

# Structural Morphology and Properties of Star Styrene–Isoprene–Butadiene Rubber and Natural Rubber/Star Styrene–Butadiene Rubber Blends

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**ABSTRACT:** Star styrene–isoprene–butadiene rubber (SIBR) was synthesized with a new kind of star anionic initiator made from naphthalene lithium and an  $\text{SnCl}_4$  coupled agent. The relationship between the structure and properties of star SIBR was studied. Star block styrene–isoprene–butadiene rubber (SB-SIBR), having low hysteresis, high road-hugging, and excellent mechanical properties, was closer to meeting the overall performance requirements

of ideal tire-tread rubber according to a comparison of the morphology and various properties of SB-SIBR with those of star random SIBR and natural rubber/star styrene–butadiene rubber blends. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 336–341, 2004

**Key words:** blends; morphology; mechanical properties

## INTRODUCTION

The aims of the auto industry are safety, comfort, and energy savings, and the last is becoming more important with the influence of the energy crisis.<sup>1</sup> It has been reported that energy loss in the tire-tread zone accounts for 30–40% of tire total loss,<sup>2</sup> and so it is essential to develop a tread material with low hysteresis and high road-hugging. The rolling resistance and antiskid properties of rubber are contradictory, and so satisfying the aforementioned requirements with the traditional blending method is limited. Accordingly, researchers have started to use molecular design techniques to develop new kinds of rubbers.

In 1984, Nordsiek et al.<sup>3</sup> proposed the integral rubber concept, which provided a theoretical foundation for developing a tread material with an excellent combination of high antiskid properties and low rolling resistance. Their design principle was that the construction units of general-purpose rubbers, such as natural rubber (NR), butadiene rubber (BR), and styrene–butadiene rubber (SBR), were concentrated into a single molecular chain via anionic polymerization, which could both integrate the advantages and avoid the disadvantages of general blends for tire-tread rubbers. Accordingly, styrene–isoprene–butadiene rubber (SIBR) was produced. In recent years, more attention has been focused on SIBR. Among the numerous

research institutes, Goodyear Co. (United States) and Huels Co. (Germany) are the most fruitful.<sup>4–7</sup>

Many research workers have studied the array distribution of the monomers in SIBR to form a triblock copolymer, that is, the styrene–butadiene rubber/polyisoprene/polybutadiene copolymer. Although this copolymer has the synthetic properties of SBR, NR, and BR, its molecular chain is not very long, or the processing of SIBR becomes difficult. Furthermore, an already reported copolymer<sup>6</sup> was made with the general anionic polymerization technique (the catalyst was *n*-butyllithium in the presence of TMEDA polar modifiers), and it had a linear molecular structure. Therefore, it is not obviously deduced that internal friction heat is induced by the random movement of the free ends of SIBR linear molecular chains.

We applied for a patent<sup>8</sup> for a new kind of polymerization initiator, a star anionic initiator with four to six arms made from naphthalene lithium and an  $\text{SnCl}_4$  coupled agent. With synthetic technology, the coupled active nuclei were made first, and monomers were added in one or more steps and polymerized; a copolymer with a star molecular structure (with 100% coupling) was formed. This star copolymer had the lowest number of free molecular chain ends and the lowest internal friction loss among the macromolecules.

In this study, two kinds of SIBRs were synthesized via anionic polymerization. One was star block styrene–isoprene–butadiene rubber (SB-SIBR), consisting of an isoprene homopolymer block and a styrene–butadiene random copolymer block with a star coupled molecular structure. The other was star random styrene–isoprene–butadiene rubber (SR-SIBR) which was made from three kinds of monomers (styrene,

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TABLE I  
Sample Structures and Compositions

	SB-SIBR		SR-SIBR			NR/S-SBR
	B <sub>1</sub>	B <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	
St/Ip/Bd (%)	15/40/	20/40/	25/35/	20/40/	15/40/	—
1,2-PB/PB (%)	45	40	40	40	45	—
3,4-PI/PI (%)	28.9	27.0	—	—	—	—
St (%)	30.0	30.8	—	—	—	—
Ethylene/Bd (%)	14.9	15.0	24.3	20.0	15.0	—
M <sub>n</sub>	—	—	25.3	21.8	18	—
NR/S-SBR	200,000	246,000	174,000	181,000	170,000	—
	—	—	—	—	—	40/60
Composition	Rubber		100	Homogenizing Agent		3.0
	Sulfur		1.8	Accelerator, (CZ/TT)		1/0.2
	Zinc Oxide		4.0	Stearic Acid		2.0
	Carbon Black <sub>1</sub> (N234)		50	Antiager (RD/4010NA)		1.0/1.0
	Solid Wax		1.0	Liquid coumarone		5.0

St = styrene; Ip = soprene; Bd = butadiene; CZ = *N*-cyclohexyl-2-benzothiazole sulphenamide; TT = tetramethyl thiuram disulfide; RD = olymeried 2,2,4-trimethyl-1,2-dihydroquinoline (resin); 4010NA = *N*-Isopropyl-*N'*-phenyl-*p*-phenylene di-anime.

isoprene, and butadiene) fed into a polymerization apparatus simultaneously in certain proportions to form a random copolymer with a star coupled molecular structure. For contrast, a natural rubber/star styrene-butadiene rubber (NR/S-SBR) blend was made in our laboratory.

The structural morphology and properties of SB-SIBR, SR-SIBR, and NR/S-SBR blends were studied to explore the outstanding features of SIBR and to provide a theoretical basis for the molecular design of SIBR in the future.

## EXPERIMENTAL

### Materials and compositions

SB-SIBR and star random styrene-butadiene rubber (SR-SBR) samples were synthesized in our laboratory. NR 1 was produced by Hainan Rubber Industry Co., Ltd. (China). S-SBR 2305 was synthesized by Yanshan Petrochemical Industry Co., Ltd. (China). Carbon black N234 was produced by Tianjin Haitun Carbon Black Co., Ltd. (China). The homogenizing agent was produced in our laboratory. Other common additives were produced in China.

The structural information and compositions for six samples are listed in Table I.

### Processing techniques and property testing

#### Mixing procedures

The compounds were mixed in conventional cycles with a laboratory two-roll mill, except that carbon black N234 was added to the rubber before stearic acid.

#### Curing procedures

All the physicomechanical test specimens were cured at 145°C for 20 min.

#### Testing methods and conditions

The physicomechanical properties of the samples were measured according to the state standards in China (e.g., GB/T 531-92 for Shore A hardness, GB/T 528-98 for tensile strength and elongation, GB 1681-82 for rebound, GB 530-81 for tear strength, and GB/T 1689-98 for Akron wear loss). For each compound, five specimens were tested, and the average results were reported.

For transmission electron microscopy (TEM) studies, small, thin pieces of SR-SBR, SB-SIBR, and NR/S-SBR blends were made by the microtome cutting of the vulcanizates frozen with liquid N<sub>2</sub> and stained with OsO<sub>4</sub>. OsO<sub>4</sub> preferentially stained isoprene microdomains, leading to enhanced electron scattering contrast between the isoprene homopolymer block and styrene-butadiene random copolymer block, or NR and SBR. The TEM images were obtained at 100 kV with an H-800-1 TEM instrument made by Hitachi Co., Ltd. (Japan) at magnifications of 5000× and 8000×.

Scanning electron microscopy (SEM) photographs of the wear surfaces were obtained with an S-2501 SEM instrument made by Combridge Co., Ltd. (Britain) at an acceleration voltage of 1.5 kV for samples coated with Au.

The measurements of the dynamic mechanical properties were carried out on a DDV-11-EA dynamic viscoelastometer working in the tensile mode. The

TABLE II  
Physicomechanical Properties of SIBR and NR/S-SBR Vulcanizates

	SB-SIBR		SR-SIBR			NR/S-SBR
	B <sub>1</sub>	B <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	
Shore A Hardness	70	72	67	70	64	70
300% Modulus (MPa)	15.9	16.1	9.5	13.6	12.2	14.1
Tensile Strength (MPa)	21.6	23.1	21.5	19.4	17.1	21.2
Elongation (%)	396	408	500	456	388	452
Set (%)	8	8	8	8	8	16
Tear Strength (KN/M)	41	42	41	39	33	42
Rebound (%)	35	36	20	35	37	39
Temperature rise at dynamic compression (°C)	19	19	18	20	16	26

dynamic storage modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) were determined. The temperature was  $-100$  to  $100^\circ\text{C}$ , the frequency was 11 Hz, the heating rate was  $3^\circ\text{C}/\text{min}$ , and the deformation amplitude was 0.5%.

The temperature rise in the compression fatigue was determined with an YS-25 compression fatigue tester made in China (GB/T1687-93). The preheating time was 20 min, the compression time was 20 min, room temperature was  $50^\circ\text{C}$ , the compression frequency was 30 Hz, the stroke was 6 mm, and the load was 1.01 MPa.

## RESULTS AND DISCUSSION

### Physicomechanical properties

The physicomechanical properties of six vulcanizates are shown in Table II. The styrene content and the number-average molecular weight ( $M_n$ ) of B<sub>2</sub> are greater than those of B<sub>1</sub>, and the butadiene content of B<sub>2</sub> is lower than that of B<sub>1</sub>. As the content of styrene

increases, the tensile strength, break elongation, and 300% modulus of star block styrene–butadiene rubber (SB-SBR) increase, and the tear strength and rebound of SB-SBR hardly change. The mechanical properties of B<sub>2</sub> show higher levels. As the contents of styrene and ethylene increase, the tensile strength, break elongation, tear strength, and rise in temperature at dynamic compression of SR-SBR increase, and the rebound of SR-SBR decreases.

There are no obvious differences in the physicomechanical properties of B<sub>1</sub>, B<sub>2</sub>, R<sub>1</sub>, R<sub>2</sub>, and the NR/S-SBR blend, but the rise in temperature at dynamic compression for the NR/S-SBR blend is much higher than that for the star SIBR samples. Therefore, one of the advantages of star SIBR is low hysteresis.

### Morphological structure

Figure 1 shows TEM photomicrographs of raw SB-SIBR (B<sub>2</sub>), SR-SIBR (R<sub>2</sub>), and NR/S-SBR blends (no other additives except for the homogenizing agent).

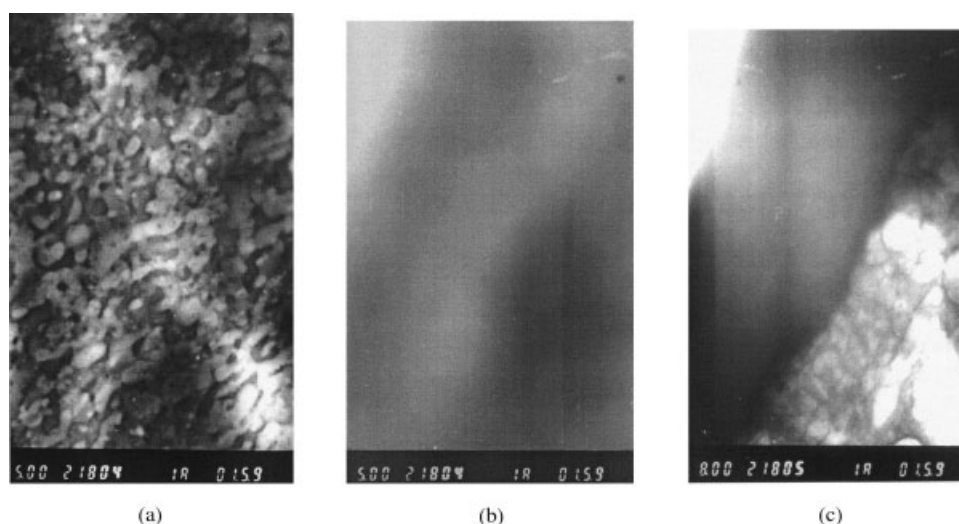


Figure 1 TEM photomicrographs of (a) SB-SIBR (original magnification =  $5000\times$ ), (b) SR-SIBR (original magnification =  $5000\times$ ), and (c) NR/S-SBR blends (original magnification =  $8000\times$ ).



**TABLE III**  
**Wear Loss of Three Vulcanizates**

Wear loss, (cm <sup>3</sup> /1.61/km)	Vulcanizate		
	B (SB-SIBR)	R (SR-SIBR)	NR/S-SBR
	0.167	0.206	0.197

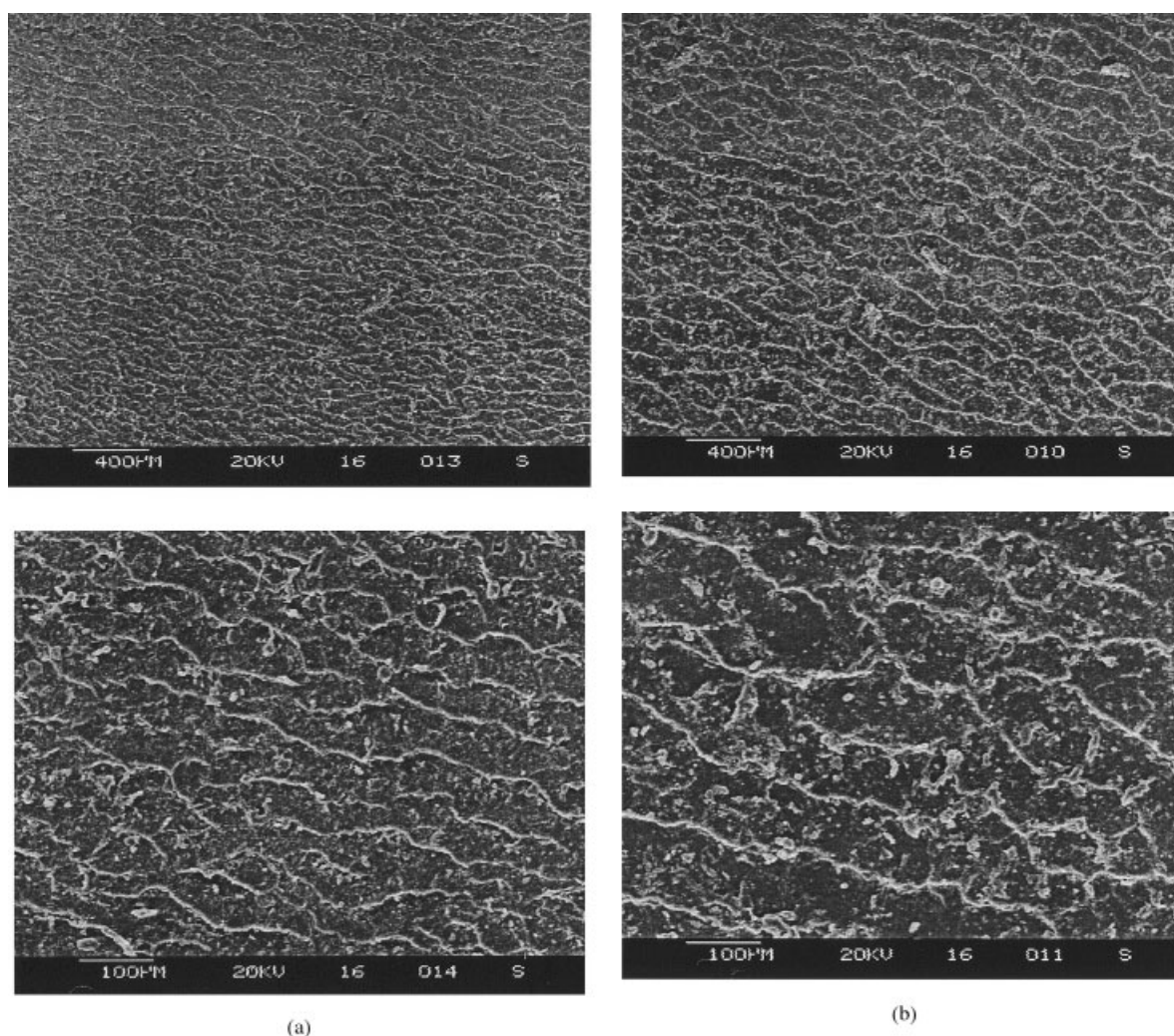
As shown in Figure 1(a), SB-SIBR forms a two-phase interlock phase structure that consists of a polyisoprene block and a styrene-butadiene random copolymer block (SBR). The size of the polyisoprene block phase is about 400–500 nm, and the interfacial layer is not obvious. The morphology of SR-SIBR is characteristic of the homopolymer [Fig. 1(b)]. Even after NR/S-SBR has been blended in a homogenizing agent for a long time, Figure 1(c) shows that the phase of NR in the NR/S-SBR blend is much bigger, and its interfacial layer is more distinct, with respect to SB-SIBR. Accordingly, a reasonable copolymerization composition and

a certain block array profile can contribute macrohomogeneity and microheterogeneity to the copolymer, whereas the mechanical blending is beyond comparison.

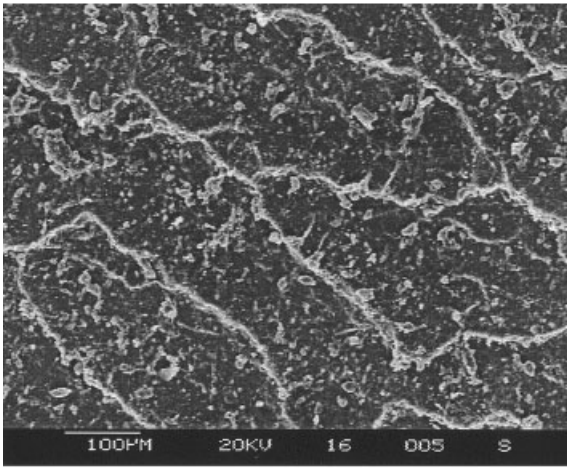
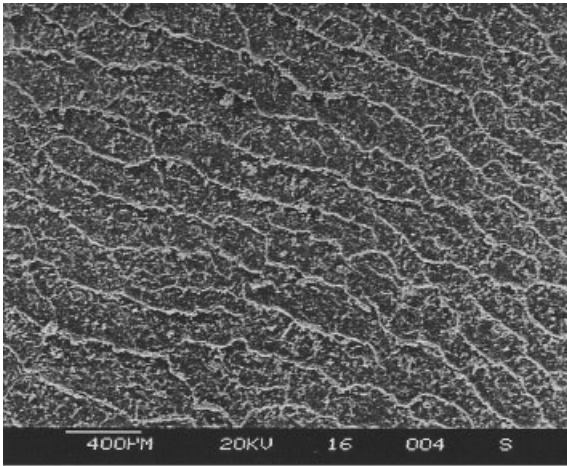
#### Wear loss and morphology of the wear surface

The Aklon abrasion loss of three vulcanizates (B<sub>2</sub>, R<sub>2</sub>, and NR/S-SBR) are given in Table III. The wear volume of SB-SIBR is the smallest, and this indicates that its resistance to wear is superior to that of the other two rubbers.

Figure 2 shows that the morphology of the wear surfaces of the three vulcanizates is characterized by abrasion patterns.<sup>9,10</sup> The wear streak lines of the NR/S-SBR blend are relatively thick and sparse, those of SB-SIBR are thin and dense, and those of SR-SIBR are between the lines of the former two rubbers. This is because NR does not have good heat resistance, and its abrasion mechanism rolls up wear. The phase size



**Figure 2** SEM photomicrographs of the wear surfaces of three vulcanizates: (a) SB-SIBR, (b) SR-SIBR, and (c) NR/S-SBR.



(c)

Figure 2 (Continued from the previous page)

of NR in the NR/S-SBR blend is bigger, and the link force in the boundary between NR and S-SBR is weaker. Therefore, with respect to abrasion, the NR/S-SBR blend behaves like NR. For SB-SIBR, the homogeneous phase structure and strong link force in the boundary between the polyisoprene and SBR phase make the SB-SIBR stock transfer of the stress to the road surface more even, and this results in SB-SIBR with good abrasion resistance. SR-SBR does not behave like NR or SBR and is a new kind of copolymer.

#### Dynamic viscoelasticity

Figure 3 shows  $E'$  and  $E''$  as functions of temperature for three kinds of vulcanizates.  $E'$  of  $B_2$  in the glass state is higher than that of  $R_2$  and the NR/S-SBR compound because the macromolecules of  $B_2$  with the block copolymer and coupled structure pile up closely together and the free volume among the macromolecules is smaller; therefore, the force needed for  $B_2$  to deform is greater. Although  $R_2$  also has a coupled

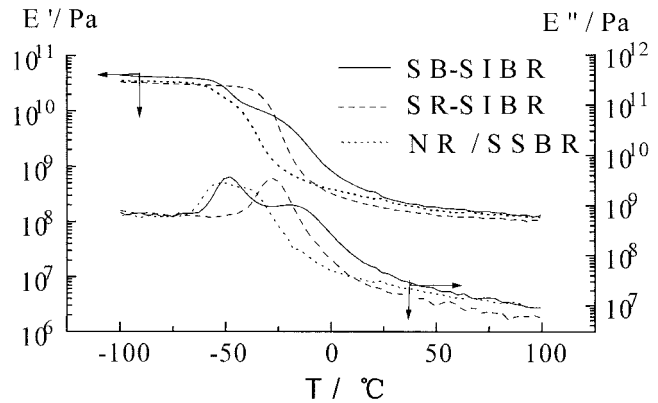


Figure 3  $E'$ -temperature ( $T$ )- $E''$  curves of three vulcanizates.

structure, the random array distribution of the monomer makes the macromolecules pile up not closely; the free volume is larger, and  $E'$  of  $R_2$  is smaller. The action force of the boundary between NR and S-SBR for the NR/S-SBR blend is weaker, and the movement of molecular chains is easy, so  $E'$  of the NR/S-SBR blend is also smaller.

$E'$  of  $B_2$  and  $R_2$  samples is higher than that of the NR/S-SBR blend in the glass-transition zone because the macromolecular chain ends of the two kinds of SIBRs are fixed by the  $\text{SnCl}_4$  coupler, and so the end effect makes the macromolecules relax with difficulty.

It is generally accepted that rubber used in tire tread must have high abrasion resistance, good antiskid properties under wet conditions, and low rolling resistance. Satio<sup>2</sup> found that a high  $\tan \delta$  value in the region of  $-20$  to  $10^\circ\text{C}$  was desirable for a tire tread, providing a tire with good wet traction, and a low  $\tan \delta$  value in the region of  $50$ – $60^\circ\text{C}$  was desirable for a tire tread, providing a tire with low rolling resistance.

Figure 4 shows  $\tan \delta$  as a function of temperature for three vulcanizates. In the test temperature range, the  $\tan \delta$  curve of SB-SIBR shows two loss peaks,

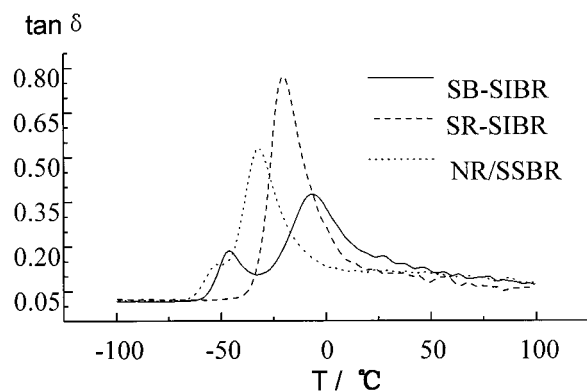


Figure 4  $\tan \delta$ -temperature ( $T$ ) curves of three vulcanizates.

representing the glass-transition processes of the isoprene homopolymer segment and the styrene-butadiene random copolymer segment. The  $\tan \delta$ -temperature curve for the NR/S-SBR blend also shows two loss peaks for NR and S-SBR, and for SR-SIBR, only one glass-transition peak appears. The glass-transition-temperature ranges of B<sub>2</sub>, R<sub>2</sub>, and the NR/S-SBR blend are  $-60$  to  $10^\circ\text{C}$ ,  $-30$  to  $0^\circ\text{C}$ , and  $-65$  to  $0^\circ\text{C}$ , respectively. This shows that SB-SIBR has a higher  $\tan \delta$  value in the  $-10$  to  $10^\circ\text{C}$  range, and this predicts a tread with better antiskid properties than the other two rubbers have. At  $60^\circ\text{C}$ , the  $\tan \delta$  values of the two kinds of SIBRs are lower, and this implies a small rolling resistance. In summary, SB-SIBR has a good balance between antiskid properties and low rolling resistance and might be used for ideal tire-tread rubbers.

### CONCLUSIONS

Two kinds of star SIBRs (SR-SBR and SB-SBR) have been synthesized successfully with a new kind of star anionic initiator invented by us. In comparison with SR-SBR, SB-SBR with 20% styrene, 27% 1,2-polybutadiene/polybutadiene, and 30% 3,4-polyisoprene/

polyisoprene has good antiskid properties, resistance to wear loss, resistance to low temperatures, and excellent mechanical properties. In comparison with the NR/S-SBR blend, SB-SIBR(B<sub>2</sub>) has macrohomogeneity, microheterogeneity, and a smaller phase size, and it shows low hysteresis loss, high wet traction, and good mechanical properties. In summary, SB-SIBR satisfies the overall property requirements of high-performance tire-tread rubber, and it is a new kind of integral rubber.

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