areas. The high molecular weight coupled polymer was isolated in 92% yield by fractional precipitation.

The isolated polymer showed a sharp monomodal SEC distribution (see Figure 2B). The M_w value measured by SLS was 216 kg/mol and quite consistent with the target value of 217 kg/mol assuming that all reaction sites reacted completely. ^1H NMR analysis of the polymer indicates that all of the benzyl bromide functionalities had completely reacted. Accordingly, the efficiency was 100% in this case.[37] Furthermore, the reaction of **3a** with either of the two higher molecular weight polymer anions (M_w = 24.5 kg/mol + 5.70 kg/mol = 30.2 kg/mol, and M_w = 55.1 kg/mol + 5.70 kg/mol = 60.8 kg/mol) proceeded virtually quantitatively.

Table 3. Synthesis of High-Density Branched Polymers by Coupling Reaction of 3 with Polymer Anions Comprised of Two Polystyrene Chains in THF at −40 °C for 168 h

3		PSLi	PS-D[a]	polymer anion	branched polymer[b] $M_w \times 10^{-3}$			
$M_w \times 10^{-3}$	DP_w	$M_w \times 10^{-3}$	$M_w \times 10^{-3}$	$M_w \times 10^{-3}$	calcd	SEC	SLS	CE[c] (%)
6.08	19.3	5.34	5.70	11.2	217	69	216	100
6.08	19.3	24.5	5.70	30.2	582	206	587	100
6.08	19.3	55.1	5.70	60.8	1173	424	1150	98
6.77	21.3	12.8	11.8	24.3	523	150	523	100
17.0	53.9	4.87	5.35	10.2	551	109	546	99
17.0	53.9	21.8	5.70	27.5	1480	267	1540	104
17.0	53.9	49.2	5.35	54.6	2942	596	3060	105
17.0	53.9	14.9	11.8	26.7	1442	243	1110	77
33.7	107	4.65	5.35	10.0	1070	168	843	79
33.7	107	27.2	5.35	32.6	3487	482	2720	78
33.7	107	29.1		29.1	3140	461	3144	100

[a] Chain-end-functionalized polystyrene with DPE moiety. [b] $M_w/M_n = 1.02{\sim}1.04$. [c] Coupling efficiency.

Table 4. Synthesis of High-Density Branched Polymers by Coupling Reaction of 3b (M_w = 17.0 kg/mol, DP_w = 53.9) with Polymer Anions Comprised of Two Polystyrene Chains in THF at −40 °C for 168 h

reaction time (h)	PSLi	PS-D[a]	polymer anion	branched polymer[b] $M_w \times 10^{-3}$			
	$M_w \times 10^{-3}$	$M_w \times 10^{-3}$	$M_w \times 10^{-3}$	calcd	SEC	SLS	CE[c] (%)
1	19.5	5.35	24.8	1340	260	1070	80
24	19.6	5.35	24.9	1343	295	1340	100
168	21.8	5.70	27.5	1480	267	1540	104

[a] Chain-end-functionalized polystyrene with DPE moiety. [b] $M_w/M_n = 1.02{\sim}1.03$. [c]Coupling efficiency.

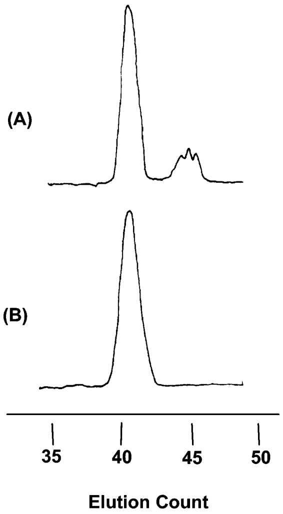


Figure 2. SEC profiles of reaction mixture (**A**) and branched polymer isolated by fractional precipitation (**B**).

A relatively high molecular weight polymer anion comprised of two polystyrenes similar in molecular weight (M_w = 12.5 kg/mol + 11.8 kg/mol = 24.3 kg/mol) also reacted completely with **3a′** (M_w = 6.77 kg/mol, DP_w = 21.3 very close to **3a** in molecular weight).

To follow the progress of the reaction, the reaction of **3b** with the polymer anion (M_w = ca. 20 kg/mol + ca. 5.5 kg/mol = ca. 25 kg/mol) was monitored in THF at −40 °C for 1, 24, and 168 h. The results are summarized in Table 4. It was observed that the reaction proceeded in 80% yield even after 1 h and was complete within 24 h (presumably within a few hours). Nevertheless, the reaction time of 168 h was set throughout this study, since higher molecular weight backbone polymers and polymer anions were used in the reaction.

The reaction of another backbone polymer having a higher molecular weight, **3b**, (M_w = 17.0 kg/mol, DP_w = 53.9), with either of three polymer anions having M_w values (10.2∼54.6 kg/mol) proceeded with quantitative efficiency (Table 3). A high-density branched polymer with a M_w value of up to 3×10^6 could be synthesized. Thus, the presence of the spacer between the main polystyrene chain and the benzyl bromide functionality is very important and essential for introducing two branch segments in each repeating unit of **3**. As mentioned above, the reaction of **3b** with the polymer anion (M_w = 21.8 kg/mol + 5.70 kg/mol = 27.5 kg/mol) was complete, whereas a similar molecular weight polymer anion (M_w = 26.7 kg/mol) comprised of different polystyrene segments in molecular weight (M_w = 14.9 kg/mol + 11.8 kg/mol = 26.7 kg/mol) could not react quantitatively with **3b** under the identical conditions. In this case, the efficiency was 77%. Thus, the branched structure of polymer anion (or the position of anion in polymer chain) is also an important factor for achieving the introduction of two polymer segments.

With use of a backbone polymer with the highest molecular weight in this study, **3c**, (M_w = 33.7 kg/mol, DP_w = 107), difficulty arose even in the reaction with a low molecular weight polymer anion (M_w = 4.15 kg/mol + 5.35 kg/mol = 9.50 kg/mol). The reaction proceeded with only 79% efficiency and far from complete after 168 h. Similarly, the reaction of **3c** with a relatively high molecular weight polymer anion (M_n = 27.2 kg/mol + 5.35 kg/mol = 32.6 kg/mol) proceeded with 78% efficiency. The effect of molecular weight of **3** on the reaction with polymer anion is thus very critical. A similar trend was observed in the related reactions previously reported by Deffieux et al.,[23] Hadjichristidis et al.,[30] and us.[27,28,30] This can be explained by changing from flexible to a stiff chain conformation of **3** with increasing the number of branch segments and thereby increasing steric hindrance around the reaction site.[6,38−45] We observed in a separate experiment that a high molecular weight PSLi end-capped with DPE (M_w = 29.1 kg/mol) quantitatively reacted with **3c** to introduce one branch into each repeating unit (see Table 3). This result indicates that, in addition to the above-mentioned chain conformation change, the steric hindering effect arising from the polymer anion comprised of two polymer segments and the branch chains already introduced into **3** may be also responsible for the incomplete reaction.

Table 5. g' Values of High-Density Branched Polystyrenes

	DP_w		g' value	
ex. no.	backbone	branch	calcd (arm number) from eq 2	obsd
1	19.3	51.3, 54.8	0.12 (38.6), 0.21 (19.3)	0.13
2	19.3	530, 54.8	0.12 (38.6), 0.21 (19.3)	0.22
3	21.3	123, 114	0.11 (42.6), 0.20 (21.3)	0.11
4	53.9	46.8, 51.4	0.054 (108), 0.094 (53.9)	0.059
5	53.9	473, 51.4	0.054 (108), 0.094 (53.9)	0.089

Intrinsic Viscosity and g' Value of Branched Polymer Carrying Two Branch Chains in the Repeating Unit. It is generally recognized that branched polymers have more compact structures and smaller hydrodynamic volumes than those of the linear counterparts and their branched architecture significantly affected both structure and hydrodynamic volume. Therefore, new high-density branched polymers synthesized herein are of interest in this regard. Since polymerization degrees of the backbone chains are comparable or smaller than those of the branched chains in the present high-density branched polymers successfully synthesized, these polymers may possibly adopt starlike rather than rodlike structures in solution. As previously reported, the effect of branching on the molecular dimension of a star-branched polymer can be expressed by the parameter g' value defined as $[\eta]_{branch}/[\eta]_{linear}$ where $[\eta]_{branch}$ and $[\eta]_{linear}$ are intrinsic viscosities of branched polymer and linear polymer with the same molecular weight under the same conditions. The relationship between the g' value and arm (or branching) number of star-branched polymer has been well-established based on theoretical models and experimental results.[46−50]

We have selected representative five polymer samples (nos. 1−5) carrying two branch segments in each repeating unit (CE = ca. 100% in each sample) and measured their $[\eta]_{branch}$ values in toluene at 35 °C. The intrinsic viscosities of the corresponding linear polystyrenes with same molecular weights were calculated from eq 1[51]

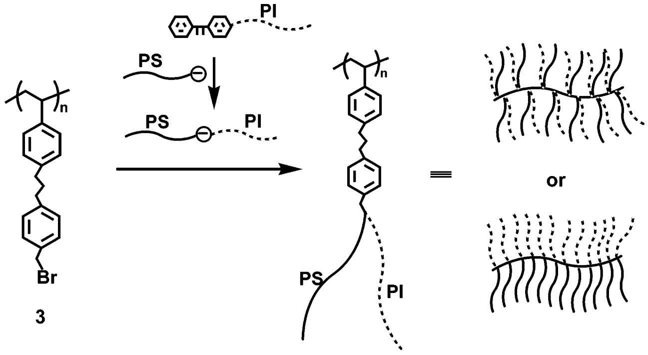
$$[\eta] = 1.26 \times 10^{-4} M_w^{\,0.71} \qquad (1)$$

With these values, the g' values for such polymer samples were obtained. Since Roovers proposed eq 2

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

based on the experimental results,[52] g' values for 38.6-arm (19.3 × 2), 42.6-arm (21.3 × 2), and 108-arm (53.9 × 2) star-branched polymers were calculated by using this equation. In addition, g' values for 19.3-, 21.3-, and 53.9-arm star-branched polymers were also calculated. The data are given in Table 5. As can be seen, experimental g' values of three samples (nos. 1, 3, and 4) are 0.13, 0.11, and 0.059, respectively, and very close to the values calculated as 38.6-, 42.6-, and 108-arm star-branched polymers. Thus, the three polymer samples appear to behave like star-branched polymers with the same numbers of arm segments. On the other hand, very interestingly, another two branched polymer samples (nos. 2 and 5) comprised of two branch polymer segments quite different in molecular weight (so-called molecular weight asymmetry) showed g' values similar to those calculated as 19.3- and 53.9-arm star-branched polystyrenes. Accordingly, these two polymers behave like star-branched polymers comprised of only longer branch segments. The results thus obtained seem reasonable in terms of the architecture of the resulting polymers in which polymerization degrees of the backbone chains are comparable or smaller than those of the branched chains. Although the high-density branched polymers synthesized in this study may belong to comblike branched polymers in structure, they behave like star-branched polymers with the corresponding numbers of arm segments in good solvents such as toluene.

Scheme 4. Reaction of 3 with Polymer Anion Comprised of Polystyrene and Polyisoprene Chains



Reaction of Poly(4-(3-(4-bromomethylphenyl)-propyl)styrene) with Block Copolymer Anion Comprised of Polystyrene and Polyisoprene Segments. The advantageous feature of the present methodology using the polymer anion over the previously reported methodology is that two different polymer segments both in molecular weight and composition can be simultaneously introduced by a one-step reaction via one benzyl bromide functionality. In the preceding section, we successfully introduced two polystyrene chains different in molecular weight into each repeating unit of **3** as listed in Table 3.

In this section, we have prepared new block copolymer anions from (PSLi)s and chain-end-functionalized polyisoprenes (PI)s with DPE moiety and in situ reacted with **3**. As illustrated in Scheme 4, the resulting polymers are novel graft-block copolymers with extremely high-density branched architectures. The SEC profiles of the reaction mixtures all were very similar to Figures 1A and 2A. The requisite coupled polymers eluted at higher molecular weight sides were isolated by fractionation with HPLC and characterized by SEC, ^{1}H NMR, and SLS measurements. A typical ^{1}H NMR spectrum of the resulting graft-block copolymer (DP_w of backbone polymer = 19.3, copolymer anion (M_w = 20.6 kg/mol (PS) + 5.40 kg/mol (PI) = 26.0 kg/mol)) is shown in Figure 3. The results are summarized in Table 6.

The polymer obtained by the reaction of **3a** with the copolymer anion (M_w = 6.47 kg/mol (PS) + 5.40 kg/mol (PI) = 11.9 kg/mol) showed a sharp monomodal SEC distribution (M_w/M_n = 1.02). Agreement of the M_w values between predicted and measured by SLS is quite satisfactory. As expected, the composition ratio measured by ^{1}H NMR agreed with that calculated from the feed ratio. Similarly, the reaction of **3a** with a higher molecular weight copolymer anion (M_w = 20.6 kg/mol (PS) + 5.40 kg/mol (PI) = 26.0 kg/mol) proceeded with virtually quantitative efficiency. Thus, we have succeeded in synthesizing novel extremely high-density graft-block copolymers whose polystyrene and polyisoprene branch segments are exactly aligned in alternat-

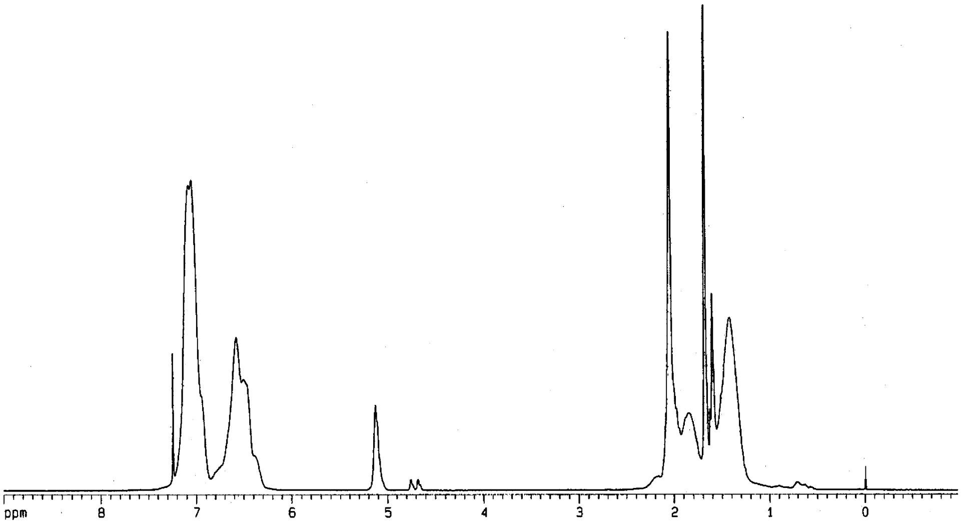


Figure 3. ^{1}H NMR of graft-block copolymer.

Table 6. Synthesis of High-Density Graft-Block Copolymers by Coupling Reaction of 3 with Block Copolymer Anions Comprised of Polystyrene and Polyisoprene Chains in THF at −40 °C for 168 h

3		PSLi	PI-D[a]	polymer anion	branched polymer[b] $M_w \times 10^{-3}$			
$M_w \times 10^{-3}$	DP$_w$	$M_w \times 10^{-3}$	$M_w \times 10^{-3}$	$M_w \times 10^{-3}$	calcd	SEC	SLS	CE[c] (%)
6.08	19.3	6.47	5.40	11.9	229	92	239	104
6.08	19.3	20.6	5.40	26.0	502	192	528	105
17.0	53.9	5.40	5.74	11.1	600	140	528	88
17.0	53.9	23.6	5.74	29.3	1580	355	1110	70

[a] Chain-end-functionalized polyisoprene with DPE moiety. [b] M_w/M_n = 1.02~1.03. [c] Coupling efficiency.

Table 7. Effect of Molecular Weights of Backbone Polymers and Polymer Anions on Coupling Efficiency

		polymer anion, $M_n \times 10^{-3}$ (PS−PS)[a] or (PS−PI)[b]					
polymer	DP$_w$	~10[a] (5−5)	~25[a] (20−5)	~60[a] (55−5)	~25[a] (12.5−12.5)	~10[b] (5−5)	~25[b] (20−5)
PBMS[a]	23.3	79	46				
PBMS	88.7	75	35				
3a	19.3	100	100	100	100	100	100
3b	53.9	100	100	100	77	88	70
3c	107	79	78				

[a] Polymer anion comprised of two polystyrene chains. [b] Copolymer anion comprised of polystyrene and polyisoprene chain.

ing sequence along the backbone polymer as shown in Scheme 4.

The reaction of **3b** (M_w = 17.0 kg/mol, DP_w = 53.9) with the copolymer anion (M_w = 5.40 kg/mol (PS) + 5.74 kg/mol (PI) = 11.1 kg/mol) proceeded not quantitatively but with an efficiency of 88% under the identical conditions. Increasing the molecular weight of the copolymer anion (M_w = 23.6 kg/mol (PS) + 5.74 kg/mol (PI) = 29.3 kg/mol) further decreased the efficiency to 70%. Since the reaction of **3b** with the similar molecular weight polymer anions comprised of two polystyrene segments proceeded virtually quantitatively, such incomplete efficiencies might be attributable to the incompatibility between polystyrene and polyisoprene segments under the conditions at a low temperature of −40 °C. Finally, all data on the coupling reaction are summarized in Table 7 in order to compare more clearly the effect of DP$_w$ values of backbone chain and polymer anion on the reaction efficiency. As can be seen, the reaction efficiency is significantly affected by the molecular weight of **3**. It is somewhat surprising that high molecular weight polymer anions (~60 kg/mol) can be efficiently introduced into **3**.

It has been well established that the conformation of poly(macromonomer) can vary from starlike sphere to rodlike structures, depending on the degrees of polymerization of the backbone and the branch segments.[6,38−45] Since backbone and branch segments of the high-density branched polymers successfully synthesized in this study range from 19 to 54 and from 47 to 530 in DP$_w$ value, respectively, these branched polymers may possibly adopt starlike sphere rather than rodlike structures.

Conclusions

We have successfully synthesized extremely high-density branched polymers carrying two branch segments in each repeating unit by the reaction of **3** with polymer anions comprised of two polymer segments based on “grafting-onto” methodology. Quite new graft-block copolymers with similar high-density branched architectures have also been synthesized by the same approach using copolymer anions comprised of polystyrene and polyisoprene segments. The resulting branched polymers were well-defined in densely branched architecture and precisely controlled in chain lengths of both backbone and branch segments. The reaction efficiency was however significantly affected by several factors such as DP$_w$ of **3** and branched and chemical structures of the polymer anion. A key point of the reaction is to employ **3** as a backbone polymer that is specially designed in such a way that the benzyl bromide reaction site is separated from the main chain by three methylene units. This strongly suggests that the introduction of a longer spacer than three methylene units would further improve the reaction efficiency in the present system. The resulting high-density branched polymers appear to adopt starlike structures, estimating from their g' values. In the branched polymers comprised of two branch chains different in molecular weight (molecular weight asymmetry), however, they behave like the star-branched polymers comprised of only longer branch chains.

Note Added After ASAP Posting

This article was released ASAP on 5/27/2004. On page 1, line 5, the first author name was changed from Sang Wong Ryu to Sang Woog Ryu. The correct version was posted on 6/16/2004.

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(37) Even if the reaction efficiency is carefully determined, there may be at least ±5% experimental errors, estimating from the analytical limits of M_w values by SEC and SLS, respectively. It is therefore considered that the efficiencies from 95 to 105% are virtually “quantitative” in the present system.
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