

Polar Polystyrene-Isoprene-Styrene Copolymers with Long Polybutadiene Branches

Zhongfu Zhao,^{1,2} Zhanyue Wang,¹ Chunqing Zhang,^{1,2} Yongzhao Wang,¹
Zhansheng Li,^{1,2} Yanming Hu,^{1,2} Xuesong Xiao³

¹Department of Polymer Science and Engineering, Dalian University of Technology, No. 2 Linggong Road, Ganjingzi District, Dalian 116024, China

²State Key Laboratory of Fine Chemicals, Dalian University of Technology, No. 2 Linggong Road, Ganjingzi District, Dalian 116024, China

³Yifang Industry Factory, Liaoyang Petrochemical Company, PetroChina Company Limited, No. 143 Hongwei Road, Hongwei District, Liaoyang, Liaoning Province 111003, China

Correspondence to: C. Q. Zhang (E-mail: zhangcq@dlut.edu.cn) and Z. F. Zhao (E-mail: zfzhao@dlut.edu.cn)

ABSTRACT: Polar polystyrene-isoprene-styrene (SIS) copolymers having epoxide groups and long polybutadiene (PB) branches were synthesized via the combination of *in situ* epoxidation, anionic polymerization and graft-onto reaction. They were characterized with ¹H NMR, GPC, FT-IR, DSC, and contact angle test. Their polarity was determined by the epoxidation degree and graft efficiency. The epoxidation degree linearly increased with the epoxidation time. The graft efficiency decreased with the branch length, but increased with the epoxidation degrees. Although their glass transition temperature (T_g) of diene blocks and flexibility properties had been negatively affected by *in situ* epoxidation, they could be modulated by the epoxidation degree, branch length, and branch density. Their T_g could be tailored by the branch length and branch density since they fitted the Fox equation very well, especially as the longer branches were grafted. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40303.

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INTRODUCTION

As an important family of materials in the category of thermoplastic elastomers, polystyrene-isoprene-styrene (SIS) and polystyrene-butadiene-styrene (SBS) tri-block copolymers are widely used in rubber soles in footwear, asphalt modification, elastic film, soft molded parts, viscosity modification for oils and gels, adhesives,^{1–4} nanostructured thermosetting matrices,^{5–7} nanoparticle filled composites,^{8,9} competitive double-networked copolymers,¹⁰ thermoplastic compounds,¹¹ actuation applications as a kind of electric field-activated electroactive polymers,¹² biomedicines,^{13,14} and membranes due to their microphase-separated structures.^{15,16} The styrene phase provides excellent strength as physical crosslinks and the soft conjugated diene phase exhibits the behaviors of vulcanized rubber at their service temperature by covalently bonding the thermodynamically incompatible styrene phase.^{17,18} SBS has much higher elasticity modulus while the side methyl of isoprene provides excellent cohesive strength and adhesive property to SIS copolymers.^{19–21} They are synthesized through anionic polymerization so that it is hard to directly insert polar monomers in their molecular chains, which limits their applications.

To increase their compatibility with polar materials, various strategies are used to introduce polar functional groups in both the styrene and diene blocks, including graft, sulfonation, plasma, and epoxidation treatments.^{6,7,15,22–26} Among these methods, the epoxidation procedures are utilized to incorporate epoxide groups into the diene blocks of the copolymers, in which some oxidants, such as metal catalyzed/hydrogen peroxide, dimethyldioxirane, meta-chloroperbenzoic acid and *in situ* peracetic acid, have been adopted.^{6,27–29} To synthesize templates for nanostructured thermosets, metal catalyzed/hydrogen peroxide, dimethyldioxirane and meta-chloroperbenzoic acid have been utilized to epoxidize SIS or SBS copolymers with high epoxidation degrees (>60 mol %).^{6,7,28,30,31} Comparatively, the *in situ* peracetic acid is preferred to epoxidize polybutadienes, styrene-butadiene rubber, SBS, natural rubber and SIS due to its environment-friendly feature, stability, and easy manipulation.^{25,32–38}

However, their glass transition temperature (T_g) of the diene phase increases with the epoxidation degree and their flexibility at their service temperature sacrifices to some extent.^{7,37–39} This kind of situation becomes even worse for SIS copolymers since

they have much higher glass transition temperature (-50 to -60°C) than SBS copolymers ($< -80^\circ\text{C}$). The further increment of their T_g would greatly limit their application in low temperature surroundings, especially in the field of SIS-based hot melt pressure sensitive adhesives.

Long chain branches (LCBs) are of great interest in both academic and industrial relevance over the past few decades since the presence of LCBs yields a significant improvement on polymer viscoelastic properties and processing behavior without compromising mechanical properties.^{40–43} Their advantages activate numerous investigations of different polymers with LCBs. For example, several approaches have been developed to synthesize LCBs grafted polypropylene with high melt strength and strain hardening, such as melt radical grafting, electron beam irradiation, and copolymerization with macromonomers.^{44–49} Yamazaki and co-workers synthesized a poly (butyl acrylate) elastomer via copolymerization, which contained considerable amounts of branches with uniform lengths and exhibited noticeable viscoelastic relaxation.⁵⁰ Castillo et al. prepared a well-defined poly (lactic acid) containing poly (ethylene glycol) branches for application in cytology.⁵¹ The LCBs are responsible for the observed strong melt strength and a dramatic improvement of shear thinning and zero shear viscosity at a low level of LCBs when compared with linear polymers.^{52,53} As the branch length and branch density increase, a linear increase in mechanical properties of tensile strength, strain, and elongation at break was obtained.⁵⁴

In this article, long PB branches grafted SIS copolymers (SIS-*g*-PB) have been synthesized via the combination of *in situ* epoxidation, anionic polymerization and graft-onto reaction. The *in situ* epoxidation provides active sites to the grafting reaction and the excessive epoxide groups can enhance the polarity of SIS-*g*-PB copolymers. Furthermore, the long PB branches not only can significantly improve polymer properties, but also can compensate the flexibility loss and significantly lower the T_g of diene blocks according to the Fox equation since the long PB branches, having a much lower glass transition temperature than polyisoprene (PI), are mixed with SIS copolymers at a molecule level. Besides, *cis*-1,4-PB chains have a much smaller entanglement molecular weight (1.7 kg/mol) than PI chains (7.0 kg/mol).⁴ Thus, the long PB branches were utilized to modulate the molecular structures and properties of SIS copolymers.

EXPERIMENTAL

Materials

SIS tri-block copolymer (YH-1209, $M_n \sim 9 \times 10^4$ kg/mol diblock <1%, styrene 29 wt %) was obtained from the Sinopec Baling Petroleum and Chemical Co., Toluene (AR grade) and formic acid (AR grade, 88 vol %) were purchased from Tianjin Fuyu Fine Chemical Co. Hydrogen peroxide (AR grade, 30 vol %) and tetrahydrofuran (AR grade) was obtained from Guangdong Xilong Chemical Co. *n*-BuLi (from J&K Scientific) was analyzed by the double-titration method with 1,2-dibromoethane. Cyclohexane was refluxed over calcium hydride and distilled under argon atmosphere. 1,3-butadiene (from Jinzhou Petrochemical Corp.) were purified with a small amount of *n*-BuLi and then vaporized to use.

Synthesis of SIS-*g*-PB Copolymers

First, SIS copolymer was treated via *in situ* epoxidation. Typically, SIS (5 g) was dissolved in toluene (95 g) in a 250 mL three-necked round-bottom flask with an electric stirrer. After being cooled to 4°C , the solution was mixed with 3 g formic acid for 10 min. After 5.5 g hydrogen peroxide was added dropwise into the solution, the reaction was conducted for different time. The epoxidized SIS (ESIS) was precipitated in an excess of 95% ethanol and washed with distilled water until neutral. The product was dried in a vacuum at 30°C for 48 h prior to preparing 5 wt % ESIS solution in cyclohexane. Secondly, given amounts of butadiene and cyclohexane were transferred into a 300 mL glass reactor through stainless steel capillaries. After being initiated by a stoichiometric amount (according to a designed molecular weight of PB LCBs) of *n*-BuLi, the polymerization was continued to synthesize living PB lithium macroanions at 50°C for 4 h. Thirdly, the reactor was injected with 5 wt % ESIS solution and stirred at 50°C for 8 h. The mole ratio of PB lithium macroanions to epoxide groups was set as 4:5. The graft reaction was terminated by a small amount of degassed ethanol and the product was precipitated by an excess amount of ethanol. Finally, ethanol and tetrahydrofuran were utilized to carefully remove the unreacted PB homopolymer.⁵⁵

Characterization

^1H NMR spectrum was recorded on a Varian INOVA 400 MHz spectrometer in CDCl_3 at ambient temperature. The number molecular weight (M_n), molecular weight distribution (PDI), and intrinsic viscosity were measured by gel permeation chromatograph (GPC). The chromatographic system consisted of a Viscotek TDA-302 (Viscotek), equipped with tetra detectors [refractive index (RI), UV, viscosity (VISC), and two-angle laser light scattering]. THF was used as eluent at a flow rate of 1.0 mL/min at 30°C , and polystyrene standards were used to calibrate the instrument. Their T_g was measured by differential scanning calorimetry (NETZSCH DSC 204 instrument, Germany). All the samples of 10.0 ± 0.1 mg were prepared in an aluminum pan. These samples were first scanned from room temperature to 150°C , kept for 5 min. Then, they were cooled to -120°C with a cooling rate of $10^\circ\text{C}/\text{min}$ in N_2 stream and kept for 5 min. Finally, they were reheated to 150°C with a heating rate of $10^\circ\text{C}/\text{min}$. Fourier transform infrared spectroscopy (FT-IR) was utilized to characterize specimens with a Bruker Vertex-70 FT-IR spectrometer by a solution-film casting method. The film with the thickness of 1–3 μm was prepared by casting the specimen solution (in chloroform) on to the KBr disc. JY-85 contact angle tester was utilized to characterize the polarity of SIS or ESIS copolymers. SIS or ESIS copolymers were dissolved in cyclohexane to form solution with a concentration of 10 mg/mL. The solutions were dropped on to fresh mica substrate to obtain thin films. They were dried in vacuum oven overnight before their contact angles were measured with distilled water.

RESULTS AND DISCUSSION

Epoxidation of SIS Copolymer

As described in experimental section, a series of ESIS was synthesized by *in situ* epoxidation. They are named of ESIS-*x* and *x*

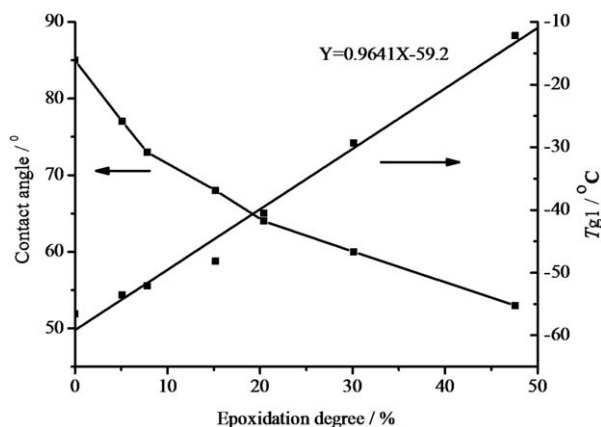


Figure 1. Dependence of T_g and contact angle on the epoxidation degree of various ESIS.

denotes their epoxidation degree. Their epoxidation degree is defined as the percentage of epoxidized double bonds occupied all PI double bonds of the parent SIS copolymer and calculated by

$$\text{Epoxidation Degree} = \frac{A(2.69)}{A(2.69) + A(5.12) + 0.5A(4.75) + 0.5A(4.67)} \times 100\% \quad (1)$$

where $A(i)$ is the integral area of the peak at i ppm in the $^1\text{H-NMR}$ spectra. Theoretically, their maximum epoxidation degree equals to the content of 1,4-isoprene units ($\sim 87.6\%$ in the case of YH-1209).

Different epoxidation time (2, 3, 5, 8, 12, and 20 h) is used to prepare ESIS-5.1, ESIS-7.8, ESIS-15.2, ESIS-20.4, ESIS-30.1, and ESIS-47.6, respectively. Their polarity, characterized by their contact angle, is described together with their T_g in Figure 1. Prior to modification, SIS copolymers' contact angle is 85° due to their apolar feature. As the epoxide groups are incorporated into their isoprene units, their contact angle evidently decreases with the epoxidation degree. In the case of ESIS-47.6, the contact angle can be lowered to 53° . Meanwhile, their T_g increases linearly with the epoxidation degree, as shown in Figure 1. The T_g of SIS copolymers' PI phase locates at about -56.6°C . By comparison, ESIS-47.6 has its T_g increased to about -12.2°C . Such great increment of T_g will damage their flexibility performance to some extent and affect their application at service temperature. Furthermore, high epoxidation degree is accompanied by low epoxidation efficiency and gel formation in the following grafting reaction. Thus, ESIS-5.1, ESIS-7.8, and ESIS-15.2 are utilized to synthesize SIS-g-PB copolymers due to their moderate epoxidation degree.

The molecular structures of these ESIS copolymers have been varied as shown in Figure 2. Parent SIS copolymer has obvious peaks at 5.12, 4.67–4.75 ppm in the $^1\text{H-NMR}$ spectrum, which are ascribed to olefinic protons of 1,4-isoprene (87.6%) and 3,4-isoprene (12.4%) units, respectively. After being epoxidized, there appears a new peak at 2.69 ppm, assigned to the methane protons attached to epoxide groups. As the epoxidation reaction time is prolonged, the intensity of the new peak increases while the peaks of 1,4-isoprene units are weakened. The peaks of

3,4-isoprene are not influenced. The FT-IR results also (Table I) shows that the content of 3,4-isoprene units is constant for these ESIS copolymers. Clearly, the epoxidation reaction mainly occurs at the 1,4-isoprene units. These samples were further characterized with GPC (Table II). It is found that the M_n of SIS5.1, SIS7.8, and SIS15.2 slightly increases due to the introduction of epoxide groups.

Synthesis of Living PB Lithium Macroanions

Because 1,4-olefinic units have lower glass transition temperature and better elasticity than 1,2-olefinic units in polybutadiene chains, cyclohexane is used as solvent without polar additives to synthesize living PB lithium macroanions with high content of 1,4-butadiene units. It is well-known that the properties of grafted polymers are markedly affected only if the molecular weight of branch chains is well above their critical molecular weight for entanglements. It has been reported that 1.7 kg/mol is the critical molecular weight for entanglements of polybutadiene.⁴ Thus, 1.0, 2.5, and 5.0 kg/mol are designed as the M_n of PB lithium macroanions, corresponding to unentangled, marginally entangled and entangled branch chains, respectively. Their measured M_n is 1.1, 2.4, and 4.9 kg/mol, respectively. However, their PDI becomes much higher due to their lower molecular weight. These PB lithium macroanions are named of PBy and γ denotes their measured M_n (Table I).

These PB lithium macroanions are further characterized with FT-IR and DSC (Table I). They obtain high content of 1,4-butadiene units (about 91%, *cis*-1,4-butadiene nearly 50%) in non-polar cyclohexane solvent. The content of *cis*-1,4 units is close to the commercial SBS (YH-796, *cis*-1,4-BD 52%, styrene 20 wt %, Sinopec Baling Petroleum and Chemical Co.), in which the *cis*-1,4 units provide excellent elasticity. Although their microstructures are independent of the molecular weight, their T_g increases with the molecular weight (Figure 3). The T_g of PB1.1, PB2.4 and PB4.9 are -104.3 , -100.5 and -98.8°C , respectively.

Synthesis of SIS-g-PB Copolymers

As described in the experimental section, SISx-g-PBy copolymers are successfully synthesized by grafting PB lithium macroanions onto the molecular backbones of ESISx. SIS7.8-g-PB2.4

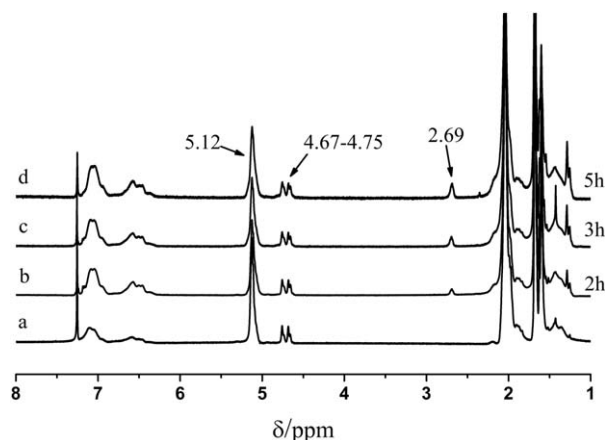


Figure 2. $^1\text{H-NMR}$ spectra of (a) SIS, (b) SIS5.1, (c) SIS7.8, and (d) SIS15.2.

Table I. Molecular Microstructures and T_g of SIS, ESIS, and PBLMs

Sample ID	M_n^a (kg/mol)	1,4- <i>ip</i> ^b (%)	3,4- <i>ip</i> ^b (%)	<i>cis</i> -1,4-Bd ^b (%)	<i>Trans</i> -1,4-Bd ^b (%)	T_g^c (°C)	PDI ^a
SIS	90.0	87.6	12.4			-56.6	1.06
SIS5.1	90.8	82.5	12.4			-53.6	1.06
SIS7.8	91.2	79.8	12.4			-52.1	1.06
SIS15.2	92.3	72.4	12.4			-48.2	1.06
PB1.1	1.1			48.5	42.8	-104.3	1.21
PB2.4	2.4			47.9	42.7	-100.5	1.19
PB4.9	4.9			48.3	42.4	-98.8	1.19

^a Measured by GPC with tetra detectors.^b Calculated by FT-IR.⁵⁶^c Determined by DSC.

is taken as an example. As shown in Figure 4, the mixture of PB2.4 and SIS7.8-*g*-PB2.4 has two peaks in their GPC trace [Figure 4(b)]. These two peaks overlap with the peak of PB2.4 [Figure 4(a)] and the peak of SIS7.8-*g*-PB2.4 [Figure 4(c)], respectively. SIS7.8-*g*-PB2.4 (160 kg/mol) has much higher molecular weight than SIS7.8 (91.2 kg/mol) due to the introduction of PBy. Figure 5 depicts its evolution of molecular structures according to the ¹H-NMR typical resonance peaks of ESIS, PBy, and SIS7.8-*g*-PB2.4. Besides the characteristic peak (2.69 ppm) of epoxide group, ESIS shows peaks at 5.12 and 4.67–4.75 ppm, which are ascribed to olefinic protons of 1,4-isoprene and 3,4-isoprene units, respectively. While PBy branches have sharp peaks at 5.57, 4.91–4.87, and 5.32–5.37 ppm, corresponding to the olefinic protons of 1,2-butadiene units (–CH=), 1,2-butadiene (=CH₂) units and 1,4-butadiene (–CH=CH–) units, respectively. These peaks remain in the ¹H-NMR spectrum of SIS7.8-*g*-PB2.4 except for the characteristic peak (2.69 ppm) of epoxide group. There is a remainder peak at 2.69 ppm since the epoxide groups are partially consumed by the graft-onto reaction.

The same strategy is utilized to graft various PBy branches onto the molecule backbones of SIS5.1, SIS7.8, and SIS15.2. Their microstructures are illuminated with branch lengths, branch

density, and graft efficiency (GE) in Table II. The branch density is defined as the average branch number per 1000 C atoms, where the total C atoms consist of 4 C atoms of 1,4-isoprene units and two atoms of 3,4-isoprene units, calculated according to the molecular structure of SIS. The branch number (N_b) tethered to per SIS molecule is calculated by

$$N_b = \frac{M_g - M_s}{M_b} \quad (2)$$

where M_g , M_s , and M_b are molecular weight of SIS x -*g*-PBy, SIS copolymer and PBy, respectively. The GE is defined as the percentage of epoxide groups consumed by the PBy branches, and calculated by eq. 3. The un-reacted epoxide groups functionalize the SIS x -*g*-PBy copolymers.

$$GE = \frac{N_b}{71M_s \cdot ED/68} \times 100\% \quad (3)$$

When compared with SIS copolymer, SIS5.1-*g*-PBy copolymers have higher molecule weight due to the introduction of the branch chains. Table II shows that their molecular weight increases in an order of SIS5.1-*g*-PB1.1, SIS5.1-*g*-PB2.4, and SIS5.1-*g*-PB4.9. As the branch length is prolonged, their molecular weight increases but their GE and branch density decrease. A similar trend takes place for SIS7.8-*g*-PBy copolymers. When

Table II. Characterization of SIS x -*g*-PBy Copolymers

Sample ID	M_n^a (kg/mol)	Bd ^a (wt %)	PS ^b (wt %)	GE (%)	Branch density	PDI ^a
SIS	90		29.0			1.06
SIS5.1- <i>g</i> -PB1.1	112	19.6	23.3	45.8	6.24	1.07
SIS5.1- <i>g</i> -PB2.4	128	29.7	20.4	31.7	4.25	1.07
SIS5.1- <i>g</i> -PB4.9	155	41.9	16.8	27.1	3.69	1.09
SIS7.8- <i>g</i> -PB1.1	124	27.4	21.1	46.3	9.64	1.07
SIS7.8- <i>g</i> -PB2.4	160	43.7	16.3	38.2	7.94	1.08
SIS7.8- <i>g</i> -PB4.9	224	59.8	11.7	36.6	7.66	1.07
SIS15.2- <i>g</i> -PB1.1	159	43.2	16.5	48.6	19.57	1.07
SIS15.2- <i>g</i> -PB2.4	237	62.1	11.0	41.7	16.73	1.07
SIS15.2- <i>g</i> -PB4.9	357	74.8	7.3	37.4	15.03	1.09

^a Measured by GPC with tetra detectors.^b Calculated by M_n of SIS and SIS x -*g*-Pby.

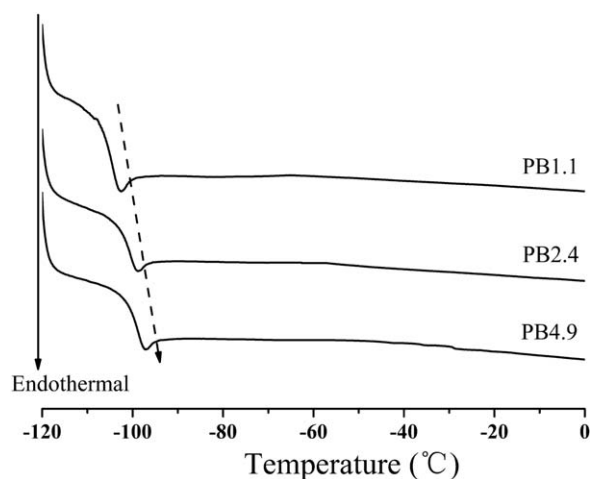


Figure 3. DSC curves of (a) PB1.1, (b) PB2.4, and (c) PB4.9.

compared with SIS5.1-*g*-PBy copolymers, SIS7.8-*g*-PBy copolymers have their molecular weight increased more quickly with the branch length. In the case of SIS15.2-*g*-PBy copolymers, they have much higher molecule weight and branch density than the SIS7.8-*g*-PBy copolymers having a same branch length. As their epoxidation degree of ESIS is constant, their molecular weight increased with the branch length. However, their GE gradually decreases due to the steric effect of the PBy on the graft-on reaction. The longer the branch chains are, the more pronounced the steric effect becomes.

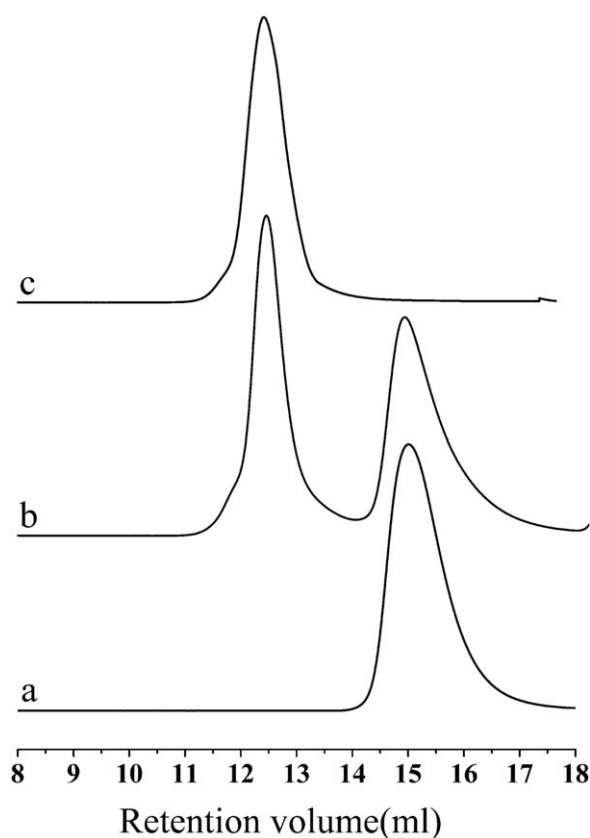


Figure 4. GPC traces of (a) PB2.4, (b) the mixture of PB2.4 and SIS7.8-*g*-PB2.4, (c) SIS7.8-*g*-PB2.4.

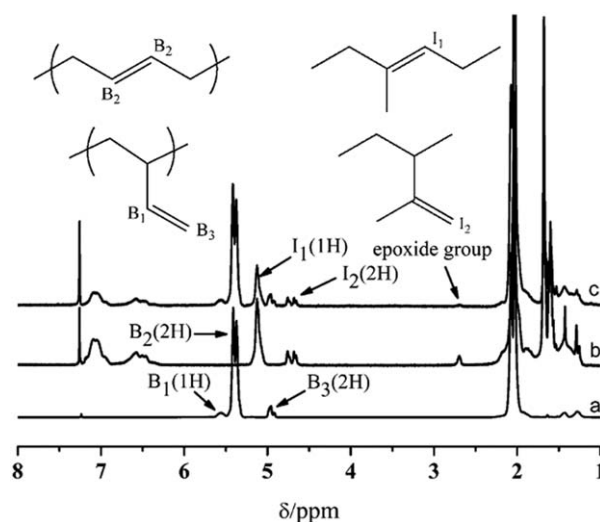


Figure 5. $^1\text{H-NMR}$ spectra of (a) PB2.4, (b) SIS7.8, and (c) SIS7.8-*g*-PB2.4.

Table II also displays that the epoxidation degree of ESIS has great effect on GE, branch density and molecular weight of SIS x -*g*-PBy copolymers. Their GE positively increases with the epoxidation degree for SIS x -*g*-PB1.1, SIS x -*g*-PB2.4, and SIS x -*g*-PB4.9 since the presence of more epoxide groups enhances the reaction probability between SIS and PBy. Therefore, their branch density and molecular weight also increase with the epoxidation degree.

The results indicate that the GE of SIS x -*g*-PBy copolymers increases with the epoxidation degree of ESIS, but decreases with the branch length. Although their GE can be enhanced by controlling these two factors or adding promoters, i.e., BF_3 , N,N,N,N -tetramethylethylenediamine and lithium salts,⁵⁷ higher GE is not required in preparing LCBs grafted copolymers. Higher GE not only reduces functional groups but also leads to hyper-branched SIS x -*g*-PBy copolymers. The latter will greatly lower the volume fraction of styrene phase. If the volume fraction of styrene phase is less than 15 wt %, the physical cross-linking effect of the styrene phase will be damaged. As a result, they will lose their excellent mechanical strength and thermo-reversible property. Thus, the obtained products, such as SIS7.8-*g*-PB4.9, SIS15.2-*g*-PB2.4, and SIS15.2-*g*-PB4.9, cannot work as thermoplastic elastomers.

Tunable Glass Transition of SIS x -*g*-PBy Copolymers

Although the introduction of epoxide groups can increase the T_g of mid-segments of ESIS5.1, ESIS7.8, and ESIS15.2, the SIS x -*g*-PBy copolymers should theoretically have much lower glass transition temperature of diene phase according to the Fox equation since the grafted chains have much lower glass transition temperature, as mentioned in Table I.

DSC is utilized to investigate the effect of the branch chains on the glass transition of the SIS x -*g*-PBy copolymers, as described in Table III. Figure 6 representatively illuminates that the T_g of SIS5.1-*g*-PBy remarkably moves to even lower temperature with the branch length even though their branch density slightly decreases in sequence. Undoubtedly, their T_g is mainly affected by the branch length rather than by the branch density for the SIS5.1-*g*-PBy copolymers. Similar trend takes place for the

Table III. Measurements and Calculations of the Glass Transition of SISx-g-PBy Copolymers

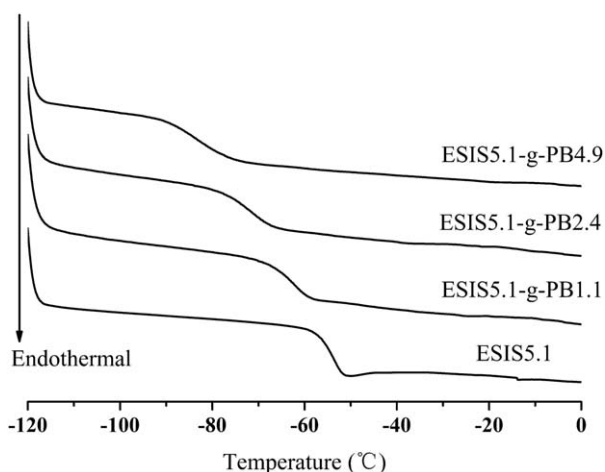
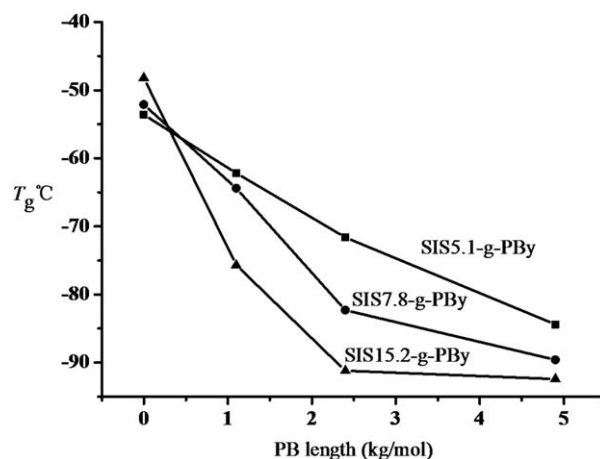
Sample ID	T_g^a (°C)	T_{g1}^b (°C)	Δ_1 (°C)	T_{g2}^c (°C)	Δ_2 (°C)
SIS	-56.6				
SIS5.1-g-PB1.1	-62.2	-68.1	-5.9	-71.2	-9.0
SIS5.1-g-PB2.4	-71.6	-73.8	-2.2	-75.4	-3.8
SIS5.1-g-PB4.9	-84.4	-80.7	+3.7	-80.1	+4.3
SIS7.8-g-PB1.1	-64.4	-68.9	-4.5	-74.9	-10.5
SIS7.8-g-PB2.4	-82.3	-80.3	+2.0	-82.6	-0.3
SIS7.8-g-PB4.9	-89.6	-87.4	+2.2	-87.1	+2.5
SIS15.2-g-PB1.1	-75.7	-81.1	-5.4	-84.2	-8.5
SIS15.2-g-PB2.4	-91.2	-87.6	+3.6	-89.3	+1.9
SIS15.2-g-PB4.9	-92.4	-90.8	+1.6	-91.8	+0.6

^aDetermined by DSC.

^bCalculated with the T_g of ESIS by the Fox equation.

^cCalculated with T_g of SIS by the Fox equation; Δ_1 is the difference between the measured T_g and the T_{g1} ; Δ_2 is the difference between the measured T_g and the T_{g2} .

SIS7.8-g-PBy copolymers and the SIS15.2-g-PBy copolymers, as shown in Figure 7. However, their T_g shifts even faster to low temperature with the branch length than the SIS5.1-g-PBy copolymers. Furthermore, the branch length has different effects due to the variation of their branch density. For SISx-g-PBy copolymers with low branch density, their T_g is evidently affected by the branch length. However, the branch length nearly has no effect on the T_g of the SISx-g-PBy copolymers bearing high branch density. As the branch length is constant, the T_g of SISx-g-PBy copolymers decreases with the branch density. However, this change is also greatly affected by the branch length. The T_g of SISx-g-PB1.1 and SISx-g-PB4.9 decreases with the branch density in a narrow temperature range. However, the branch chains can greatly lower the T_g of SISx-g-PB2.4. Clearly, the T_g of SISx-g-PBy copolymers can decrease with the branch density in a wider temperature range as the branch length approaches its critical molecular weight for entanglements.

**Figure 6.** DSC curves of (a) SIS-5.1, (b) SIS5.1-g-PB1.1, (c) SIS5.1-g-PB2.4, and (d) SIS5.1-g-PB4.9.**Figure 7.** Dependences of T_g on the branch length of the SISx-g-PBy copolymers.

The SISx-g-PBy copolymers consist of PB branches, PS segments and PI segments. The PB branches have the lowest T_g among the three components. They factually act as plasticizers to the rest of the SISx-g-PBy copolymers. Their free dangling ends increase the free volume of the system and subsequently lower the T_g of the SISx-g-PBy copolymers. Their effects can be described by the Fox equation (4–6) due to their mixing at molecular level.

$$\frac{1}{T_g} = \frac{W_a}{T_{g,a}} + \frac{W_b}{T_{g,b}} \quad (4)$$

$$W_a = \frac{71\%M_s}{71\%M_s + (M_g - M_s)} \quad (5)$$

$$W_b = \frac{M_g - M_s}{71\%M_s + (M_g - M_s)} \quad (6)$$

where $T_{g,a}$, $T_{g,b}$, M_g and M_s are the T_g of ESIS, the T_g of PBy, the molecular weight of the SISx-g-PBy copolymers and the molecular weight of ESIS, respectively. To calculate the T_g of the diene phase, the effect of the molecular weight of polystyrene segments is ignored since the branch chains are grafted on to the PI segments. The calculated T_{g1} are listed in Table III. In most cases, the difference (Δ_1) between T_{g1} and the measured T_g is below 5°C, except for the SISx-g-PB1.1 copolymers. Clearly, the SISx-g-PBy copolymers can not fit the Fox equation quite well if the branch length is short. If the $T_{g,a}$ of ESIS is replaced by the T_{g1} of parent SIS resins in eq. 4, the difference (Δ_2) between the calculated T_{g2} and the measured T_g becomes even greater for the SISx-g-PB1.1 copolymers. However, the T_{g2} fits the Fox equation quite well for other SISx-g-PBy copolymers having longer branch length since the Δ_2 decreases with the branch length. Thus, the T_g of parent SIS resins can be directly used in the Fox equation. In this case, $T_{g,a}$ and M_s are constant in eqs. (4–6) so that the glass transition of SISx-g-PBy copolymers can be designed by the branch length and the branch number, which determine the $T_{g,b}$ and $(M_g - M_s)$.

CONCLUSIONS

The SIS-g-PB copolymers have well-defined long chain branched molecular structures, which can be tailored by variable epoxidation degree, branch length and branch density. The *in*

situ epoxidation can be controlled by the reaction time in the experimental range. The epoxide groups partially react with PB lithium macroanions. The GE decreases with the branch length and the epoxidation degree. The unreacted epoxide groups can provide polar functional groups to the SIS-g-PB copolymers. As their epoxidation degree is constant, the branch density decreases with the branch length, but their molecular weight increases with the branch length. While the branch density and the molecular weight increase with the epoxidation degree.

Apart from the molecular structures, the LCBs can compensate the flexibility loss of polar SIS copolymers by significantly lowering the T_g of diene blocks. Their glass transition can be designed by the epoxidation degree, branch length and branch density since their T_g can fit the Fox equation, especially as the long branches are grafted. Although the T_g of polar SIS increases with the epoxidation degree, the T_g of the SIS-g-PB copolymers evidently decreases with the branch length. The T_g of copolymers bearing much shorter or longer branch length decreases with the branch density in a narrow temperature range. Only if the branch length approaches its critical molecular weight for entanglements, the T_g markedly decreases with the branch density in a wider temperature range. However, the content of polystyrene phase is greatly lowered due to the introduction of LCBs. Thus, SIS copolymer with high content of polystyrene phase is preferably chosen to synthesize SIS-g-PB thermoplastic elastomers with low branch density and longer branch length. Consequently, SIS-g-PB copolymers not only can have high enough content of polystyrene phase (>10 wt %) to meet the requirement of processing properties of thermoplastic elastomers, but also have their performance tailored in a wider range. This correlation between the molecular structures and performance can be utilized to synthesize SIS-g-PB copolymers with special molecular structures meeting the requirement of different practical uses.

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REFERENCES

- Holden, G.; Kricheldorf, H. R.; Quirk, R. Thermoplastic Elastomers; Hanser Publishers: Munich, **2004**; Chapter 4, pp 69.
- Drobny, J. G. Handbook of Thermoplastic Elastomers; William Andrew Inc.: New York, **2007**; Chapter 5, pp 161–178.
- Lynd, N. A.; Oyerokun, F. T.; O'Donoghue, D. L.; Handlin, D. L.; Fredrickson, G. H. *Macromolecules* **2010**, *43*, 3479.
- Benedek, I.; Feldstein, M. M. In Technology of Pressure-Sensitive Adhesives and Products; Benedek, I., Feldstein, M. M.; CRC Press: Florida, **2009**; Chapter 3, pp 3-1 - 3-45.
- Meng, F. L.; Zheng, S. X.; Zhang, W. A.; Li, H. Q.; Liang, Q. *Macromolecules* **2006**, *39*, 711.
- Ramos, J. A.; Espósito, L. H.; Fernández, R.; Zalakain, I.; Goyanes, S.; Avgeropoulos, A.; Zafeiropoulos, N. E.; Kortaberria, G.; Mondragon, I. *Macromolecules* **2012**, *45*, 1483.
- Garate, H.; Mondragon, I.; Goyanes, S.; D'Accorso, N. B. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 4505.
- Garate, H.; Fascio, M. L.; Mondragon, I.; D'Accorso, N. B.; Goyanes, S. *Polymer* **2011**, *52*, 2214.
- Ocando, C.; Tercjak, A.; Mondragon, I. *Eur. Polym. J.* **2011**, *47*, 1240.
- Singh, N. K.; Lesser, A. J. *Macromolecules* **2011**, *44*, 1480.
- Shih, R. S.; Kuo, S. W.; Chang, F. C. *Polymer* **2011**, *52*, 752.
- Thongsak, K.; Kunanuruksapong, R.; Sirivat, A.; Lerdwijitjarud, W. *Mater. Sci. Eng. A* **2010**, *527*, 2504.
- Kennedy, J. E.; Higginbotham, C. L. *Mater. Sci. Eng. C* **2011**, *31*, 246.
- Yang, J. M.; Tsai, S. C. *Mater. Sci. Eng. C* **2010**, *30*, 1151.
- Barreto, S. M. A.; Suleiman, D. *J. Membr. Sci.* **2010**, *362*, 471.
- Buonomenna, M. G.; Golemme, G.; Tone, C. M.; De Santo, M. P.; Ciuchi, F.; Perrotta, E.; Zappone, B.; Galiano, F.; Figoli, A. *J. Membr. Sci.* **2011**, *385*, 162.
- Drazkowski, D. B.; Lee, A.; Haddad, T. S. *Macromolecules* **2007**, *40*, 2798.
- Deng, T.; Breen, C.; Breiner, T.; Swager, T. M.; Thomas, E. L. *Polymer* **2005**, *46*, 10113.
- Kim, D. J.; Kim, H. J.; Yoon, G. H. *Int. J. Adhes. Adhes.* **2005**, *25*, 288.
- Adedeji, A.; Grünfelder, T.; Bates, F. S.; Macosko, C. W.; Stroup-Gardiner, M.; Newcomb, D. E. *Polym. Eng. Sci.* **1996**, *36*, 1707.
- Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639.
- Wang, C. X.; Han, W.; Tang, X. Z.; Zhang, H. *AAPS Pharm. Sci. Tech.* **2012**, *13*, 556.
- Wilhelm, H. M.; Felisberti, M. I. *J. Appl. Polym. Sci.* **2002**, *83*, 2953.
- Yang, J. M.; Tsai, S. C. *Mater. Sci. Eng. C* **2010**, *30*, 1151.
- Li, H. Q.; Zeng, X. R.; Wu, W. Q. *J. Elastomers Plast.* **2008**, *40*, 317.
- Choi, S.; Han, C. D. *Macromolecules* **2003**, *36*, 6220.
- Serrano, E.; Larranaga, M.; Remiro, P. M.; Mondragon, I.; Carrasco, P. M.; Pomposo, J. A.; Mecerreyes, D. *Macromol. Chem. Phys.* **2004**, *205*, 987.
- Antonietti, M.; Forster, S.; Hartmann, J.; Oestreich, S. *Macromolecules* **1996**, *29*, 3800.
- Grubbs, R. B.; Broz, M. E.; Dean, J. M.; Bates, F. S. *Macromolecules* **2000**, *33*, 2308.
- Ocando, C.; Tercjak, A.; Serrano, E.; Ramos, J. A.; Corona Galvañ, S.; Parellada, M. D.; Fernández-Berridi, M. J.; Mondragon, I. *Polym. Int.* **2008**, *57*, 1333.
- Serrano, E.; Tercjak, A.; Ocando, C.; Larranaga, M.; Parellada, M. D.; Corona-Galvañ, S.; Mecerreyes, D.;

- Zafeiropoulos, N. E.; Stamm, M.; Mondragon, I. *Macromol. Chem. Phys.* **2007**, *208*, 2281.
32. Zhang, Y.; Chen, X. Z.; Zhang, Y.; Zhang, Y. X. *J. Appl. Polym. Sci.* **2001**, *81*, 2987.
33. Jian, X.; Hay, A. S. *J. Polym. Sci. Part A: Polym. Chem.* **1991**, *29*, 1183.
34. Udipi, K. *J. Appl. Polym. Sci.* **1979**, *23*, 3301.
35. Udipi, K. *J. Appl. Polym. Sci.* **1979**, *23*, 3311.
36. Akinlabi, A. K.; Okieimen, F. E.; Aigbodion, A. I. *J. Appl. Polym. Sci.* **2005**, *98*, 1733.
37. Tanrattanakul, V.; Wattanathai, B.; Tiangjunya, A.; Muhamud, P. *J. Appl. Polym. Sci.* **2003**, *90*, 261.
38. Li, H. Q.; Zeng, X. R.; Wu, W. Q. *Polym. Plast. Technol. Eng.* **2008**, *47*, 978.
39. Wang, Q.; Wang, Y. Z.; Zhao, Z. F.; Fang, B. *Int. J. Adhes. Adhes.* **2012**, *34*, 62.
40. Kapnistos, M.; Vlassopoulos, D.; Roovers, J.; Leal, L. G. *Macromolecules* **2005**, *38*, 7852.
41. Lohse, D. J.; Milner, S. T.; Fetters, L. J.; Xenidou, M.; Hadjichristidis, N.; Mendelson, R. A.; García-Franco, C. A.; Lyon, M. K. *Macromolecules* **2002**, *35*, 3066.
42. Liao, R. G.; Yu, W.; Zhou, C. X. *Polymer* **2010**, *51*, 568.
43. Ruymbeke, E. V.; Bailly, C.; Keunings, R.; Vlassopoulos, D. *Macromolecules* **2006**, *39*, 6248.
44. Zhang, Z. J.; Wan, D.; Xing, H. P.; Zhang, Z. J.; Tan, H. Y.; Wang, L.; Zheng, J.; An, Y. J.; Tang, T. *Polymer* **2012**, *53*, 121.
45. Zhang, Z. J.; Xing, H. P.; Qiu, J.; Jiang, Z. W.; Yu, H. O.; Du, X. H.; Wang, Y. H.; Ma, L.; Tang, T. *Polymer* **2010**, *51*, 1593.
46. Gotsis, A. D.; Zeevenhoven, B. L. F.; Tsenoglou, C. *J. Rheol.* **2004**, *48*, 895.
47. Graebing, D. *Macromolecules* **2002**, *35*, 4602.
48. Hadjichristidis, N.; Xenidou, M.; Iatrou, H.; Pitsikalis, M.; Poulos, Y.; Avgeropoulos, A.; Sioula, S.; Paraskeva, S.; Velis, G.; Lohse, D. J.; Schulz, D. N.; Fetters, L. J.; Wright, P. J.; Mendelson, R. A.; García-Franco, C. A.; Sun, T.; Ruff, C. J. *Macromolecules* **2000**, *33*, 2424.
49. Yan, D.; Wang, W. J.; Zhu, S. *Polymer* **1999**, *40*, 1737.
50. Yamazaki, H.; Takeda, M.; Kohno, Y.; Ando, H.; Urayama, K.; Takigawa, T. *Macromolecules* **2011**, *44*, 8829.
51. Castillo, J. A.; Borchmann, D. E.; Cheng, A. Y.; Wang, Y. F.; Hu, C. H.; García, A. J.; Weck, M. *Macromolecules* **2012**, *45*, 62.
52. Nikopoulou, A.; Iatrou, H.; Lohse, D. J.; Hadjichristidis, N. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 2597.
53. Kempf, M.; Barroso, V. C.; Wilhelm, M. *Macromol. Rapid Commun.* **2010**, *31*, 2140.
54. Zhu, Y. Q.; Burgaz, E.; Gido, S. P.; Staudinger, U.; Weidisch, R.; Uhrig, D.; Mays, J. W. *Macromolecules* **2006**, *39*, 4428.
55. Knauss, D. M.; Huang, T. Z. *Macromolecules* **2003**, *36*, 6036.
56. Shen, Z. Q.; Song, X. Y.; Xiao, S. X.; Yang, J. P.; Kan, X. L. *J. Appl. Polym. Sci.* **1983**, *28*, 1585.
57. Yuan, Z. S.; Gauthier, M. *Macromolecules* **2005**, *38*, 4124.