

# Molecular Weight and Arm Number of a Star-Shaped Styrene–Butadiene Block Copolymer Synthesized on a Pilot-Vessel Scale

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**ABSTRACT:** To improve the rheological properties and processability of industrial rubbers, star-shaped styrene–butadiene–styrene (SBS) block copolymers were synthesized and characterized in this work. Through the variation of the ratio of divinylbenzene to the diblock anion, a series of SBS samples with three to six arms were prepared. Multi-angle laser light scattering (MALLS) and size exclusion chromatography (SEC) combined with light scattering (LS) were used to determine the weight-average molecular weight ( $M_w$ ), radius of gyration ( $\langle S^2 \rangle^{1/2}$ ), arm number, and chain conformation. The results from MALLS indicated that the  $M_w$  values of the star-shaped SBS copolymers were 9.0, 13.0, 14.9, and  $18.1 \times 10^4$ , which corresponded to three, four, five, and six arms, respectively. There was a lot of  $M_w$  and  $\langle S^2 \rangle^{1/2}$  data for the many frac-

tions in the SEC chromatograms of the SBS copolymers in tetrahydrofuran (THF) detected by LS, so the exponent of  $\langle S^2 \rangle^{1/2} = KM_w^\alpha$  was determined to range from 0.59 to 0.30 for the samples having three to six arms. An analysis of the results revealed that the star SBS copolymers existed in a sphere conformation in THF, and their chain density increased with an increase in the arm number. The viscosity of the six-arm SBS copolymer was reduced significantly, compared with that of the SBS samples having three to five arms, when their  $M_w$  values were similar. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1853–1859, 2007

**Key words:** branched; chain; light scattering; living polymerization; star polymers

## INTRODUCTION

Nowadays, star-shaped block copolymers are attracting much attention because of their unique behaviors and properties in the bulk, solution, and melt states,<sup>1–6</sup> in addition to the well-defined correlation of the structure to the properties.<sup>7–10</sup> The star-shaped styrene–diene block copolymer has become one of the fronts in industrial rubber materials. Styrene–butadiene (SB) block copolymers are well known to exhibit an excellent combination of elasticity and thermoplasticity.<sup>11,12</sup> Compared with linear styrene–butadiene–styrene (SBS), star-shaped SBS has a more compact morphology, reduced bulk and solution viscosities, and better mechanical, rheological, and processing properties.<sup>8,9</sup> However, its further development and applications have been restricted by the complexity of the structure. An industrial application would require the process to be scaled up first at the pilot-plant level. Therefore, it is very important to clarify the

structure and chain conformation of the products when we consider its vast applications in industry. Usually, for the convenience of both academic study and industrial application, star polymers with controlled molecular weights, narrow molecular weight distributions, and tailored molecular architectures are required.<sup>13,14</sup> The development of the living anionic polymerization technique has provided powerful tools for obtaining such tailored star polymers.<sup>15–18</sup> A sensitive and efficient technique for the determination of the molecular architecture of star-shaped SBS is essential for the successful investigation of the secondary structure. Size exclusion chromatography (SEC) is a simple and rapid method for separation, molecular characterization, and quality control of polymers.<sup>19,20</sup> Furthermore, size exclusion chromatography/laser light scattering (SEC–LS) is an absolute method for molecular weight determination and may provide more useful information about the molecular weight and its distribution, the chain conformation, and the molecular size.<sup>21,22</sup>

The properties of star-shaped SBS are strongly influenced by the molecular weight, conformation, and degree of branching. We have accumulated experience in the fractionation and characterization of the molecular weights and chain conformations of polymers.<sup>23–27</sup> In this work, we attempted to prepare star-shaped SBS copolymers by living anionic polymeriza-

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tion with divinylbenzene (DVB) as a linking agent on a pilot-vessel scale, and then we studied their molecular weights, arm numbers, and chain shapes. We hope that this work contributes toward a meaningful pathway that can help us develop the production of star-shaped SBS copolymers. In addition, the characterization of the molecular size and conformation of star-shaped copolymers by laser light scattering (LS) and SEC-LS may give some meaningful information for understanding the molecular architecture of star SBS.

## EXPERIMENTAL

### Synthesis of the star-shaped SBS copolymer

Styrene, butadiene, and *n*-butyllithium were gifts of Yanshan Petrochemical Co. (Beijing, China). Cyclohexane (Jinxi Chemical Plant, Lianyungang, China) was treated with 5-Å molecular sieves and then deoxygenated. Styrene was purified via stirring and degassing over CaH<sub>2</sub>, followed by distillation. DVB was analytical-grade. DVB was purchased from Shanghai Chemical Plant (Shanghai, China) and was purified by the same procedure used for styrene. *n*-Butyllithium was vacuum-distilled and then diluted with benzene. Tetrahydrofuran (THF) and ethanol were analytical-grade; they were purchased from Tianjing Fucheng Chemical Reagent Corp. (Tianjing, China).

All the polymerization experiments were carried out in a 5-L reaction vessel at a pilot level under high-vacuum conditions. Under a slight nitrogen overpressure, cyclohexane was added to the vessel. Styrene (40 wt %) was then polymerized at 50°C for 2 h with *n*-butyllithium as the initiator. The color became red, indicating the presence of living polystyryllithium anions. Then, 60 wt % butadiene was added to the mixture to obtain the diblock anion SB, whose molar concentration was equal to that of *n*-butyllithium. Finally, the linking agent DVB was added to the resulting mixture solution, and the linking reaction was carried out at 50°C for 3 h to obtain the star-shaped SBS copolymer. Finally, the reaction was terminated with degassed ethanol. The functionality of the stars was controlled by changes in the amount of DVB ([DVB]/[SB] = 1, 2, 3, or 4) that was added,<sup>28,29</sup> and the resultant SBS samples were coded S2D, S4D, S6D, and S8D, respectively.

The SBS copolymer solution was subjected to centrifugation at 8000 rpm for 15 min to remove some impurities and microgels. Moreover, a 1% solution of the SBS copolymer in THF was prepared. The solvent/nonsolvent fractionation method was used to separate the unreacted diblock arm SB from the SBS sample. Ethanol was slowly added with stirring until a distinct turbidity appeared. The solution was heated until the turbidity disappeared and then was left

overnight to allow the formation of two phases. The precipitate was collected with a centrifugation method and then was vacuum-dried at 50°C for 24 h to obtain a white powder.

### LS and SEC-LS

The LS intensities of the polymer solutions were measured with a multi-angle laser light scattering (MALLS) instrument equipped with a He-Ne laser ( $\lambda = 633$  nm; Dawn DSP, Wyatt Technology Co., St. Barbara, CA) at angles of 43, 49, 56, 63, 71, 81, 90, 99, 109, 118, 127, 136, and 152° at 25°C. Redistilled THF was used as the solvent. Polymer solutions of the desired concentrations were prepared, and optical clarification of the solutions was achieved by filtration through a 0.45- $\mu$ m pore size filter [Puradisc 13-mm polytetrafluoroethylene (PTFE) syringe filters, Whatman, England] into the scattering cell. The refractive-index increments ( $dn/dc$ ) were measured with a double-beam differential refractometer (DRM-1020, Otsuka Electronics Co., Osaka, Japan) at 633 nm and 25°C. The  $dn/dc$  values of the SBS samples in THF solutions were determined to be 0.1349, 0.1362, 0.1386, and 0.1451 mL/g for star-shaped SBS samples having three, four, five, and six arms, respectively, and 0.1250 mL/g for diblock copolymer SB. Astra software (version 4.70.07) was used for data acquisition and analysis. The weight-average molecular weight ( $M_w$ ) and the average root-mean-square radius of gyration ( $\langle S^2 \rangle^{1/2}$ ) of the polymers in dilute solutions could be obtained from a Zimm plot:

$$\frac{Kc}{R_0} = \frac{1}{M_w} \left( 1 + \frac{16\pi^2 n^2}{3\lambda_0^2} \langle S^2 \rangle \sin^2(\theta/2) + \dots \right) + 2A_2c \quad (1)$$

$$K = \frac{4\pi^2 n^2}{N_A \lambda_0^4} \left( \frac{dn}{dc} \right)^2 \quad (2)$$

where  $A_2$ ,  $N_A$ ,  $n$ ,  $\lambda_0$ , and  $c$  are the second virial coefficient, Avogadro's number, the solvent refractive index, the wavelength of the light in a vacuum, and the concentration, respectively.

SEC-LS was carried out on a size exclusion chromatograph combined with a previously mentioned multi-angle laser light scattering instrument and a P100 pump (Thermo Separation Products, San Jose, CA), which was equipped with G4000H8 columns (MicroPak, TSK, Japan) combined with G3000H8 columns (MicroPak, TSK) and a differential refractive-index detector (RI-150, Kyoto, Japan), at 25°C. The carrier solution was redistilled, dust-free-treated, and degassed with THF. The samples were dissolved in THF overnight with stirring to obtain transparent solutions. The THF and polymer solutions were purified

with a 0.45- $\mu\text{m}$  filter (Puradisc PTFE 13-mm syringe filters, Whatman) and degassed before use. The injection volume was 200  $\mu\text{L}$  with a concentration of 0.2% for each sample, and the flow rate was 1.0 mL/min. Astra software was used for data acquisition and analysis.

### Dynamic light scattering (DLS)

$M_w$ ,  $\langle S^2 \rangle^{1/2}$ , and the hydrodynamic radius of the S8D sample in THF at 30 and 40°C were also determined with a Precision Detector two-angle (15 and 90°) DLS photometer ( $\lambda = 680$  nm; Precision Detector, Inc., Bellingham, MA) with a refractive-index detector.

### Viscometry measurements

The viscosity of the samples was measured at  $25 \pm 0.1^\circ\text{C}$  with an Ubbelohde viscometer. THF was used as the solvent and was treated through the same process as the LS measurement mentioned previously. The kinetic energy correction was always negligible. The Huggins and Kraemer equations were used to estimate the intrinsic viscosity ( $[\eta]$ ) by the extrapolation of concentration  $c$  to zero as follows:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c \quad (3)$$

$$(\ln \eta_r)/c = [\eta] - k''[\eta]^2c \quad (4)$$

where  $k'$  and  $k''$  are constants for a given polymer at a given temperature in a given solvent,  $\eta_{sp}/c$  is the reduced specific viscosity, and  $(\ln \eta_r)/c$  is the inherent viscosity.

### Characterization of the structure

$^1\text{H-NMR}$  spectra were recorded on a Mercury 600 NB NMR spectrometer (Varian, Inc., PaloAlto, CA) at 600 MHz and 25°C. The spinning speed, pulse delay, and total number of scans were 15 Hz, 15 s, and 2048, respectively. The sample was dissolved in deuterated

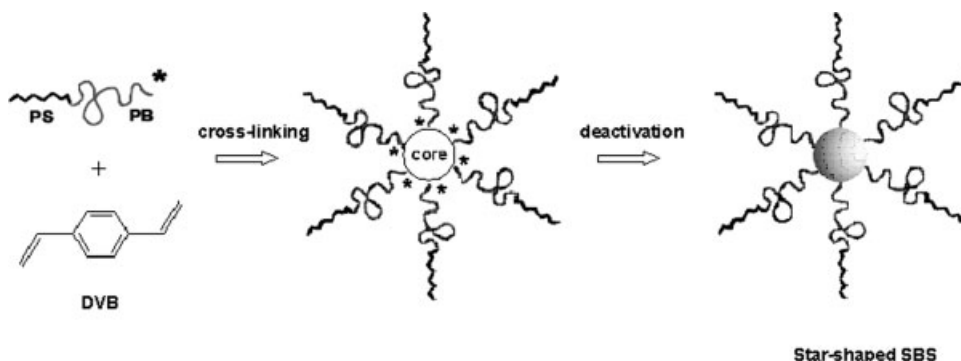
chloroform ( $\text{CDCl}_3$ ) to prepare the solution at a concentration of 150 mg/mL.

## RESULTS AND DISCUSSION

### Structure of star SBS

The synthesis of the star-shaped SBS block copolymer is depicted in Scheme 1. The diblock precursor arm is a block copolymer comprising one block of polystyrene (PS) and one block of polybutadiene (PB). In this case, the diblock polymer arm is a living polymer containing a single lithium atom bonded to a terminal carbon atom. With the addition of the crosslinking agent DVB, the diblocks undergo intermolecular coupling to yield the star-shaped SBS block copolymers.<sup>30</sup> Because of the presence of two active sites, the polymerization causes the formation of small-scale networks, which are the junctions for the linking of the arms. Therefore, the arm numbers of the target star always have statistical distributions.<sup>31</sup> Meanwhile, this could hardly cause obvious error in the data for  $M_w$  and the arm number.

$^1\text{H-NMR}$  spectra of the diblock copolymer SB and star-shaped SBS are shown in Figure 1. In the spectra, the peaks at 1.43 (a) and 1.5 ppm (b) are assigned to protons of methylene in 1,2-butadiene ( $\text{H}_V$ ) and vinyl groups of PS ( $\text{H}_b$ ). The peak at 2.03 ppm (c) belongs to the protons of methylene in 1,4-butadiene ( $\text{H}_A$  and  $\text{H}_D$ ). Two peaks at 4.98 (d) and 5.41 ppm (e) represents protons of the double bonds of 1,2- and 1,4-butadiene units ( $\text{H}_K$ ,  $\text{H}_M$ ,  $\text{H}_T$ ,  $\text{H}_F$ , and  $\text{H}_B$ ). Furthermore, the peaks with a chemical shift of 6.57–7.01 ppm (f and g) are signals of the aromatic ring of the PS block ( $\text{H}_m$ ,  $\text{H}_p$ , and  $\text{H}_o$ ). By comparison with the peak intensities, we can conclude that the 1,4-PB block predominates in the star-shaped SBS. This is similar to Holden's report.<sup>32</sup> Obviously, the chemical composition of the star-shaped SBS copolymers from S2D to S8D is basically identical. The compositions of the PS and PB blocks in the copolymers have been calculated from the peak intensities, and the PS contents are listed in Table I.



**Scheme 1** Schematic polymerization process of the six-arm star SBS crosslinked by DVB.

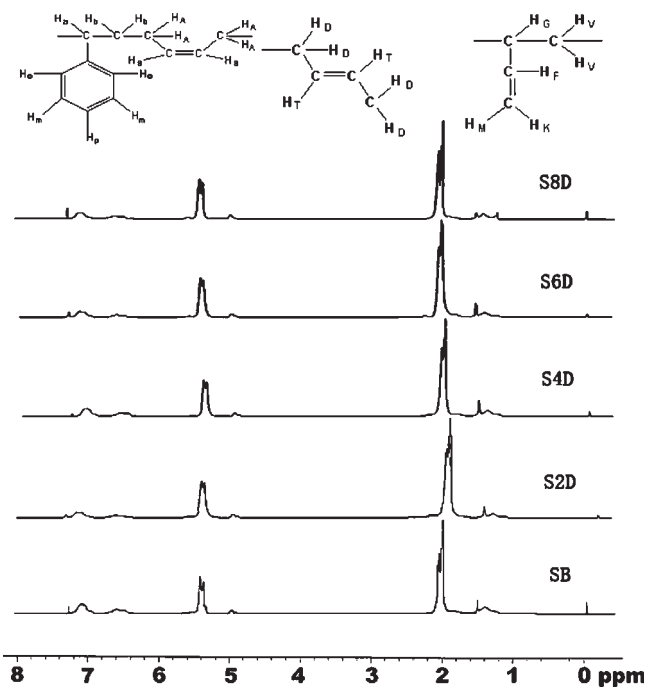


Figure 1  $^1\text{H}$ -NMR spectra of the SBS samples.

### Molecular weight and arm number

Figure 2 shows the SEC chromatograms of the S2D, S4D, S6D, and S8D samples. The SEC traces of the samples show sharp and monomodal distributions [weight-average molecular weight/number-average molecular weight ( $M_w/M_n$ ) = 1.1–1.3], indicating that they are purified without obvious aggregates and crosslinking macromolecules. With Astra software, the number-average molecular weight ( $M_n$ ) was estimated from the molecular weight ( $M_w$ ) of many fractions detected by MALLS. This led to the rise in the  $M_n$  values and the reduction of the molecular weight distribution ( $M_w/M_n$ ). Thus, the  $M_w/M_n$  value required calibration through calculation.<sup>19,33</sup> The values of  $M_w$ ,  $M_w/M_n$ ,  $[\eta]$ , and the arm number for the samples are summarized in Table I. In view of the results, the  $M_w$

value of diblock-arm precursor SB is basically consistent with the designed theoretical molecular weight ( $2.8 \times 10^4$ ). The result clearly indicates that the samples were monodispersed star polymers having narrow molecular weight distributions; that is, the polymerization occurred in a living and controlled manner. In addition, the  $M_w$  values of the SB and S4D samples were determined by MALLS with a Zimm plot, and the results are shown in Figure 3. SB and S4D are diblock-arm precursor SB and the star polymer having four arms, respectively. The  $M_w$  values measured by SEC-LS are similar to those by MALLS and DLS, suggesting a good agreement of these methods. Thus, the values of  $M_w$  of the SBS samples are believable. In view of the results mentioned previously, the  $M_w$  values of S8D, S6D, S4D, and S2D are about 6, 5, 4, and 3 times that of SB, so the statistical average arm numbers of the SBS copolymers have been confirmed to be 3, 4, 5, and 6. Moreover, the change tendency of  $M_w$  of the samples is similar to their arm numbers on the whole. Usually,  $[\eta]$  has the dimensions of a specific volume, that is, the volume per unit of mass. The relatively small  $[\eta]$  value reflects a small molecular size or volume of the SBS samples. According to the data in Table I, the  $[\eta]$  values slightly increase with a rapid increase in  $M_w$  for the star-shaped SBS, except for S8D. This suggests that when the number of arms of the SBS samples increases from three to six, their molecular volume becomes relatively small; that is, the density of the chains increases. An analysis of the  $M_w$  and  $[\eta]$  data indicates that the  $[\eta]$  value of S8D decreases significantly, compared with that of SBS samples having three to five arms, suggesting a relatively low viscosity of the SBS copolymer having six arms.

According to Einstein's viscosity relationship and Stoke's law, the equivalent sphere viscometric radius ( $R_\eta$ ) can be calculated as follows:<sup>34</sup>

$$R_\eta = \frac{1}{2} [12 / (5\pi N_A)]^{1/3} (M[\eta])^{1/3} \quad (5)$$

TABLE I  
Experimental Results for  $[Z]$ ,  $M_w$ ,  $M_w/M_n$ ,  $\langle S^2 \rangle^{1/2}$ ,  $\alpha$ ,  $R_\eta$ , and Arm Number ( $n$ ) of the SBS Samples

Sample	PS (%)	MALLS		SEC-LS			$[\eta]$ ( $\text{cm}^{-3} \text{g}^{-1}$ )	$R_\eta$ (nm)	$n$
		$M_w \times 10^{-4}$ (g/mol)	$\langle S^2 \rangle^{1/2}$ (nm)	$M_w \times 10^{-4}$ (g/mol)	$\alpha^c$	$M_w/M_n$			
S2D	30	9.0	5.3	8.2	0.59	1.1	75.5	10.0	3
S4D	32	13.0	6.9	12.7	0.43	1.2	98.5	12.6	4
S6D	33	14.9	8.1	14.6	0.35	1.1	116.7	14.2	5
S8D	34	18.1	12.7	17.8	0.30	1.3	83.9	13.6	6
		17.5 <sup>a</sup>	12.6 <sup>a</sup>					15.0 <sup>a</sup>	
		17.5 <sup>b</sup>	12.5 <sup>b</sup>					15.1 <sup>b</sup>	
SB	45	2.9	—	—	—	—	40.2	—	1

<sup>a</sup> Data obtained by DLS at 30°C.

<sup>b</sup> Data obtained by DLS at 40°C.

<sup>c</sup>  $\langle S^2 \rangle_z^{1/2} = f(M_w)$ .

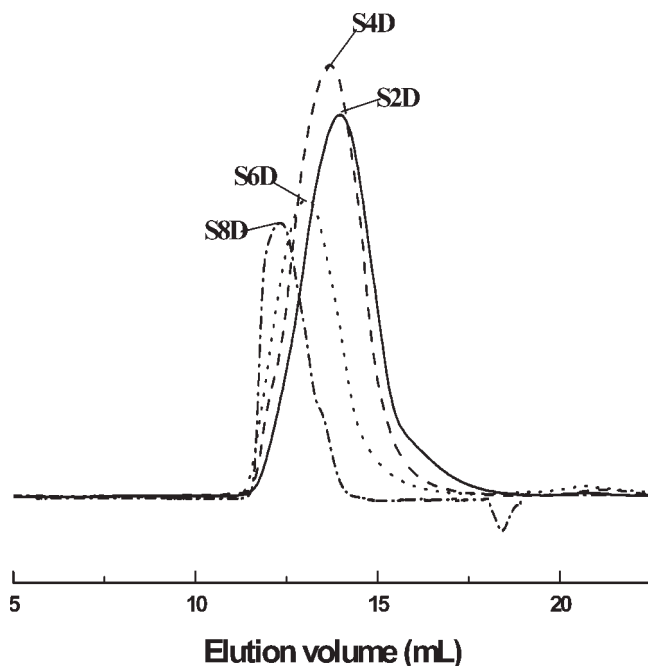


Figure 2 SEC chromatograms of star-shaped SBS.

The  $R_{\eta}$  values calculated here are summarized in Table I. This indicates that the  $R_{\eta}$  value with a high arm number slowly increases with an increase in  $M_w$ .  $R_{\eta}$  is related to the radius of an equivalent hard sphere.<sup>35</sup> Therefore, the molecules of S8D exist as a more compact sphere conformation in THF than those of S2D, S4D, and S6D. Clearly, the good fluidity of S8D is related to the compact conformation.

The  $\langle S^2 \rangle$  value is related to the actual space of the polymer chain in the solution. The  $\langle S^2 \rangle^{1/2}$ - $M_w$  rela-

tionship can be established from a polymer with the same structure. The  $\langle S^2 \rangle^{1/2}$  value detected by MALLS here almost lies in the lower measurable limit (8 nm) of the LS technique, leading to the inaccuracy of the  $\langle S^2 \rangle^{1/2}$  absolute value obtained by LS. However, from the SEC chromatogram detected by MALLS, we can obtain  $M_w$  and  $\langle S^2 \rangle^{1/2}$  values of many fractions, which can be estimated from many experimental points in the SEC chromatograms. Moreover, the continuous  $\langle S^2 \rangle^{1/2}$  and  $M_w$  values can be used for the calculation of the slope of the power law  $\langle S^2 \rangle^{1/2} = f(M_w)$ . Information about chain stiffness can be obtained from  $\langle S^2 \rangle^{1/2} = KM_w^{\alpha}$ . Figure 4 shows the molecular weight dependences of  $\langle S^2 \rangle^{1/2}$  for S2D, S4D, S6D, and S8D by SEC-LS in THF at 25°C. The slope ( $\alpha$ ) of log-log plots of  $\langle S^2 \rangle^{1/2}$  against  $M_w$  was determined to be 0.59, 0.43, 0.35, and 0.30 for S2D, S4D, S6D and S8D, respectively. Usually,  $\alpha$  is 0.5–0.6 for flexible polymers in a good solvent but 0.2–0.4 for highly branched molecules or compact coils and 0.3 for global shapes.<sup>36</sup> It has been further confirmed that star-shaped SBS exists as a compact sphere conformation in a THF solution, and the density of the chains increases as the arm number of the copolymer rises. The good agreement of these results indicates that the molecular size and shape and the arm number of star-shaped copolymers can be reliably characterized with MALLS and SEC-LS techniques.

The SEC chromatograms and the molecular weight data as a function of the elution volume of the star-shaped SBS samples in THF at 25°C are shown in Figure 5. The plots of  $M_w$  against the elution volume exhibit a U-shape, rather than the normal linear decrease with increasing elution volume. The U-cur-

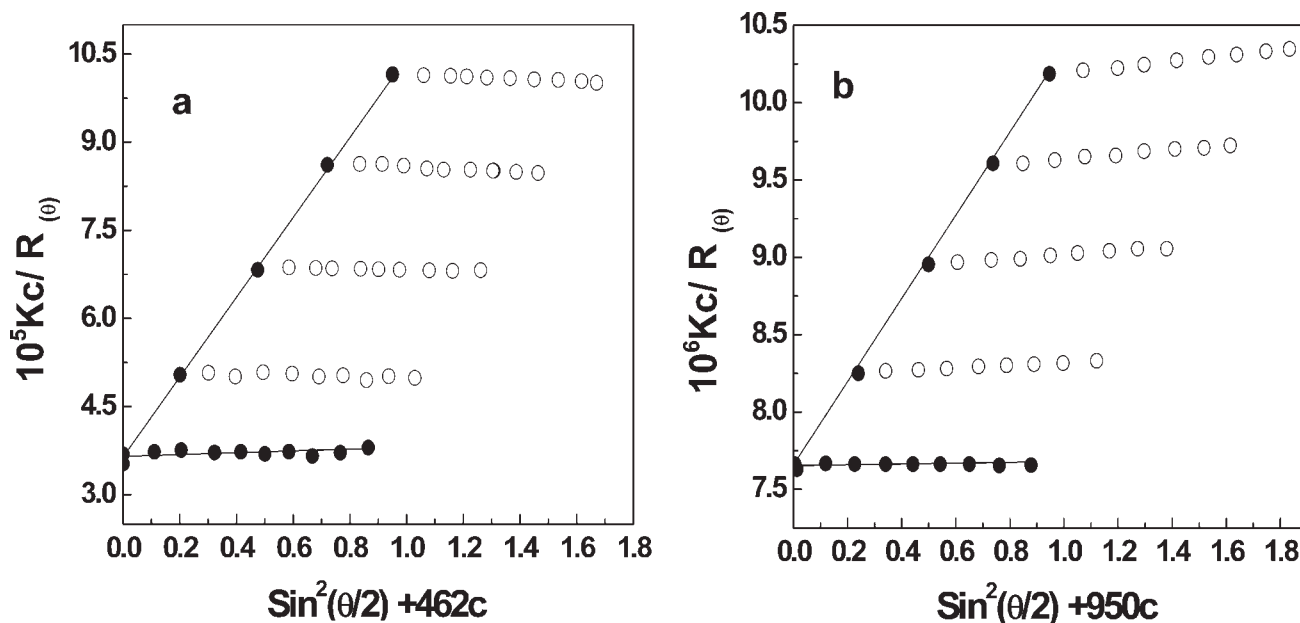


Figure 3 Zimm plots of (a) SB and (b) S4D in THF at 25°C.

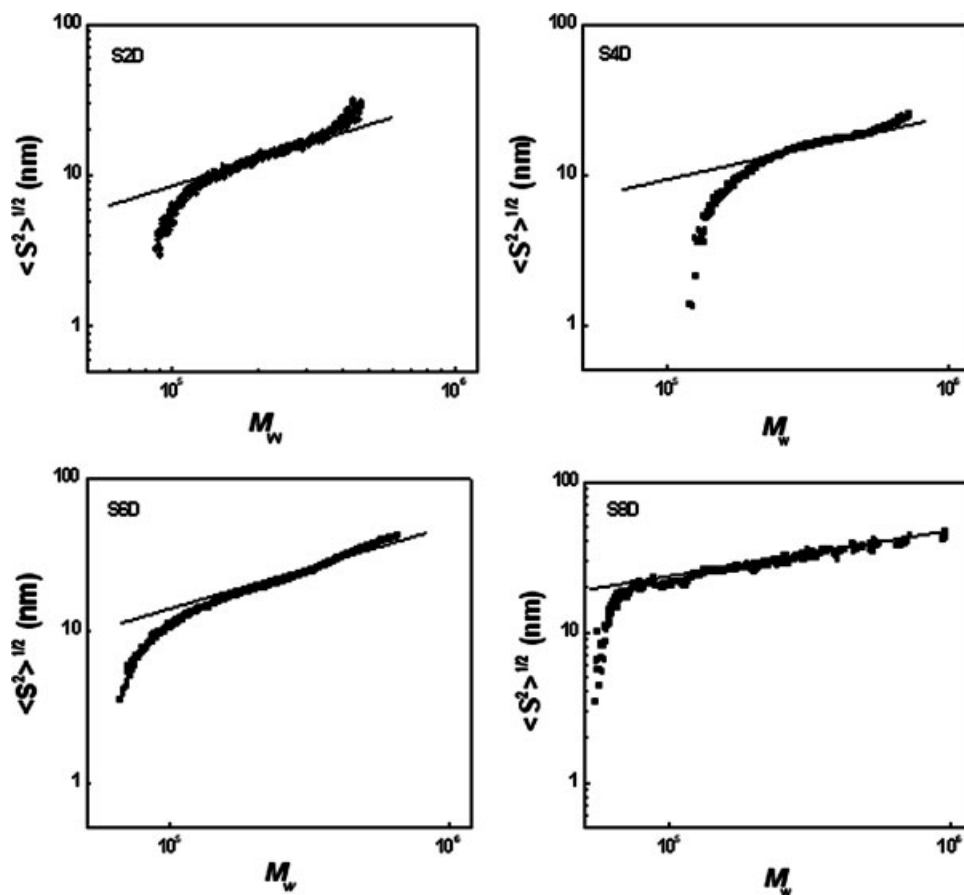


Figure 4 Molecular weight dependence of  $\langle S^2 \rangle_z^{1/2}$  for star-shaped SBS.

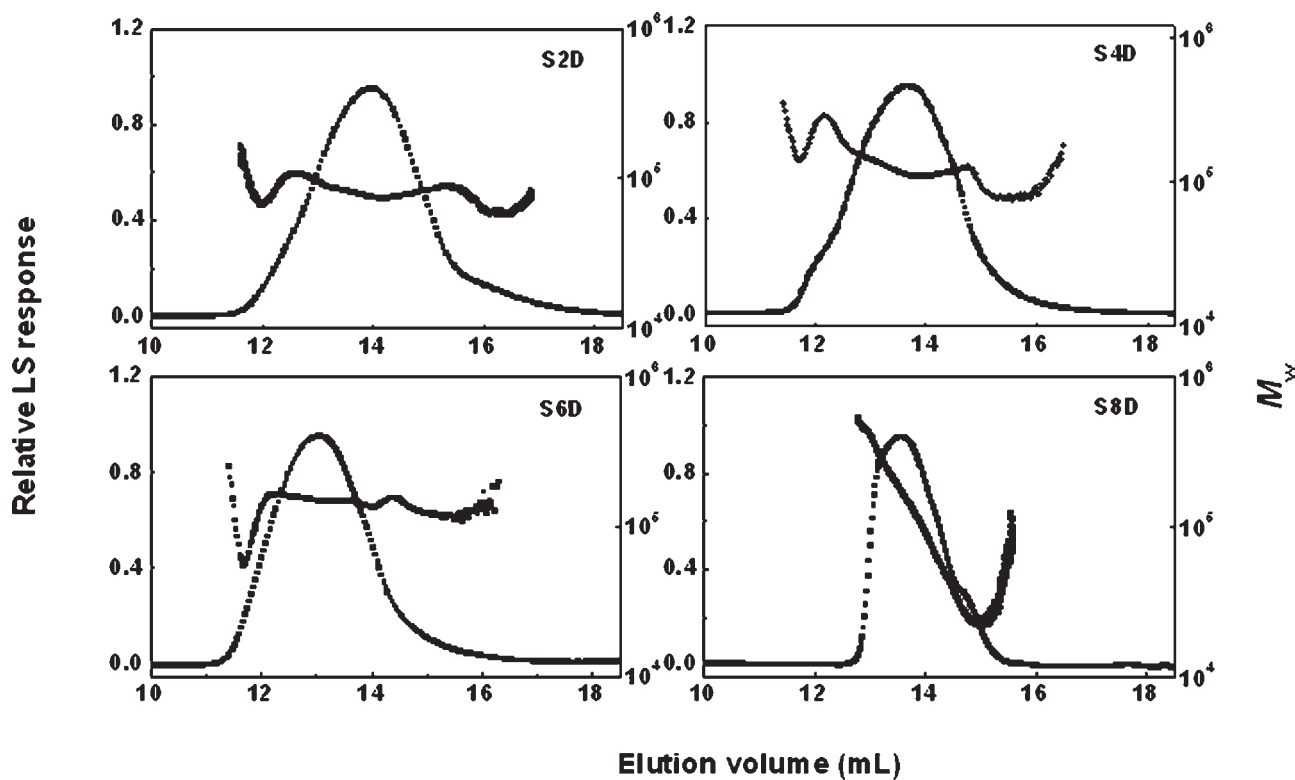


Figure 5 SEC chromatograms and plots of  $M_w$  versus the elution volume for star-shaped SBS.

vature of SEC elution of the SBS samples is typical for highly branched polymers, whereas samples with less branching behave similarly to linear polymers.<sup>22,37</sup> The retardation of the large molecules in the size exclusion separation reflects the hyperbranched molecular architecture; the origin of the retardation, however, remains unclear.<sup>38,39</sup> Core-core coupling or entanglement of the partial, large branched molecules in the pore of the column packing may be the explanation of the delay in size exclusion separation. Moreover, the hydrodynamic radii of the partial, large molecules for star-shaped SBS become relatively small as a result of core-core coupling or molecule entanglement. Then, the large molecules may behave as separate molecules, penetrate the column packing, and anchor the entire molecule. Therefore, the retardation of some large molecules in the column packing means that increased values of the molecular weight are measured at high volumes, exhibiting a U-shaped curve rather than the normal decrease for linear polymers. Thus, with the U-shaped curvature, we can further confirm the branched characteristics of star-shaped SBS.

## CONCLUSIONS

By changing the DVB content, we synthesized star-shaped SBS block copolymers with three to six arms by living anionic polymerization on a pilot-vessel scale. The molecular weight, chain shape, and arm number of the SBS copolymers were successfully characterized with MALLS, SEC-LS, and viscometry. The results confirmed well that the arm numbers of the SBS samples synthesized with different DVB contents were three, four, five, and six, respectively. Furthermore, there was a lot of  $M_w$  and  $\langle S^2 \rangle^{1/2}$  data for many fractions in the SEC chromatograms of the star-shaped SBS copolymers detected by LS, leading to the establishment of the  $\langle S^2 \rangle^{1/2} = KM_w^\alpha$  equation. The exponent of the equation was determined to be 0.59–0.30 for three to six arms; this indicated an increase in the branching leading to the rise in the chain density. In view of the results from the molecular parameters, star SBS copolymers existed as a compact sphere conformation in THF, and their chain density increased with an increase in the arm number. The viscosity of the six-arm SBS copolymer was relatively low, compared with that of the SBS samples having three to five arms, indicating good fluidity.

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