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Synthesis of Branched Polymers by Means of Anionic Polymerization. 11. Anionic Synthesis of Densely Branched Polystyrenes Carrying Double Branches in Each Repeating Unit

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Summary: We have demonstrated the first successful synthesis of well-defined densely branched polystyrenes carrying double branches in each of all repeating unit of backbone polymer by the coupling reaction of 1,1-diphenylethylene-end-capped polystyryllithiums with novel polystyrene derivatives having two benzyl bromide moieties in each monomer unit. The coupling reaction efficiently and quantitatively proceeded without any steric limitations to introduce two polystyrene branches in each repeating unit under certain conditions in THF at -40°C. Thus, a series of 36.4- and 181-arm densely branched polystyrenes were synthesized (M_w = 365 ~ 2 000 kg/mol, M_w/M_n = 1.01 ~ 1.03). In the 36.4-arm branched polystyrenes thus synthesized, the maximum M_w value of the introduced polystyrene as a branch segment was 55.1 kg/mol. The experimental g‘ values of the 36.4-arm branched polystyrenes deterimined in the range of 0.14 ~ 0.15 were very close to the value of 0.13 calculated from the empirical equation previously reported by Roovers.

Introduction

Branched polymers belong to one of the most important class of specially shaped polymeric materials and exhibit interesting and unique properties originated from their inherent branch structures. Therefore, these polymers have been extensively studied from synthetic as well as theoretical points of view. [1-3] For their synthesis, “grafting-onto method“ is one of the most generally established and practical synthetic procedures. It has however long been believed that the maximum number of branch to be introduced into backbone chain is definitely limited by steric hindrance arising from the crowding of branch.[3]

Recently, Deffieux and Schappacher have first demonstrated that one branch chain can be introduced into each of all repeating unit of backbone polymer by means of a coupling reaction based on the grafting-onto method.[4,5] Their method involves the synthesis of poly(2-chloroethyl vinyl ether) by the living cationic polymerization and the subsequent

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coupling reaction of the resulting polymer with polystyryllithium. Surprisingly, the coupling reaction proceeded quantitatively in benzene in the presence of N,N,N‘,N‘-tetramethylethylenediamine. Thus, a series of densely branched polymers having single branch in each repeating unit were successfully synthesized. Moreover, their branch and backbone chains were precisely controlled in molecular weight and molecular weight distribution, since they were obtained by the living anionic and cationic polymerizations.

More recently, we have successfully synthesized similar well-defined densely branched polystyrenes and graft copolymers by the coupling reaction of living anionic polymers of styrene, isoprene, 2-vinylpyridine, and *tert*-butyl methacrylate with precisely controlled poly(3-halomethylstyrene)s in chain length prepared *via* living anionic polymerization.[6-8] In the coupling reaction with use of the poly(3-bromomethylstyrene) ($DP_w = 30$) as a backbone chain under the conditions in THF at -40°C, a high molecular weight polystyrene branch with the M_w value of 68.8 kg/mol ($DP_w = 662$) could quantitatively be introduced. Almost at the same time, Hadjichristidis et al. have demonstrated that the poly(4-chloromethylstyrene)s obtained by the TEMPO-mediated living radical polymerization quantitatively reacted with DPE-end-capped either polystyryllithiums or polyisoprenyllithiums to afford various densely branched polymers with well-defined architectures.[9] In general, the above-mentioned coupling reactions efficiently and quantitatively proceed without any steric limitations as predicted when the polymerization degrees of the backbone chains are less than around 100, although the coupling efficiency seems to gradually decrease with increasing the polymerization degree of the backbone polymer. In the coupling reaction of poly(2-chloroethyl vinyl ether) with polystyryllithium, however, a very high efficiency of 85 % was still attained in the reaction between a high molecular weight poly(2-chloroethyl vinyl ether) ($M_n = 111$ kg/mol, $DP_n = 1042$) and polystyryllithium ($M_n = 3.00$ kg/mol).

During our synthetic studies, we found a very interesting and suggestive paper on the synthesis of graft copolymers previously reported by Roovers et al.[10] In this paper, they reported that the coupling reaction of poly(1,3-butadienyl)lithium with the hydrosilylated poly(1,3-butadiene) having $SiCl_2$ group underwent essentially to completion to introduce two poly(1,3-butadiene) segments at all of the available $SiCl_2$ groups. Although the number of the reaction sites that were hydrosilylated was not quantitative, the maximum average number of the introduced poly(1,3-butadiene) branch reached to *ca.* 1.6 branches in each repeating unit. This strongly suggests the possible synthesis of more densely branched polymers by means of the similar coupling reactions based on grafting-onto approach.

In this contribution, we report on the first successful synthesis of densely branched polystyrenes carrying double branches in each repeating unit by the coupling reaction of living anionic polystyrenes with novel polystyrene derivatives having two benzyl bromide moieties in each monomer unit.

Experimental Part

Purification of all the solvents and reagents (purchased from Tokyo Kasei, Japan) used in this study was carried out according to our previous papers.[6-8]

4-[3-(4-*Tert*-butyldimethylsilyloxymethylphenyl)propyl]styrene (1)

The title compound, **1**, was synthesized in 50 % yield by the Li_2CuCl_4-mediated coupling reaction of 4-(3-bromopropyl)styrene with the Grignard reagent prepared from 1-bromo-4-*tert*-butyldimethylsilyloxymethylbenzene and magnesium in THF by modifying the method previously reported [11]: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.10 (s, 6H, Si-CH_3), 0.93 (s, 9H, Si-C-CH_3), 1.95 (m, 2H, $CH_2C\mathit{H_2}CH_2$), 2.60 (t, 4H, $C\mathit{H_2}CH_2C\mathit{H_2}$), 4.71 (s, 2H, O-$CH_2$), 5.20 (d, 1H, CH_2=), 5.70 (d, 1H, CH_2=), 6.70 (q, 1H, CH=), 7.12 ~ 7.34 (m, 8H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ -5.12 ($SiCH_3$), 18.5 (Si-C), 26.1 ($SiCCH_3$), 33.0, 35.2 ($CH_2CH_2CH_2$), 65.0 (CH_2OSi), 112.9 (CH_2=), 136.8 (CH=), 126.3, 128.4, 128.7, 135.2, 138.9, 140.9, 142.1 (Ar C).

Anionic Polymerization of 1

The anionic polymerization of **1** was carried with *sec*-BuLi in THF at -78 °C for 0.2 ~ 0.5 h under high vacuum conditions (10^{-6} torr) using break-seal technique. The reaction mixture always showed a characteristic red color, which remained unchanged during the course of the polymerization. The polymerization reaction was terminated with degassed methanol and the polymer was precipitated in methanol. Yields of polymers were always quantitative under the conditions. They were reprecipitated twice from THF to methanol and freeze-dried from their benzene solutions. The results are summarized in Tab. 1. SEC profiles of the resulting polymers showed sharp monomodal distributions, M_w/M_n values being less than 1.06. The observed M_n values agreed well with those predicted. These results clearly indicate the living character of the polymerization of **1**. In the case for a longer reaction time to 2 h or at a higher [M] to [I] ratio of 200, a small amount of high molecular weight shoulder (< 10 %) was often formed. These high molecular weight reactions if formed were removed by SEC fractionation and used in the next reaction.

Table 1. Anionic polymerization of **1** with *sec*-BuLi in THF at -78 °C for 0.2 - 0.5 h[a)]

[**1**] / [*sec*-BuLi]	M_n (kg/mol)			M_w/M_n[b)]
	cacld	SEC	^{1}H NMR	
19.1	7.08	6.00	6.98	1.03
56.0	20.5	15.5	19.4[c)]	1.02
95.3	34.9	26.1	33.2[c)]	1.06

[a)] Yields of polymers were 100 % in all cases.

[b)] Determined by SEC.

[c)] M_w (kg/mol) determined by SLS.

Synthesis of Polystyrene Having One Benzyl Bromide Moiety in Each Repeating Unit, PS-1Br

The synthesis of **PS-1Br** was carried out by the transformation reaction of the poly(**1**) by treatment with a 50-fold excess of $(CH_3)_3SiCl$-LiBr in a mixture of acetonitrile and chloroform (3/5, *v/v*) at 40 °C for 24 h according to our previous procedure.[11] The transformation reaction proceeded cleanly and quantitatively to afford **PS-1Br**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.67 (m, CH_3), 1.29 ~ 2.30 (m, CH_2-CH- and $CH_2C\mathit{H_2}CH_2$), 2.56 (t, $C\mathit{H_2}CH_2C\mathit{H_2}$), 4.47 (s, CH_2Br), 6.51 ~ 7.29 (m, ArH). IR (thin film on silicon wafer): 604, 1220cm^{-1} (CH_2-Br), 780, 1200, 1507cm^{-1} (Ar-H). Elemental analysis: $(C_{18}H_{19}Br)_n$ calculated; C 68.58, H 6.07, Br 25.35, observed; C 68.54, H 6.26, Br 25.93.

Synthesis of Polystyrene Having Two Benzyl Bromide Moieties in Each Monomer Unit, PS-2Br

The title polymer, **PS-2Br**, was synthesized by the coupling reaction of **PS-1Br** with a 1.2-fold excess of the functionalized anion in THF at -78 °C for 72 h prepared from 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**2**) and *sec*-BuLi, followed by treatment with a 50-fold excess of $(CH_3)_3SiCl$-LiBr under the same conditions as mentioned before.[12] Both the reactions proceeded cleanly and quantitatively to afford **PS-2Br** as desired: ^{1}H NMR (300

MHz, $CDCl_3$): δ 0.48 ~ 0.68 (m, CH_3), 0.95 ~ 1.95 (m, CH_2-CH- and $CH_2C\mathit{H}_2CH_2$), 2.46 (t, $C\mathit{H}_2CH_2C\mathit{H}_2$), 4.36 (s, CH_2Br), 6.37 ~ 7.17 (m, ArH). IR (thin film on silicon wafer): 573 cm^{-1} (CH_2-Br), 794, 1210, 1511cm^{-1} (Ar-H). Elemental analysis: $(C_{38}H_{42}Br_2)_n$ calculated; C 69.30, H 6.43, Br 24.27, observed; C 69.41, H 6.52, Br 24.12.

Synthesis of Densely Branched Polymers Carrying Double Branches in Each Repeating Unit of Backbone Chain

The title densely branched polymer was synthesized by the coupling reaction of **PS-2Br** with DPE-end-capped polystyryllithium. The **PS-2Br** dissolved in THF (*ca.* 5 wt %) was added to the living polymer solution at -78 °C and the mixture was allowed to stand at -40 °C for 24 h. The living anionic polymer was usually used in a 1.5-fold excess to the benzyl bromide moiety. The reaction was quenched with degassed methanol and the polymer mixtures were precipitated in methanol. The resulting branched polymer was then isolated by fractional precipitation at 5 °C using a mixture of cyclohexane and hexane (5/1, *v/v*) and freeze-dried from its benzene solution.

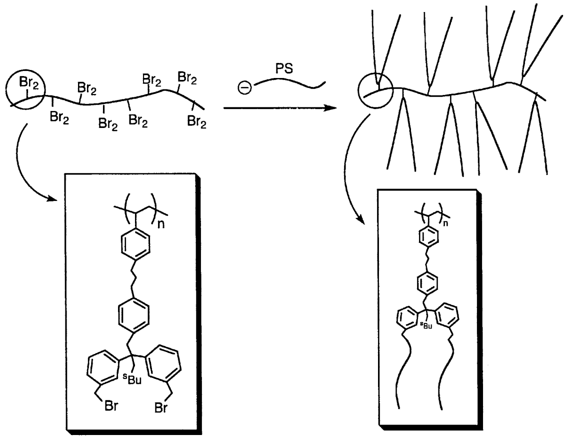
Measurements

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 shits were reported in ppm downfield relative to $(CH_3)_4Si$ (δ 0) for ^1H NMR and $CDCl_3$ (δ 77.1) for ^{13}C NMR spectra as standard. Size-exclusion chromatography (SEC) was obtained at 40 °C with 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. Three polystyrene gel columns ($TSK_{gel}G4000H_{XL}$ + $G3000H_{XL}$ + $G2000H_{XL}$ or $G5000H_{XL}$ + $G4000H_{XL}$ + $G3000H_{XL}$) were used. Measurable molecular weight ranges in these columns are from 10^3 to 4 x 10^6 g/mol. A calibration curve was made to determine M_n and M_w/M_n values with standard polystyrene samples. Fractionation by SEC was performed at 40 °C using a TOSOH HLC 8020 fully automatic instrument equipped with a TSK-4000H_{HR} column (measurable molecular weight range: 10^3 ~ 5 x 10^5 g/mol). All runs for fractionation were made with THF as an eluent. The concentration of the polymer solution was adjusted to 10 ~ 20 *w/v* %, depending on the molecular weight of the sample. Static light scattering (SLS) measurements were performed with an Ootsuka Electronics Photal SLS-600R instrument (He-Ne laser, 633nm) in THF or benzene. The refractive index increments (dn/dc) of the polymers have been measured by an Ootsuka Electronics Photal DRM-1020. Intrinsic viscosity was measured by Ubbelohde-type capillary viscometer in toluene at 35 °C. FT-IR spectra were run with a JIR-AQS20M, JEOL. A THF solution (0.2g/mL) of polymer was spin-coated on the well-washed silicon wafer and dried for 20 min under an atmosphere of nitrogen prior to measurement.

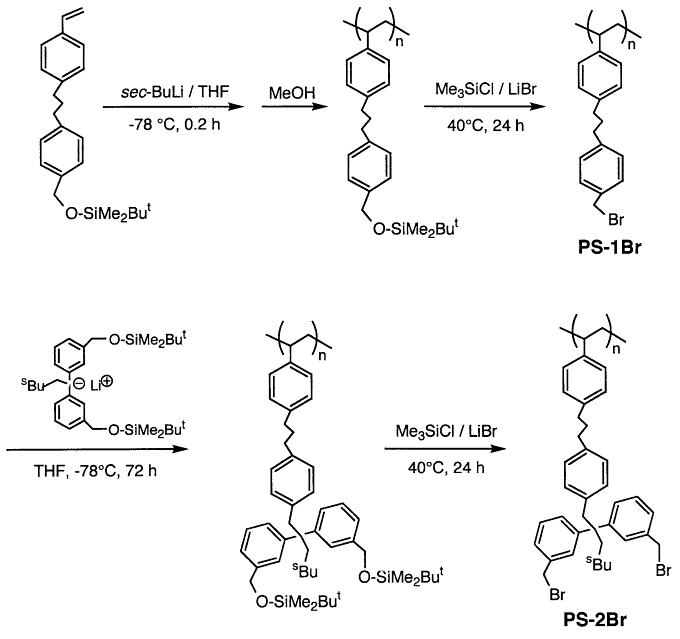
Results and Discussion

Synthesis of Novel Well-Defined Polystyrenes Having Two Benzyl Bromide Moieties in Each Monomer Units, PS-2Br

As illustrated in Scheme 1, densely branched polystyrenes carrying double branches in each repeating unit were synthesized by the coupling reaction of **PS-2Br** with living anionic polymers of styrene. For this synthesis, **PS-2Br** used as a reactive backbone chain was prepared as illustrated in Scheme 2. At first, the precisely controlled poly(**1**) in chain length was obtained by the living anionic polymerization of **1**. The resulting polymer was quantitatively transformed into a polystyrene having one benzyl bromide moiety in each monomer unit, **PS-1Br**, by treatment with LiBr-$(CH_3)_3SiCl$. It was then reacted with the functionalized anion prepared from **2** and *sec*-BuLi. The two *tert*-butyldimethylsilyloxymethylphenyl groups thus introduced were again quantitatively transformed into two benzyl bromide moieties by treatment with LiBr-$(CH_3)_3SiCl$, thus forming a polystyrene having two benzyl bromide moiety in each monomer unit, **PS-2Br**. Two **PS-2Br** samples having different molecular weights were prepared in this study. The characterization results are summarized in Tab. 2.



Scheme 1



Scheme 2

Table 2. Characterization of **PS-2Br**

M_n (kg/mol)			M_w (kg/mol) (DP_w)		M_w / M_n [a]
cacld	SEC	^{1}H NMR	cacld	SLS	
12.0	7.36	11.9	12.1	12.0 (18.2)	1.01
56.4	26.8	56.6	57.7	59.6 (90.5)	1.02

[a] Determined by SEC.

The expected structure of **PS-2Br** was clearly confirmed by IR, ^{1}H and ^{13}C NMR measurements, and elemental analysis. SEC profiles of the resulting polymers show symmetrical monomodal distributions (see Fig. 1). Their molecular weight distributions were very narrow, the M_w/M_n values being less than 1.02.

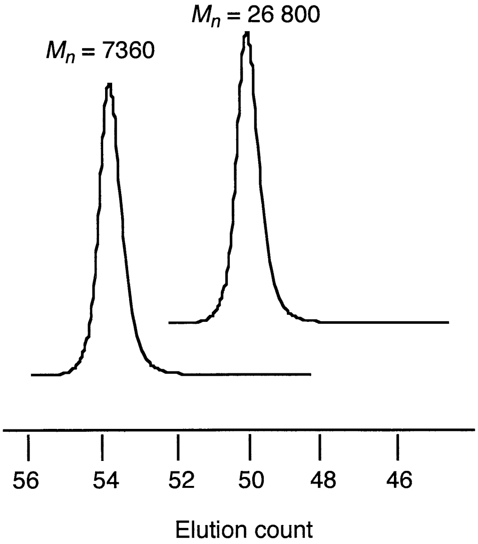


Figure 1. SEC profiles of **PS-2Br** samples

Although the M_n values estimated from SEC using polystyrene standard samples were always much smaller than those calculated, the molecular weights determined by ^{1}H NMR and SLS were in good agreement with those calculated. Thus, two polymers were precisely controlled in chain length and well defined in chemical structure as designed. Needless to say, the molecular weight of **PS-2Br** can readily be controlled by the stage of the living anionic polymerizations of **1**. The results also clearly indicate that all of the reactions used in the synthesis of **PS-2Br** cleanly and quantitatively proceed.

Synthesis of Densely Branched Polystyrenes Carrying Two Branches in Each Repeating Unit with Well-Defined Architecture

The coupling reaction of **PS-2Br** with DPE-end-capped polystyryllithium was carried out in THF at -40 ° C. The reaction time of 24 h was set in each case. The end-capping of polystyryllithium with DPE was essential in the coupling reaction to suppress presumable side reactions such as Li-Br exchange and single-electron transfer reactions occurred in the analogous reaction of poly(3-bromomethylstyrene) and polystyryllithium previously reported. Two **PS-2Br** samples (M_w = 12.0 and 59.6 kg/mol) and three DPE-end-capped polystyryllithiums (M_w = 9.40, 22.9, and 55.1 kg/mol) were used. The living polymer was always used in a 1.5-fold molar excess relative to the benzyl bromide moiety. After terminating the reaction with degassed methanol, the polymer mixtures were precipitated in methanol. The objective branched polymers were then isolated nearly quantitatively by fractional precipitation.

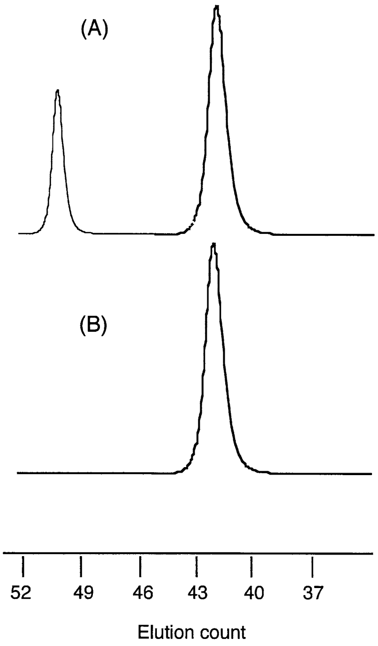


Figure 2. SEC profiles of the polymers before (A) and after (B) fractionation

Figs. 2(A) and (B) show typical SEC profiles of the polymers before and after fractionation. As you can see in Fig 2(A), there are two sharp single SEC peaks corresponding to the branched polymer and unreacted polystyrene used in excess. The branched polymer isolated by fractionation shows a sharp single SEC peak, indicating that this polymer is pure and completely free of its prepolymers (see Fig 2(B)). The characterization results are summarized in Tab. 3.

The M_w values of the resulting polymers estimated by SEC were always much smaller than those calculated as expected from their densely branched structures. On the other hand, the absolute M_w values determined by SLS agreed quite well with those calculated in all polymers obtained by the reactions of **PS-2Br** (M_w = 12.0 kg/mol, DP_w = 18.2 x 2) with DPE-end-capped polystyryllithiums (M_w = 9.40 ~ 55.1 kg/mol, DP_w = 90 ~ 529). This clearly indicates that all of the available benzyl bromide moieties react quantitatively with living polystyrene to introduce two branches in each repeating unit of the backbone polymer in each reaction. The coupling reaction of a high molecular weight **PS-2Br** (M_w =59.6 kg/mol, DP_w = 90.5 x 2) with DPE-end-capped polystyryllithium (M_w = 9.40 kg/mol, DP_w = 90) also quantitatively underwent under the same conditions. Accordingly, under the conditions employed here the steric hindering effect arising from the branch chain crowding as predicted seems to be not present in the coupling reaction.

Table 3. Synthesis of densely branched polystyrenes carrying double branches in each repeating unit[a)]

PS-2Br DP_w	PSDLi M_w (kg/mol) (DP_w)	M_w (kg/mol) cacld	M_w (kg/mol) SEC	M_w (kg/mol) SLS	M_w/M_n[b)]	Coupling efficiency %
18.2 x 2	9.40 (90)	351	128	365	1.03	103
18.2 x 2	22.9 (219)	843	293	859	1.02	102
18.2 x 2	55.1 (529)	2015	628	2000	1.03	99.5
90.5 x 2	9.40 (90)	1744	291	1740	1.03	99.6

[a)] Yields of polymers were 100 % in all cases.

[b)] Determined by SEC.

The small deviation of individual coupling efficiency can be ascribed to errors in the determination of M_w values of **PS-2Br**, living polystyrenes, and the resulting branched polymers. Therefore, the coupling efficiencies of the four reactions are considered to be virtually quantitative within the analytical limits. Thus, we could successfully synthesize a series of densely branched polystyrenes carrying double branches in each repeating unit. Their M_w values were in the range from 365 to 2 000 kg/mol and the total average branch numbers were 36.4 and 181, respectively. Any of the branched polymers possessed both precisely controlled branch and backbone chains and well-defined architectures.

It was observed that the coupling reaction was unexpectedly rapid under the conditions in THF at -40 °C. For example, the reaction of **PS-2Br** (M_w = 12.0 kg/mol) with DPE-end-capped polystyryllithium (M_w = 9.40 kg/mol) proceeded with 70 and 92 % efficiencies only after 3 and 10 min and was complete within 1 h. Very surprisingly, the reaction rate appears to be almost comparable to that between poly(3-bromomethylstyrene) and DPE-end-capped polystyryllithium under the same conditions.

Intrinsic viscosities of the three 36.4-arm branched polystyrenes measured in toluene at 35 °C were much smaller than those of linear polystyrenes having the same molecular weights obtained from the established equation, [13] as listed in Tab. 4. In these polymers, degrees of polymerization of the branch chains (DP_w = 90, 219, and 529) were much larger than that of the backbone polymer (DP_w = 18.2 x 2). It can be therefore assumed that they adopt spherical starlike structures rather than comblike molecular brushes in solution. The branched architecture of star-branched polymer is evidenced by the extremely low g‘ value defined as the ratio of $[\eta]_{star}/[\eta]_{linear}$ where $[\eta]_{star}$ and $[\eta]_{linear}$ are the intrinsic viscosities of star and the corresponding linear polymer with the same molecular weight, respectively.[14] The overall experimental g‘ values thus determined were in the range of 0.14 ~ 0.15 (see Tab. 4). These values were very close to the calculated value of 0.13 from the empirical equation [f (arm number) = 36.4] based on the experimental results of star-branched polymers in good solvents proposed by Roovers.[15]

$$\log g' = 0.36 - 0.80 \log f$$

This also provides a good evidence for the starlike architecture of the 36.4-arm densely branched polystyrenes herein synthesized.

Table 4. Intrinsic viscosities and g' values of branched polystyrenes carrying double branches[a)]

DP_w		M_w (kg/mol)	$[\eta]_{branch}$	$[\eta]_{linear}$[b)]	$g' = [\eta]_{branch}/[\eta]_{linear}$	
backbone	branch	SLS	(dl/g)	(dl/g)	experimental	equation[c)]
18.2 x 2	90	365	0.16	1.12	0.15	0.13
18.2 x 2	219	859	0.30	2.06	0.14	0.13
18.2 x 2	529	2000	0.52	3.75	0.14	0.13

[a)] Measured in toluene at 35 °C.

[b)] $[\eta] = 1.26 \times 10^{-4} M_w^{0.71}$.

[c)] $\log g' = 0.36 - 0.80 \log f$

Conclusions

We have successfully synthesized well-defined densely branched polystyrenes carrying double branches in each of all repeating units by the coupling reaction of DPE-end-capped polystyryllithiums with novel polystyrenes having two benzyl bromide moieties in each monomer unit, **PS-2Br**. The coupling reaction of either **PS-2Br** (M_w = 12.0 kg/mol, DP_w = 18.2 x 2) with living polystyrene (M_w = 9.40, 22.9, or 55.1 kg/mol, DP_w = 90, 219, or 529) or **PS-2Br** (M_w = 59.6 kg/mol, DP_w = 90.5 x 2) with living polystyrene (M_w = 9.40 kg/mol, DP_w = 90) quantitatively proceeded in THF at -40 °C without any steric limitations to afford 36.4 and 181-arm branched polystyrenes with well-defined architectures. As expected from branched architecture of the resulting 36.4-arm branched polystyrenes, their intrinsic viscosities measured in toluene at 35 °C were much smaller than those of linear polystyrenes having the same molecular weights. Their experimental g‘ values obtained in the range of 0.14 ~ 0.15 were very close to the calculated value of 0.13 by the empirical equation based on the previous experimental results of star-branched polymers in good solvents.

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