

Effects of Arm Number on the Properties of Transparent Elastomers Prepared from Styrene–Butadiene Block Copolymer

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ABSTRACT: A series of the SBS transparent elastomers were prepared from star-shaped SBS having different arm number by solution-casting. Their structure and physical properties were characterized by scanning electron microscope, ultraviolet spectrometer, wide-angle X-ray diffractometer, differential scanning calorimetry, dynamic mechanical thermal analysis, tensile testing, and contact angle measurements. The results revealed that the miscibility, optical transparency (T_r), tensile strength (σ_b), elongation at break (ε_b), and elasticity at low temperature of the star SBS increased with an increase of arm number. The six-arm SBS having relatively high molecular weight exhibited a simultaneous enhancement of T_r (90% at 800 nm), σ_b (6.0 Mpa), and ε_b (1260%). This indicated that the SBS materials having

six arms had higher transparency and elasticity than others. Moreover, the water contact angle on surface of the star-shaped SBS film increased with an increase of arm number that is enhancement of hydrophobicity. Therefore, the relatively high arm number and molecular weight played an important role in the improvement of the miscibility and properties of the SBS sheets as a result of the compacted architecture of the hyperbranched molecules. This work provides a convenient way to obtain materials with both high transparency and elasticity by increasing the arm number.
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Key words: star-shaped styrene–butadiene–styrene; arm number; mechanical properties; transparent elastomer

INTRODUCTION

In recent years, star-shaped block copolymers have become a field of considerable scientific and industrial interest.^{1–9} Much of the work has focused on homopolymer stars; however, star copolymers have an even richer range of existing and potential applications, such as separation processes, materials design, drug delivery, viscosity modification, steady foaming, and so on.¹⁰ It is well known that styrene–butadiene block copolymers (SBS) constitute an important class of thermoplastic elastomers.^{11–13} It is worth noting that the application of SBS and its composites greatly depends on their physical properties, which are decided by their molecular structure.^{14–20} Compared with linear SBS, the star-shaped SBS has a more compact morphology, a reduced bulk and solution viscosity, and the better mechanical, rheological, and processing properties.^{21,22} Arm number is an important pa-

rameter that not only determinates the molecular architecture of the star-shaped SBS but also indicates the efficiency of the controlled polymerization. Recently, there are several experiences in the synthesis of star polymers using linking agents, such as chlorosilanes or multifunctional initiators, via both ionic polymerization and living radical polymerizations.^{23–27} Among these synthetic techniques, multifunctional chlorosilanes process is the most prevalent as a result of their high activity and efficiency.²⁸ To prepare multiarmed products, divinylbenzene (DVB) process is undoubtedly a more promising method not only for its cheapness but also for its synthesis diversity.^{21,29–31} Star-shaped polymers are of great theoretical and commercial interests, most notably as models for long-chain branching in polymers, and as viscosifiers in motor oils due to their excellent resistance to shear-induced thermal degradation.^{32–35}

Star-shaped copolymers have been extensively studied to improve their properties. A basic understanding of the correlation of structure to properties of the SBS materials is essential for their successful application. However, the effects of the molecular weight and arm number of the star-shaped SBS on their properties have been scarcely reported. In present work, we attempted to prepare a series of star-shaped SBS by living anionic polymerization using DVB as linking agents. Furthermore, the effects of

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molecular weight and arm number on physical properties were investigated and discussed. We hope this work may contribute some meaningful information to deeply understand the molecular architecture and the effect of arm number on the properties of the star-shaped SBS.

EXPERIMENTAL

Synthesis of SBS copolymer

Styrene, butadiene, and *n*-butyllithium were the gift of Yanshan Petrochem, People's Republic of China. The cyclohexane (Jinxi Chemical Plant, Beijing, People's Republic of China) was treated with 5 Å molecular sieves, and then deoxygenated. DVB was of analytical grade, and purchased from Shanghai Chemical Plant. Tetrahydrofuran (THF) and ethanol were of analytical grade, and were purchased from Fucheng chemical Reagent (Tianjing, People's Republic of China). Linear SBS 1401 were self-made in Yanshan Petrochem, People's Republic of China.

All of the polymerization experiments were carried out in a 5-L air-free kettle condition. On the basis of sequential anionic "living" copolymerization, 40% (w/w) styrene was dissolved in cyclohexane with stirring, and then appropriate amount of *n*-butyllithium was added to the solution, resulting in the color turning red. The homopolymerization of polystyrene (PS) was carried out at 50°C for 2 h, and then 60% (w/w) butadiene was added to the mixture to obtain poly (*S-b-B*) diblock anions, which concentration is 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 star-shaped SBS copolymer. The residual active chains were terminated under vacuum with ethanol. To remove unreacted poly(*S-b-B*) diblock copolymers (SB) from the crosslinked product, the purification of the SBS sample was carried out in the THF–ethanol system at 25°C. The arm number of star copolymers usually increases with an increment of [DVB]/[SB].^{36,37} For a given concentration of *n*-butyllithium, the quantity of diblock anions is constant. Thus, we synthesized these star copolymers with various arm numbers by varying the concentration ratio of DVB to diblock anion ([DVB]/[SB]). The resultant SBS samples were coded as S2D, S4D, S6D, and S8D, respectively, corresponding to the [DVB]/[SB] ratio of 1, 2, 3, and 4.

Preparation of SBS sheets

To prepare cast sheet, 1 g of S2D, S4D, S6D, S8D, and 1401 were dissolved in 50 mL THF, respectively. The resultant solutions were cast in a Petri dish (ϕ 12 cm) at room temperature, and then dried under vacuum at

40°C until a constant weight. The sheets were coded as S2D-S, S4D-S, S6D-S, and S8D-S, corresponding to theoretical designed arm number of 3, 4, 5, and 6, respectively, and that from linear SBS 1401 was coded as 1401-S. The SBS sheets were controlled to be 0.15 mm in thickness.

Characterization

Viscosity of the samples was measured at 25 °C \pm 0.1°C by using an Ubbelohde viscometer, and THF was used as solvent. The kinetic energy correction was always negligible. Huggins and Kraemer equations were used to estimate intrinsic viscosity ($[\eta]$) by extrapolation to concentration (*c*) to be zero as follows:

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

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

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.

The light-scattering intensities of the SBS solution were determined with a multiangle laser light scattering (MALLS) instrument equipped with a He–Ne laser ($\lambda = 633$ nm; DAWN@DSP, Wyatt Technology, Santa Barbara, CA) in 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- μ m pore size filter (PTFE, Puradisc 13 mm syringe filters, Whatman, England) into the scattering cell. The refractive index increments (dn/dc) were measured by using a double-beam differential refractometer (DRM-1020 Otsuka Electronics, 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⁻¹ for star-shaped SBS having arm number from three to six, and 0.1332 mL g⁻¹ for linear SBS. Astra software (Version 4.70.07) was utilized for data acquisition and analysis. 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 can be obtained from Zimm plot by

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

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

TABLE I
Experimental Results of the Composition, M_w , $\langle S^2 \rangle_z^{1/2}$, and Arm Number (n) of the SBS Samples

Sample	PS content (%)	MALLS		$[\eta]$ ($\text{cm}^{-3} \text{g}^{-1}$)	n
		M_w ($10^{-4} \text{g mol}^{-1}$)	$\langle S^2 \rangle_z^{1/2}$ (nm)		
SB	45	2.9	—	40.2	1
S2D	30	9.0	5.3	76.1	3
S4D	32	13.0	6.9	98.3	4
S6D	33	14.9	8.1	123.5	5
S8D	34	18.1	12.7	132.4	6
1401	42	9.7	16.5	82.3	—

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

^1H NMR spectrum was recorded on a Mercury 600 NB NMR spectrometer (Varian, USA) with 600 MHz at 25°C. The spinning speed, pulse delay, and total numbers of scans were 15 Hz, 15 s, and 2048, respectively. The sample was dissolved in deuterated chloroform (CDCl_3) to prepare concentration of 150 mg ml^{-1} .

Scanning electron microscopy (SEM) was carried out on a SEM microscope (S-570, Hitachi, Japan). The sheets were frozen in liquid nitrogen and fractured immediately, and then vacuum-dried. The fractured surfaces (cross section) of the sheets were coated with gold for SEM observation. Optical transmittances were measured on an ultraviolet spectrometer (UV-160, Shimadzu, Japan) in the wavelength of 200 and 800 nm. Wide-angle X-ray diffraction (WAXD) patterns of the sheets were recorded on an X-ray diffractometer (D8 Advance, Bruker, Germany) with $\text{CuK}\alpha$ radiation at 40 kV and 100 mA ($\lambda = 1.5405 \times 10^{-10} \text{m}$). The samples were examined at 2θ ranging from 1° to 40° with a scanning rate of 4° min^{-1} .

Differential scanning calorimetry (DSC) measurements were carried out on a DSC-204 apparatus (Netzsch, Germany) under a nitrogen atmosphere at a heating rate of 20°C min^{-1} from -180 to 150°C. Before the test, samples of the desired weight ($10 \pm 1 \text{mg}$) were heated from room temperature to 100°C to remove the volatile components, and then they were cooled to -180°C by liquid nitrogen. Dynamic mechanical thermal analysis (DMTA) was carried out on a DMTA-V dynamic mechanical analyzer (Rheometric Scientific, USA) at a heating rate of 5°C min^{-1} from -180 to 120°C. The vibration frequency was 1 Hz. The specimens used were about $15 \times 10 \times 0.15 \text{mm}^3$.

The tensile testing measurement was performed on a universal tensile tester (CMT6503, Shenzhen Sans Test Machine, Shenzhen, People's Republic of China) at a tensile rate of 50 mm min^{-1} at 25°C. The values were an average from five measurements. Contact angles were measured using a Kruss DSA-10 (Ger-

many) contact angle goniometer employing the sessile drop principle. The instrument is equipped with a video camera system, and a video camera was connected to a U-matic video recorder. Experiments were performed using ultrapure triply distilled water. Contact angles were determined by depositing a water drop onto the SBS film surface through a syringe without removing the syringe tip. The drop volume was about of 10 μL , and triplicate measurements yielded a variation of $\pm 1^\circ$. The contact angles were measured just prior to movement of the three-phase line as judged from the video image.

RESULTS AND DISCUSSION

Structure of star SBS

The values of weight-average molecular weight (M_w), radius of gyration ($\langle S^2 \rangle^{1/2}$), and intrinsic viscosity ($[\eta]$) for the SBS samples are summarized in Table I. Star-shaped SBS samples with three, four, five, and six arms could be efficiently synthesized by theoretical design and controlled polymerization. By using MALLS technique, the M_w of diblock arm precursor is determined to be 2.9×10^4 , which is basically consistent with designed theoretical value (2.8×10^4). Then the arm number has been calculated from the M_w value of the SBS samples, and the data are summarized in Table I. The obtained arm numbers quite accorded with the theoretical design. In view of the results, the polymerization has occurred as a living and controlled manner, and the corresponding arm number have been well confirmed.

^1H NMR spectrum of the star-shaped SBS is shown in Figure 1. In the spectrum, the peaks at δ about 1.43 ppm (a) and 1.5 ppm (b) are assigned to protons of methylene in 1,2-butadiene (H_V) and vinyl groups of PS (H_b). The peak at $\delta = 2.03 \text{ppm}$ (c) belongs to the protons of methylene in 1,4-butadiene (H_A , H_D). Two peaks at about $\delta = 4.98 \text{ppm}$ (d) and 5.41 (e) ppm represents protons of the double bonds of 1,2- and 1,4-butadiene units (H_K , H_M , H_T , H_F , and 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

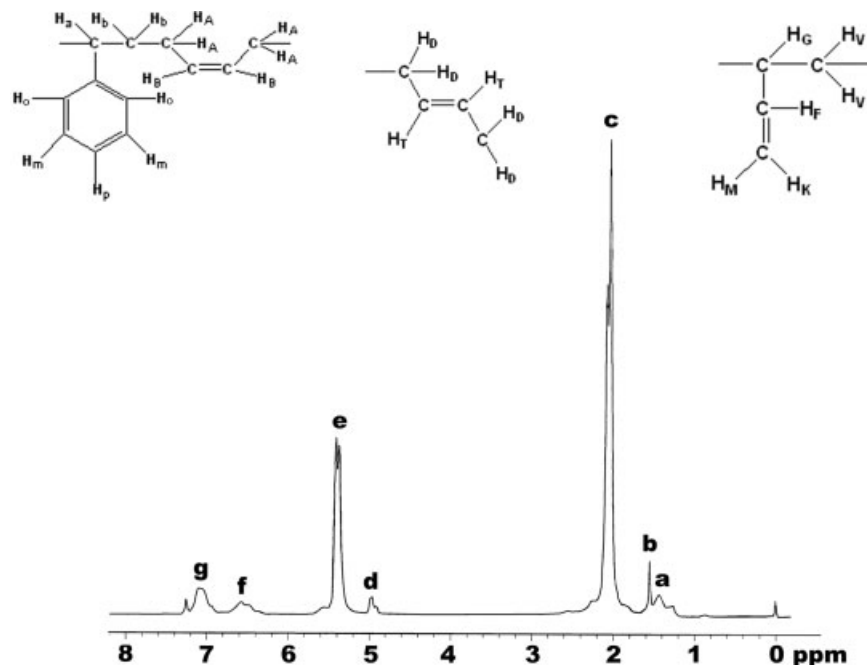


Figure 1 ^1H NMR spectrum of the sample S2D.

block (H_m , H_p , and H_o). Comparing the peak intensities, we can conclude that the 1,4-PB block predominates in the star-shaped SBS, similar to Holden's reports when the polymerization were performed without adding any polar modifiers.³⁸ The compositions of PS and polybutadiene (PB) blocks in the copolymers have been calculated from the peak intensities, and are listed in Table I.

Effect of arm number on miscibility

The SEM images of the cross section for the SBS sheets are shown in Figure 2. The cross sections of S6D-S and S8D-S are smoother than those of S2D-S and S4D-S, suggesting that the S6D-S and S8D-S sheets have better miscibility than S2D-S and S4D-S, which exhibit a slight phase-separation structure. Moreover, 1401-S obtained from linear SBS shows a more rough structure with more defect clusters. The results indicated that the miscibility of the SBS copolymer increases with an increase of the arm number. This is in agreement with Choi's results that the phase separation of star-shaped poly(ether-ester) block copolymers decreases with an increase of the branching degree.³³ The light transmittance measurement is often used as an empirical method for determining the phase separation,³⁹ which will cause losses in optical transmission because of the quantity of scattered and reflected light at the interface of particles. Furthermore, the enhancement of optical transmittance of the polymer may be relative to amorphous state, interfacial interactions, phase domain size, and match of the refractive

index of the components. As shown in Figure 3, all of the samples exhibit more than 78% optical transmittance both at 200 and 800 nm, and optical transmittance (T_r) values of the SBS samples increase with an increase of the arm number to achieve 90% for that having six arms. This can be explained that when the arm number increases from three to six, the molecular volume for the same molecular weight becomes relatively small that is the density of the chain increases. Therefore, the S6D and S8D molecules exist as dense sphere conformation in the solution, owing to strong intermolecular interaction as a result of relatively small volume and large specific surface,⁴⁰ which leads to the compact inner structure of the solution-cast sheets. The results from SEM and optical transmittance reveal that the miscibility of the SBS sheets increases with an increase of arm number. Interestingly, S8D-S possesses excellent transmittance ($T_r = 90\%$), and so it may be helpful in the field of the exploiting new optical material.

Figure 4 shows the WAXD patterns of the sheets. There is only diffuse scattering, with the maximum intensity near 20° (2θ) and a shoulder about 5.8° , which indicates the amorphous nature of the sheets. The crystallization of the SBS samples decrease with an increase of the arm number on the whole. This reflects a good miscibility of the SBS samples having five or six arms.

Effect of arm number on properties

The dependence of mechanical properties on arm number of the SBS sheets is shown in Figure 5, and the

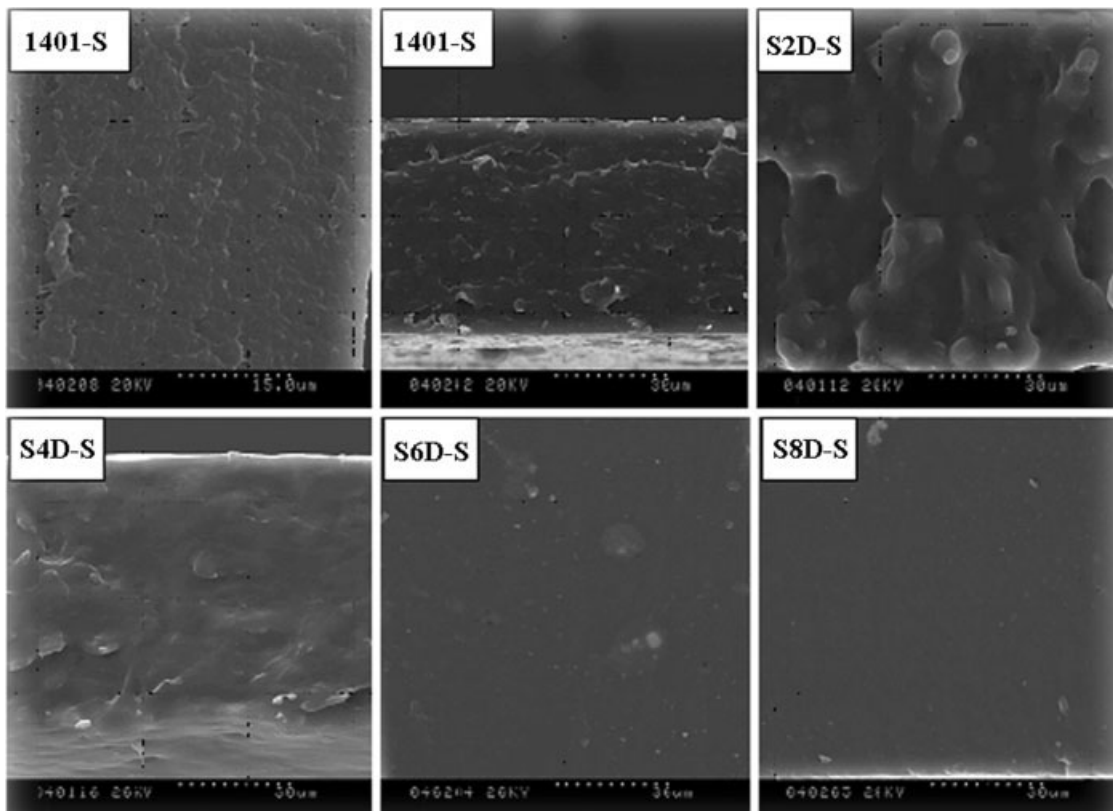


Figure 2 SEM images of the cross section for the sheets.

corresponding data are summarized in Table II. Interestingly, the tensile strength (σ_b) and the elongation at break ($\tilde{\alpha}_b$) of the SBS sheets increase simultaneously with an increase of arm number. The six-arm S8D-S possesses the highest elongation at break (1260%) and good tensile strength (6.0 Mpa). It is noted that each sample exhibits excellent elasticity, which is higher than common SBS (1401, 680%). This can be explained from the microstructure of the SBS samples and their molecular weights. The hard block (PS) provides its

modulus and the soft block (PB) makes it elastic. In this case, the content of PS block increases with the increase of arm number, which contributes to the

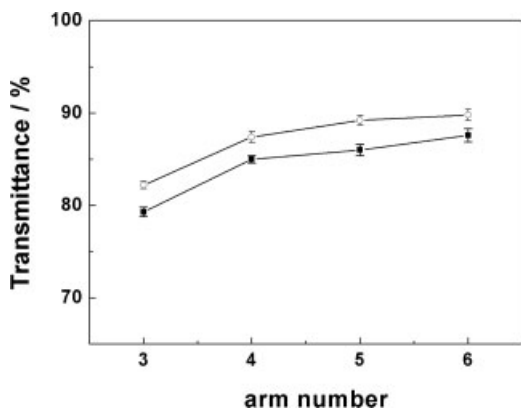


Figure 3 Dependence of T_r at 200 nm (□) and 800 nm (■) on the arm number.

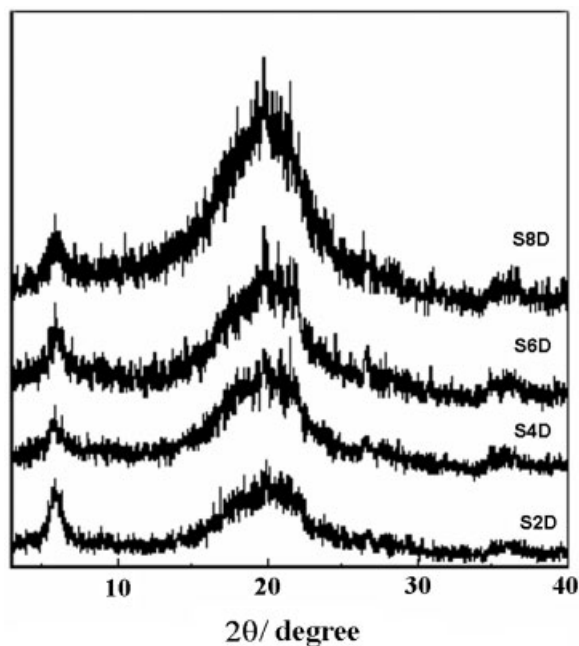


Figure 4 X-Ray diffraction patterns of the sheets.

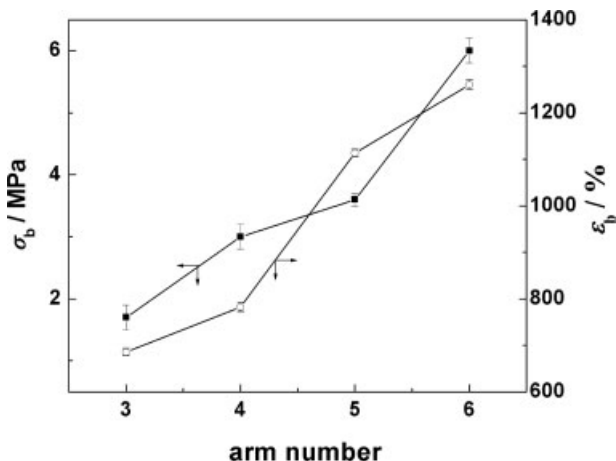


Figure 5 Dependence of tensile strength (σ_b , □) and elongation at break (ϵ_b , ■) of the SBS sheets on the arm number.

modulus. Actually, the increment of elasticity is much higher than those of modulus; it should be analyzed from the multiarm structure. The increase of the arm number leads multibranch molecules, leading to the enhancement in freedom of the molecular motion that is the increase of flexibility of the material. The M_w of S2D is lower than other stars, and its sheet is more brittle than those of others. It is obvious that the relatively high molecular weight and arm number play an important role in the improvement of such high transparency and elongation at break, as well as the tensile strength of the SBS sheets. This work provides a potential way to simultaneously enhance the transparency and elasticity of the SBS material.

Figure 6 shows DSC thermograms of S2D, S4D, S6D, S8D, and SB. In the DSC curves, the midpoint of the step of the thermogram is taken as the glass transition temperature (T_g). There is one obvious T_g value at about -90°C and one weak T_g at about 105°C , which are assigned to the glass transition temperature of the blocks PB (T_{g1}) and PS (T_{g2}), respectively.¹⁵ With an increase of the arm number, the T_{g1} shift to lower temperature that is S8D exhibits more flexibility than others. Interestingly, all the star-shaped SBS samples show lower glass transition temperature than 1401. This can be explained that the branching of the polymer leads to the decrease of the glass-transition tem-

TABLE II
Experimental Results from Mechanical Properties, DSC, and DMTA for the SBS Samples

Samples	σ_b (MPa)	ϵ_b (%)	T_{g1} ($^\circ\text{C}$)	$T_{\alpha 1}$ ($^\circ\text{C}$)
S2D	1.7 ± 0.2	685 ± 8	-89.2	-86.1
S4D	3.0 ± 0.2	782 ± 9	-97.1	-90.2
S6D	3.6 ± 0.1	1113 ± 8	-105.1	-102.6
S8D	6.0 ± 0.2	1260 ± 10	-108.2	-105.6
1401	14.1 ± 0.2	680 ± 10	-88.5	-80.3

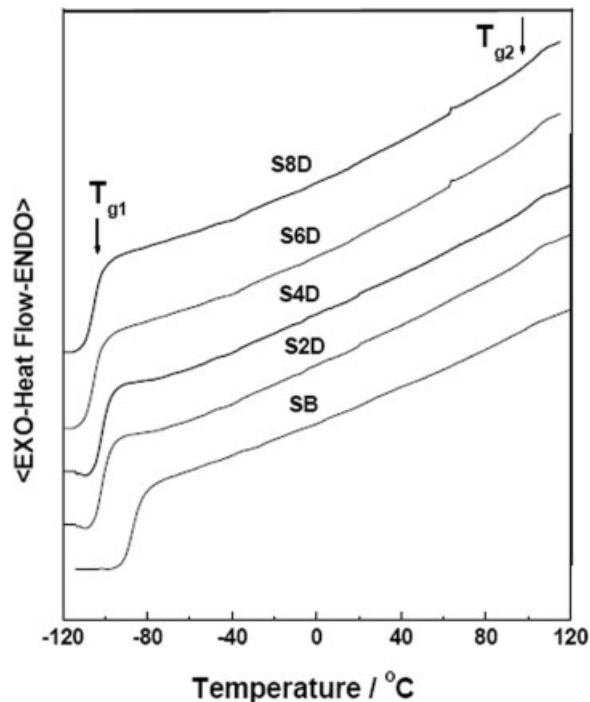


Figure 6 DSC curves of the samples.

perature as a result of the inner plasticization of the branched chains. The result supports the conclusion from the mechanical properties that is with an increase of the arm number of the star SBS the free volume in the material enhances, leading to the high elasticity of the SBS material having six arms.

Figure 7 shows temperature dependence of mechanical loss factor ($\tan \delta$) of the SBS sheets, and the peak positions of $\tan \delta$ are summarized in Table II. Generally, the $\tan \delta$ peak represents α transition, which reflects the glass transition, and may be analyzed to

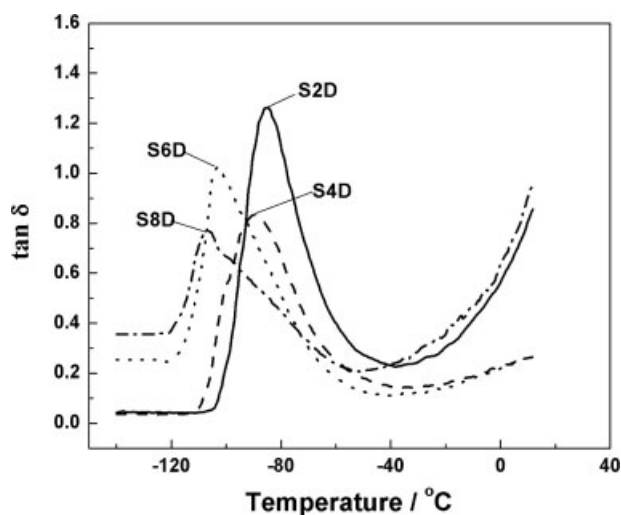


Figure 7 DMTA curves of the sheets.

provide qualitative insight into the inner structure of material.⁴¹ Similar to the results of DSC, there is one obvious α -relaxation peak at about -90°C , namely $T_{\alpha 1}$. However, $T_{\alpha 2}$ for the samples can hardly be determined, because the sheets are almost melted and the stiffness of the specimens is not enough to measure at high temperature.⁴² The results from DMTA indicated that with an increase of arm number, the $\tan \delta$ peaks of PB blocks of all the star copolymers shift toward low temperature. In this case, $T_{\alpha 1}$, corresponding to $\alpha 1$ transition, shifts from -86.1 to -105.6°C with an increase of the arm number, and this is in good agreement with the DSC results. Generally, the intensity of $\tan \delta$ peak is relative to the drop of the elastic tensile modulus,⁴³ and the freedom of the molecular motion can be reflected by the sharpness and the height of the $\tan \delta$ peak.⁴⁴ The results from DMTA indicate that the height of the $\tan \delta$ peak decreases with an increase of the arm number. This is ascribed to the decrease of the molecular segments number that is responsible for damping properties,⁴³ leading to the increase of the freedom of the molecular motion as a result of the high branching. It is well known that the lowest lasting temperature of the elastomers has much to do with their T_g .⁴⁵ In view of the aforementioned results, the elastomer can be improved by designing their molecular architecture. In this case, elasticity at low temperature of the star-shaped SBS materials has been improved by increasing their arm number.

Photograph of water drop deposited on the SBS film surface is shown in Figure 8. It illustrates that the water has a significantly lower affinity for the surface of star-shaped SBS film than that of the arm precursor SB film. Dependence of contact angle for water/SBS film interface on the arm number is shown in Figure 9. With an increase of arm number from one to six, the values of the contact angles increase from 79.1 to 92.9. Usually, a bigger contact angle indicates a more hydrophobic surface⁴⁶ that is its total surface energy is decreased. This can be explained that the star-shaped SBS exists as dense sphere chain in the solution to contribute strong intermolecular interaction, leading to the smooth surface of the solution-cast film. With an increase of arm number, the film surface becomes

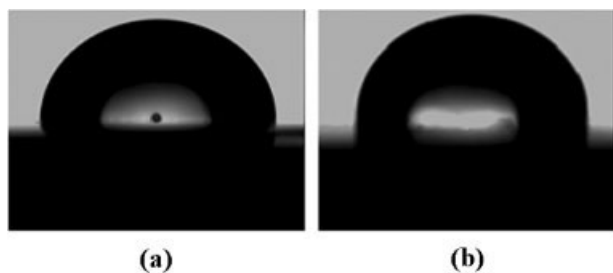


Figure 8 Photographs of a water drop on the arm precursor SB film (a) and four-arm SBS film (b) surface.

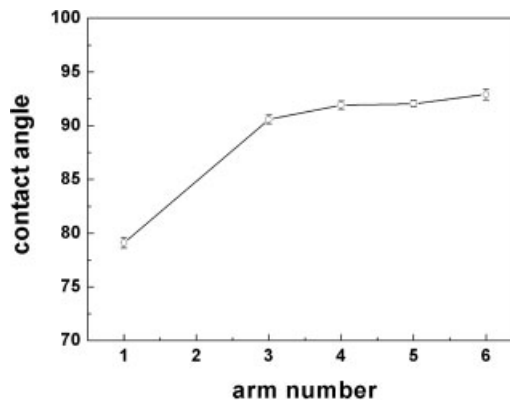


Figure 9 Dependence of contact angle for water/SBS film interface on the arm number.

more and more hydrophobic as a result of the increase of the contact angle values. The contact angle of the diblock SB film is the smallest among all the SBS films, which shows that the inner and surfacial structure of the film is not compact enough to resist the wetting of the water droplet. The results also reveal that the construction of star-shaped structure offers a direct and novel strategy without further surface modification to obtain low surface energy polymer system with tailored surface properties.

CONCLUSIONS

A series of star-shaped SBS having various arm number have been synthesized by living anionic polymerization using DVB as linking agent. With an increase of the arm number of the star-shaped SBS, their optical transparency, miscibility, tensile strength, elongation at break, and elasticity at low temperature were significantly enhanced. The SBS material having six arms exhibited the best optical transparency and elasticity. The results revealed that the relatively high arm number and molecular weight played an important role in the simultaneous enhancement of the optical transparency and the mechanical properties of the SBS sheets. Moreover, the SBS film surface becomes more and more hydrophobic with the increase of arm number, leading to the increase of the contact angle values. Therefore, the material with both high transparency and elasticity can be well designed by increasing the arm number and molecular weight.

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