Molecular Architectures of Four-Arm Star-shaped Styrene-butadiene Copolymer

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ABSTRACT: To understand the molecular architectures of styrene-butadiene four-arm star (SBS) copolymers, a size exclusion chromatography combined with laser light scattering (SEC-LLS) has been used to determine their weight-average molecular weight (M_w) and radius of gyration ($\langle S^2\rangle^{1/2}$), and a new method for the establishment of the Mark-Houwink equation from one sample has been developed. Based on the Flory viscosity theory, we successfully have reduced the $\langle S^2\rangle^{1/2}$ values of numberless fractions estimated from many experimental points in the SEC chromatogram to intrinsic viscosities ($[\eta]$). For the first time, the dependences of $\langle S^2\rangle^{1/2}$ and $[\eta]$ on M_w for the four-arm star SBS in tetrahydrofuran at 25°C were found, respectively, to be $\langle S^2\rangle^{1/2} = 2.62 \times 10^{-2} M_w^{0.54}$ (nm) and $[\eta] = 3.68 \times 10^{-2} M_w^{0.64}$ (mL/g) in the M_w range from 1.4×10^5 to 3.0×10^5. From data of $[\eta]$ and $\langle S^2\rangle^{1/2}$ for linear and star SBS, we have obtained the information about the branching, namely, the ratios (g and g') of $\langle S^2\rangle$ and $[\eta]$ for star SBS to that of the linear SBS of the same molecular weight, which agree with theoretical predictions. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 961–965, 2005

Key words: light scattering; solution properties; GPC; star-shaped SBS

INTRODUCTION

Hyperbranched polymers have generated renewed interest not only in polymer chemistry, but also in the medicine, space, automotive, and electronics industries.[1] Styrene-butadiene triblock (SBS) copolymers are thermoplastic elastomers and have been manufactured commercially with a high degree of control over the block length, molecular weight, and microstructure using anionic polymerization.[2] The SBS copolymers often have a star-shaped structure, which provides compact morphology, reduced solution viscosity, and high retention of properties under high temperature and high shear applications.[3] Recently, the molecular weight and physical properties of the four-armed star polymers and copolymers have been investigated, for example, degree of branching for SBS copolymer by gel permeation chromatography (GPC),[3] molecular weight for polystyrene-block-polybutadiene copolymers [(SB)$_4$] by GPC-ultraviolet/refractive index,[4] concentration fluctuations and chain topology for mixtures of linear poly(vinyl methyl-ether)(PVME) with a four-armed star polystyrene (PS*) by light scattering and small-angle neutron (SANS),[5] weight-average molecular weight and the ratio (g') of intrinsic viscosity of star four-branched PS to that of the linear one of the same M_w by using viscometry and light scattering techniques,[6] excluded-volume effects of four-arm star PS in benzene by light scattering and viscometry,[7] and physical properties of star-shaped poly(ether-ester) block copolymers. However, the solution properties of SBS four-arm star copolymers have been scarcely reported.

It is well known that the rheological and mechanical properties as well as the processing behavior of SBS star copolymers are strongly influenced by the molecular architecture, including molecular weight, conformation, and degree of branching. However, it is very difficult to fractionate the SBS star copolymer because of narrow molecular weight distribution with multiblock. Therefore, the Mark-Houwink equation of the SBS four-arm star copolymer has never been reported. To overcome the difficulty, a size exclusion chromatography (SEC) instrument equipped with light scattering (SEC-LS) and refractive-index (RI) detectors can be used to measure molecular weight, without needing calibration standards of similar copolymers. Moreover, we have accumulated experience in the preparation of fractionated samples and characterization of molecular weights for polymers.[8–12] In the present work, we fractionated a mixture of star copolymer into single-, two-, and four-arm copolymers by a nonsolvent addition method and then measured the molecular weight, ratio of gyration, and intrinsic viscosity of the copolymers by using viscometry, SEC-LS, and light scattering. Furthermore, we

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developed a new method for establishing a Mark-Houwink equation from one sample based on Flory's viscosity relationship and studied the branching factors.

EXPERIMENTAL PROCEDURES

Sample preparation

SBS linear copolymer coded as 1401 as well as SBS star copolymers coded as 802 and 4402 were provided by Yanshan Petrochemical Corporation of China. Another sample, four-arm SBS, coded as Y805 was purchased from (KUMHO, Korea). Tetrahydrofuran (THF) and ethanol were analytical grade and were purchased from Tianjing Fucheng Chemical Reagent Corporation in China. The SBS copolymer 802 was purified by redissolution in THF and precipitation in ethanol at room temperature. The sample 802 was further fractionated by reprecipitation from THF solution to ethanol at room temperature to obtain three fractions coded as 802-F1, 802-F2, and 802-F3, respectively. The harvested fractions were dried under reduced pressure. The final fraction was rotary evaporated under reduced pressure at 35°C to give a semisolid coded as 802-F4.

NMR analysis

^{1}H NMR spectrum was recorded on a Mercury 300 NB NMR spectrometer (Varian Inc., USA) with 300 MHz at 25°C. The spinning speed, pulse delay, and total numbers of scans were, respectively, 15 Hz, 15 s, and 2048. The sample was dissolved in deuterated chloroform ($CDCl_3$) to prepare a concentration of 150 mg/ml.

Viscometry measurement

THF as solvent was freshly distilled prior to use. Intrinsic viscosities ($[\eta]$) of the polymer solutions were measured at 25 ± 0.1°C using an Ubbelohde capillary viscometer. The kinetic energy correction was always negligible. Huggins and Kraemer equations were used to estimate the $[\eta]$ value by extrapolation to concentration (c) to be zero as follows:

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \quad (1)$$

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

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

Laser light scattering (LLS)

The light-scattering intensities of the polymer solution were determined with a multiangle laser light scattering instrument equipped with a He-Ne laser (MALLS, λ = 633 nm; DAWN®DSP, Wyatt Technology Co., Santa Barbara, CA, USA) at the angles of 43, 49, 56, 63, 71, 81, 90, 99, 109, 118, 127, 136, and 152° at 25°C. The redistilled THF was used as solvent. The polymer solutions of desired concentrations were prepared, and optical clarification of the solution was achieved by filtration through a 0.45-μm pore-size filter (PTFE, Puradisc 13-mm syringe Filters, Whatman, England) into the scattering cell (K5 mode). The refractive index increments (dn/dc) were measured using an double-beam differential refractometer (DRM-1020, Otsuka Electronics Co. Japan) at 633 nm and 25°C. The dn/dc values of the samples in THF solutions were determined to be 0.145 mL/g for four-arm SBS and 0.133 mL/g for linear SBS. Astra software (Version 4.70.07) was utilized for data acquisition and analysis.

From the LLS data, we were able to obtain the weight-average molecular weight (M_w) and the average root-mean square radius of gyration ($\langle S^2 \rangle^{1/2}$) of polymer in dilute solution from the Zimm plot by

$$\frac{Kc}{R_\theta} = \frac{1}{M_w}\left(1 + \frac{16\pi^2 n^2}{3\lambda_0^2}\langle S^2\rangle \sin^2(\theta/2) + \ldots\right) + 2A_2 c \quad (3)$$

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

where A_2, N_A, n, and λ_0 are the second virial coefficient, the Avogadro number, the solvent refractive index, and the wavelength of the light in a vacuum, respectively.

SEC-LLS measurements

SEC-LLS measurements were carried out on size exclusion chromatography combined with multiangle laser photometer mentioned above combined with a P100 pump (Thermo Separation Products, San Jose, CA) equipped with columns of G4000H8 (MicroPak, TSK) combined with G3000H8 (MicroPak, TSK) and a differential refractive index detector (RI-150, Japan) at 25°C. The carrier solution was redistilled THF. The samples were dissolved in THF overnight with stirring. The THF and polymer solution were purified by a 0.45- μm filter (PTFE, Puradisc 13-mm Syringe Filters, Whatman, England) and degassed before use. The injection volumes were 200 μL with a concentration of 0.2% for each sample, and the flow rate was 1.0 mL/min. Astra software was utilized for data acquisition and analysis.

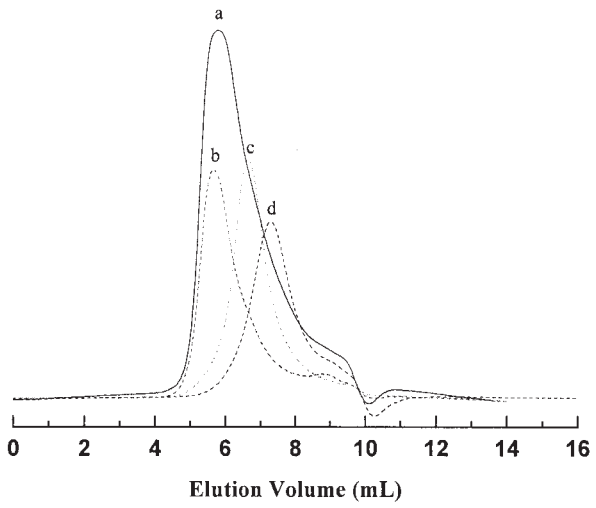

Figure 1 SEC chromatograms for the fractions and unfractioned samples from SBS 802: (a) unfractioned SBS 802; (b) 802-F1; (C) 802-F2; (d) 802-F3.

RESULTS AND DISCUSSION

Structure of star SBS

Figure 1 shows SEC chromatograms for the fractions and unfractionated sample of SBS 802. The values of M_w, $\langle S^2\rangle^{1/2}$, $[\eta]$, and arm number (f) are summarized in Table I. From the results, the M_w of 802-F1 is four times that of 802-F3, while the 802-F2 is twice that of 802-F3. This indicates that the sample 802 contains single-, two-, and four-arm copolymers and has been successfully fractionated to obtain three fractions, having different arm numbers. The predominant species of 802 is four-arm star-shaped SBS 802-F1, and its content has been estimated using the division principle of the SEC chromatogram area to be above 95%. The ^{1}H NMR spectrum and the assigned chemical shifts of the 802F1 are shown in Figure 2. The signals around 4.96 and 5.42 ppm are assigned as vinyl protons of the butadiene unit and those at 1.45, 1.58, and 2.05 ppm are assigned as methyl of the components a, b, and c, respectively. The schematic structure of the four-arm star-shaped SBS is shown in Figure 3.

Molecular weight dependence of $\langle S^2\rangle^{1/2}$ and $[\eta]$

The SEC-LLS is an absolute method, since, from the SEC chromatogram detected by LLS, we can obtain M_w and $\langle S^2\rangle^{1/2}$ values of numberless fractions, which have been estimated from many experimental points in the SEC. Figure 4 shows the comparison of the molecular weight dependence of $\langle S^2\rangle^{1/2}$ for SBS 802-F1 and that of linear SBS 1401 in THF. For low molecular weights, often the mean square radius has uncertainties larger than the values themselves and has not been considered in calculating the results. So the experimental points in the low molecular weight range have been neglected. The straight lines fitting the experimental points from SEC chromatograms are represented, respectively, by

$$\langle S^2\rangle^{1/2} = 2.62 \times 10^{-2}\, M_w^{0.54} \text{ (for star, nm)} \quad (5)$$

$$\langle S^2\rangle^{1/2} = 5.13 \times 10^{-2}\, M_w^{0.50} \text{ (for linear, nm)} \quad (6)$$

Usually, the exponent α of flexible polymers in a good solvent is in the range from 0.5 to 0.6. The α values of the star and linear SBS indicate the characteristic of flexible polymer.

Flory viscosity factor is represented by

$$\phi = [\eta]\, M_w/(6\langle S^2\rangle)^{3/2} \quad (7)$$

The values of ϕ for the samples were calculated to be 1.78×10^{23} mol^{-1} for star SBS and 1.08×10^{23} mol^{-1} for linear SBS from M_w and $[\eta]$ in Table I. Reported ϕ values of PS in benzene and cyclohexane lie in the range from 1.6×10^{23} to 3.0×10^{23} mol^{-1} and decrease first sharply and then gradually as radius expansion factor α_s ($=\langle S^2\rangle/\langle S^2\rangle_0$). Our ϕ values are lower than that of PS, owing to the heterogeneous structure of SBS and different solvent. The ϕ value of star SBS is larger than that of linear SBS because of the relatively low radius expansion factor α_s of star one. The ϕ is almost independent of M_w in the limited M_w range.[7] $[\eta]$ can be calculated accurately by the Flory viscosity equation with the substitution of measured $\langle S^2\rangle$ and Flory viscosity constant calculated from the determined $\langle S^2\rangle$ and $[\eta]$ of the same copolymer. Since, by substituting the data of $\langle S^2\rangle$ into eq. (7), a set of $[\eta]$ values was estimated roughly as shown in Figure 5, and the Mark-Houwink equations for both star and linear SBS in the M_w range from 1.0×10^5 to 3.0×10^5 are the following:

$$[\eta] = 3.68 \times 10^{-2}\, M_w^{0.64} \text{ (for star, mL/g)} \quad (8)$$

$$[\eta] = 8.73 \times 10^{-3}\, M_w^{0.77} \text{ (for linear, mL/g)} \quad (9)$$

TABLE I
Experimental Results of Molecular Weights and Intrinsic Viscosity of the SBS Star Copolymers in THF at 25°C

	SEC-LS		LS	
Sample	$[\eta]$ (mL/g)	$M_w \times 10^{-4}$	f	$M_w \times 10^{-4}$
802	98.8	15.8	Mixture (4/2/1)	—
802-F1	114.7	16.0	4	14.7
802-F2	65.2	8.2	2	—
802-F3	34.9	4.3	1	—
1401	69.2	9.6	Linear	10.1
4402	93.7	20.5	4	—
Y805	120.8	22.0	4	—

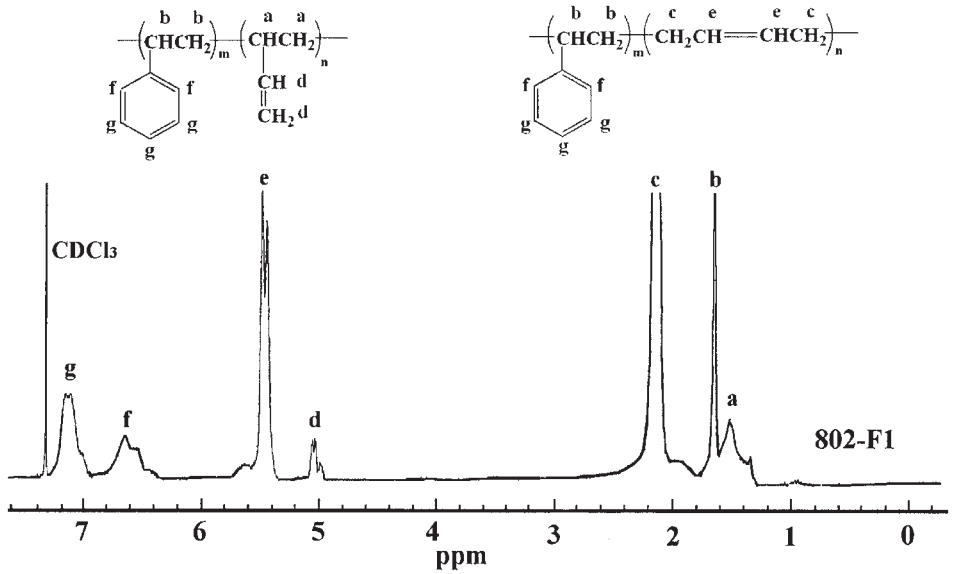

Figure 2 ^{1}H NMR spectrum and the peak assignments of the sample 802-F1.

The filled marks in Figure 5 represent the experimental values of M_w and $[\eta]$ in Table I. The M_w values of the sample 802-F1 were measured by LLS and calculated from Zimm plot as shown in Figure 6. It can be seen that the experimental points for the four-arm star SBS samples 802, Y805, and 4402 are close to the $M_w-[\eta]$ relationship. This indicates that the developed method, which can be used to establish M_w dependence of $[\eta]$ of star copolymers from one sample by SEC-LLS techniques, is feasible. The Mark-Houwink exponent of 0.64 for star SBS exhibits a somewhat lower value in the same solvent compared with linear SBS, which shows considerably higher $[\eta]$ values for the same molecular weight. In recent studies on hyperbranched polymers, the compact and globular shape are consistent with unusually low values of $[\eta]$ and the Mark-Houwink exponent (α).[13] It appears that the relatively low values for $[\eta]$ and α in our samples are a result of a compact star-shaped structure, leading to small hydrodynamic volumes.

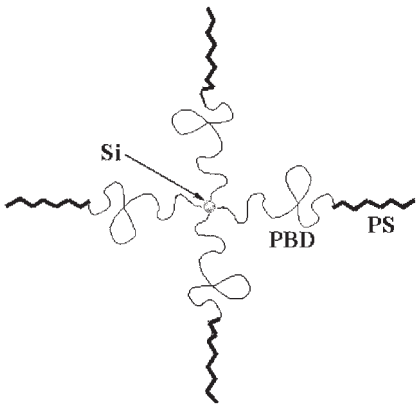

Figure 3 Schematic structure of four-arm star-shaped SBS.

Branching factors

The ratios g of $\langle S^2\rangle^{1/2}$ and g' of $[\eta]$ for the star SBS to those for the linear SBS of the same molecular weight are represented, respectively, by

$$g = \langle S^2\rangle_{z\,\mathrm{star}}/\langle S^2\rangle_{z\,\mathrm{linear}} \tag{10}$$

$$g' = [\eta]_{\mathrm{star}}/[\eta]_{\mathrm{linear}} \tag{11}$$

$$g' = g^b \tag{12}$$

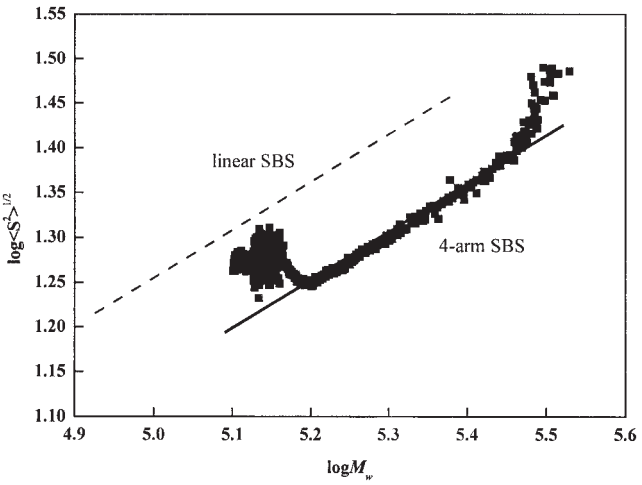

Figure 4 Molecular weight dependence on radius of gyration for four-arm star SBS (—) and linear SBS (· · ·) in THF at 25 °C.

Okumoto et al[7] and Roovers and Bywater[14] have reported that the experimental values of g' for four-arm star PS with M_w of 10^4 to 10^6 are in the range from 0.69 to 0.82 in good solvent, and agree substantially with two theoretical predictions: $g' = 0.79$ proposed by Zimm and Kilb[15] and $g' = 0.71$ by Stockmayer and Fixman.[16] Our values of g and g' were calculated from eq. (10) and (11) to be 0.60 and 0.74, respectively, which basically agree with the theoretical predictions proposed by Zimm and Kilb[15] and by Stockmayer and Fixman.[16] In addition the theoretical g_{theo} for $\langle S^2\rangle^{1/2}$ has been given by

$$g_{theo} = (3f - 2)/f^2 \quad (13)$$

for regular star polymers of equal molecular weight, where f denotes the number of arms in the molecule.[17] The g_{theo} was 0.625 for our SBS. Therefore the exponent b in eq. (12) was calculated from eq. (13) to be 0.61, which lies in the range of star polymers.

CONCLUSION

Based on the Flory viscosity theory, we successfully have reduced the $\langle S^2\rangle^{1/2}$ values of less number fractions estimated from many experimental points in the SEC chromatogram to intrinsic viscosities $[\eta]$, since the dependences of $\langle S^2\rangle^{1/2}$ and $[\eta]$ on M_w for the four-arm star SBS in THF at 25°C were found to be $\langle S^2\rangle^{1/2} = 2.62 \times 10^{-2} M_w^{0.54}$ (nm) and $[\eta] = 3.68 \times 10^{-2} M_w^{0.64}$ (mLg^{-1}) in the M_w range from 1.4×10^5 to 3.0×10^5. From data of $[\eta]$ and $\langle S^2\rangle^{1/2}$ for linear and star SBS, the values of g and g' for star SBS of the same molecular weight were 0.60 and 0.74, which agree with the theoretical predictions by Zimme and Kilb[15] and by Stockmayer and Fixman.[16]

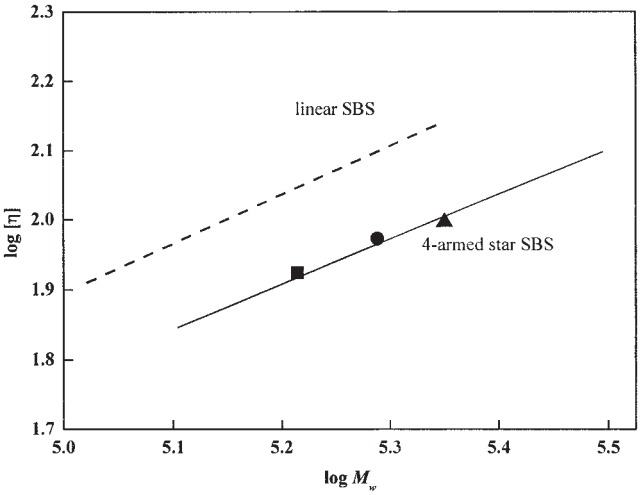

Figure 5 Intrinsic viscosity VS molecular weight relationships for linear (···) and four-arm star-shaped (—) SBS in THF at 25 °C. The marks ■, ● and ▲ represent, respectively, data for the samples, 802, 4402 and Y805 measured by viscometry and LLS.

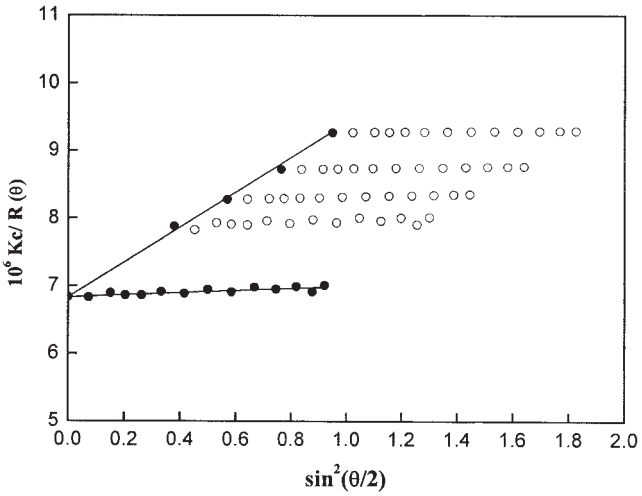

Figure 6 Zimm plot of the sample 802-F1 in THF at 25 °C.

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