Synthesis of Sulfonated Rubber Ionomers by the Ring-Opening Reaction of Epoxidized Styrene–Butadiene Rubber, Their Characterization, and Their Properties

Hong-Quan Xie,[1] Yong Chen,[2] Wei Yang,[3] Dong Xie[4]

[1]Department of Chemistry, Huazhong University of Science and Technology, Wuhan, 430074, China
[2]Hubei Research Institute of Chemistry, Wuhan 430074, China
[3]College of Material Science and Engineering, South China University of Technology, Guanzhou 510640, China
[4]Department of Biomedical Engineering, Indiana University Purdue University, Indianapolis, Indiana 46202

ABSTRACT: A novel method for the synthesis of the sulfonate ionomer of styrene-*co*-butadiene rubber (SBR) was developed. SBR was first epoxidized by performic acid formed from hydrogen peroxide and formic acid in situ in solution, and this was followed by a ring-opening reaction with an aqueous solution of $NaHSO_3$. The optimum conditions for the epoxidation of SBR in the presence of a phase-transfer catalyst and for the ring-opening reaction of epoxidized SBR with an aqueous solution of $NaHSO_3$ were studied. During the epoxidation of SBR, a phase-transfer catalyst, such as poly(ethylene glycol), could enhance the conversion of double bonds to epoxy groups. During the ring-opening reaction, both the phase-transfer catalyst and ring-opening catalyst were necessary to enhance the conversion of the epoxy groups to ionic groups. The addition of Na_2SO_3 to the reaction mixture was important to obtain 100% conversion. The products were characterized with Fourier transform infrared spectrophotometry, ^{1}H-NMR spectroscopy, differential scanning calorimetry (DSC), and transmission electron microscopy (TEM). DSC showed that the sodium sulfonate SBR ionomer possessed a dissociation temperature of ionic domains at 110°C, which appeared as black spots under TEM, after the sodium ions of the ionomer were substituted by lead ions. Some properties of the sodium ionomer, such as the water absorbency, oil absorbency, and dilute solution behavior, were studied. With increasing ionic groups, the water absorbency of the ionomer increased, whereas the oil absorbency decreased. The dilute solution viscosity of the ionomer increased abruptly with increasing ionic group content. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3090–3096, 2006

Key words: ionomers; phase transfer catalysis; rubber

INTRODUCTION

Ionomers of the ethylene–propylene–diene copolymer (EPDM) can be prepared by sulfonation in solution with acetyl sulfate and behave as thermoplastic elastomers in the presence of an ionic plasticizer.[1–3] Canter[4] obtained butyl rubber ionomers by the sulfonation of butyl rubber with the SO_3/triethyl phosphate complex, followed by neutralization with NaOH, and studied their mechanical properties. Xie and coworkers reported the melt flow properties, solution behavior, dynamic mechanical properties, and mechanical properties of sulfonated EPDM ionomers[5] and butyl rubber ionomers,[6] both of which were obtained by sulfonation with acetyl sulfate in petroleum ether and neutralization with metallic acetates or alkyl amines. They pointed out that it was not necessary to use zinc stearate during the processing of alkyl amine neutralized ionomers of sulfonated butyl rubber.[6] However, Fitzgerald and Weiss[7] pointed out that rubber with a higher unsaturation degree could not be sulfonated in solution with a concentration greater than 3% to avoid gelation. Styrene-*co*-butadiene rubber (SBR) with about 30% styrene is a synthetic rubber with a higher unsaturation degree that is obtained by emulsion polymerization. Xie and coworkers reported that in the presence of methyl ethyl ketone or acetone, (Styrene-butadiene-styrene) triblock copolymer (SBR)[8] or SBS[9] could be sulfonated in petroleum ether or cyclohexane without gelation. Jacobi et al.[10] recently reported the epoxidation of SBR by performic acid formed in situ and showed that the reaction greatly depended on the hydrogen peroxide concentration, time, and temperature. Studies related to the addition of nucleophilic reagents, such as acids, amines, and alcohols, to epoxidized polydiene were performed by Soutif et al.,[11] Jayawardena et al.,[12] and Derouet et al.,[13] respectively. Soutif et al. added naphthyl acetic acid to epoxidized 1,4-polyisoprene, using tetramethyl ammonium salt of the acid as the catalyst, and obtained about 40% con-

version at 100°C in 48 h. Derouet et al. modified epoxidized 1,4-polyisoprene via a ring-opening reaction with an alcohol, using cerium ammonium nitrate as the catalyst. Recently, Xie et al.[14] synthesized a quaternary ammonium ionomer of SBS by the ring-opening reaction of epoxidized SBS with triethylamine hydrochloride with 100% conversion.

This article deals with the synthesis conditions for the epoxidation of SBR in the presence of a phase-transfer catalyst and for the preparation of sulfonated SBR ionomers via the ring-opening reaction of epoxidized styrene-co-butadiene rubber (ESBR) with an aqueous $NaHSO_3$ solution and their characterization via Fourier transform infrared (FTIR) spectrophotometry, ^1H-NMR spectroscopy, differential scanning calorimetry (DSC), and transmission electron microscopy (TEM), as well as the study of their oil and water absorbencies and dilute solution properties, to develop a novel method for synthesizing a sulfonated ionomer from unsaturated rubber. The sulfonated ionomer prepared from the ring-opening reaction of ESBR should be different from that prepared from the sulfonation of SBR in structure because the former contains the sulfonate groups only on the polybutadiene units of SBR, whereas the latter contains those groups mainly on the polystyrene units.[8]

EXPERIMENTAL

Materials

SBR 1500 is a product made by Lanzhou Chemical Industrial Co. (Lanzhou, China) with a Mooney viscosity of 52 and a styrene content of 23.5%. Formic acid (85%), hydrogen peroxide (30%), $NaHSO_3$, Na_2SO_3, lead acetates, acetone, cyclohexane, poly(ethylene glycol) 600 (PEG 600), tetraethyl ammonium bromide (TEAB), N,N-dimethyl aniline (DMA), and ethanol were chemically pure. Antioxidant 264 (2,6-di-tert-butyl-4-methylphenol) was an industrial product. Hydrochloric acid (HCl) and KOH were analytical reagents.

Epoxidation of SBR in the presence of PEG 600

The epoxidation of SBR was carried out via the reaction of SBR in a cyclohexane solution (SBR concentration = 11 g/100 mL) with performic acid formed from HCOOH and a 30% aqueous H_2O_2 solution in situ at 70°C for 4 h, with 5 wt % PEG 600/SBR as the phase-transfer catalyst. The molar ratio of H_2O_2 to HCOOH was 1. The product was precipitated and washed several times with ethanol, and this was followed by drying in a vacuum dryer at 60°C.
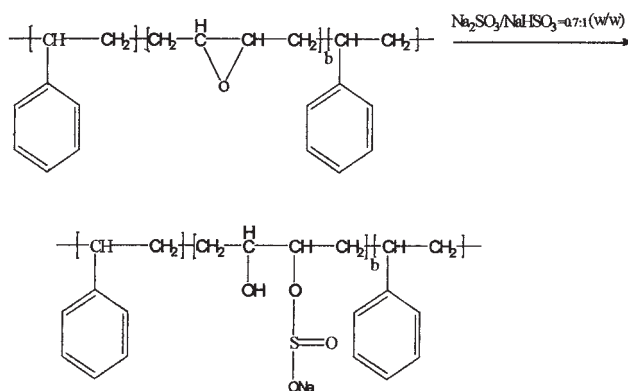
Scheme 1

Ring-opening reaction of ESBR with $NaHSO_3$ to form the ionomer (Scheme 1)

ESBR was first dissolved in toluene to form an ESBR solution with a concentration of 13 g/100 mL, to which was added 5 wt % TEAB/ESBR as a phase-transfer catalyst and 5 wt % DMA/ESBR as a ring-opening catalyst. An aqueous solution of $NaHSO_3$ and Na_2SO_3 was then added with vigorous stirring at 70°C for 6 h according to a $NaHSO_3$/epoxy group molar ratio of 1.2 and a Na_2SO_3/$NaHSO_3$ weight ratio of 70%. The reaction was terminated by the addition of a small amount of an acetone solution containing antioxidant 264. The mixture was washed with distilled water three times, precipitated by ethanol, and dried in a vacuum dryer at 50°C.

Chemical analysis

The epoxy group in ESBR was determined by the HCl–acetone method[15] as follows. An approximately 1-g sample was accurately weighed into an iodometric titration flask. A HCl–acetone (1/80) solution (25 mL) was added. The flask was stoppered, and the mixture was stirred until the sample was dissolved. After it stood in the dark for 1 h, three drops of phenolphthalein indicator were added, and the solution was titrated with a standard alcoholic KOH solution to a pink color:

$$Epoxy\ value = (V_0 - V_1)N/10W$$

where V_0 and V_1 are the volumes (mL) of the standard alcoholic KOH solution used in titration for the blank and sample, respectively; W is the weight of the sample; and N is the normality of the alcoholic KOH solution.

The conversion of the epoxy group to the sulfonate group was obtained by the subtraction of two epoxy values determined before and after the ring-opening reaction divided by the original epoxy value.
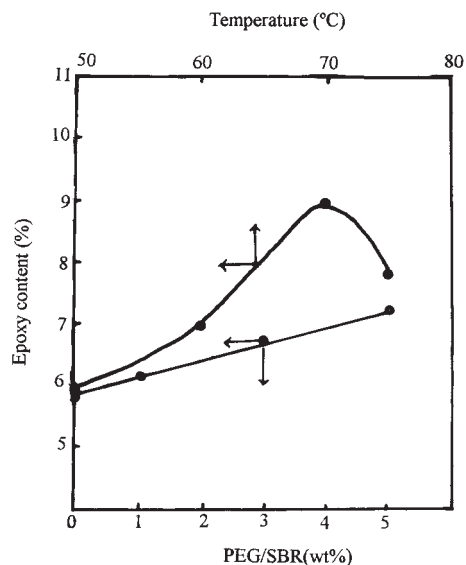
Figure 1 Effects of PEG as a phase-transfer catalyst (60°C) and the reaction temperature on the epoxy content of the epoxidized product.

Characterization

The ^{1}H-NMR spectrum of ESBR was obtained with a Varian Mercury Plus 300 NMR spectroscopy instrument, with CDCl$_3$ as the solvent and tetramethylsilane as the internal standard. The FTIR spectrum of the sulfonated SBR ionomer was taken with a Bruker Equinox 55 FTIR spectrophotometer (Ettlingen, Germany): a KBr disc was coated with a solution of the sample, and this was followed by evaporation of the solvent. A TEM micrograph of the lead-ion-neutralized SBR ionomer was obtained with a JEM 100CXII transmission electron microscope (JEOL Ltd., Japan). DSC of the sodium SBR ionomer curve was recorded with a PerkinElmer thermal apparatus (Wellesley, MA) at a heating rate of 10°C/min.

Oil or water absorbency of the ionomer

The oil absorbency or water absorbency was determined by the immersion of an accurately weighed sample (W_b) in diesel oil or water at room temperature for 48 h, followed by the removal of the liquid on the surface of the sample with filter paper and then the weighing of the sample (W_a):

$$\text{Absorbency (\%)} = (W_a - W_b) \times 100/W_b$$

Solution viscosity of the ionomer

The dilute solution viscosity (η_r/c, where η_r is the relative viscosity and c is the concentration of the solution) of the ionomers in a mixed solvent of toluene and methanol (9/1) at an approximately 0.1 g/100 mL

concentration was measured with an Ubbelohde viscometer at 25°C.

RESULTS AND DISCUSSION

### Epoxidation of SBR in the presence of a phase-transfer catalyst

Because the epoxidation reaction is carried out in both the aqueous phase and organic solution phase, it is favorable to use a phase-transfer catalyst. Poly(ethylene glycol) with a molecular weight of 600 (PEG600) is soluble in both water and cyclohexane. It can transfer hydrogen peroxide or performic acid to the cyclohexane solution of SBR, thus accelerating the epoxidation of SBR. The effect of PEG as a phase-transfer catalyst on the epoxy group content at 60°C is shown in Figure 1. With an increasing weight percentage of PEG/SBR, the epoxy percentage of ESBR increases. Five percent PEG can increase the epoxy group content about 20%. The following experiments were all carried out in the presence of 5% PEG/SBR.

Figure 1 also shows the effect of the reaction temperature on the epoxidation of SBR. With increasing reaction temperature, the epoxy groups of the product increase at first and then decrease. The optimum temperature is 70°C. This may be due to the fact that over 70°C there occur some side reactions between the epoxy groups and formic acid, forming ester and OH groups and thus decreasing the epoxy group content.

Figure 2 shows the effect of the weight ratio of formic acid to SBR in the presence of 5 wt % PEG 600 at 70°C for 2 h on the epoxy group content. The degree of epoxidation increases rapidly at first and then
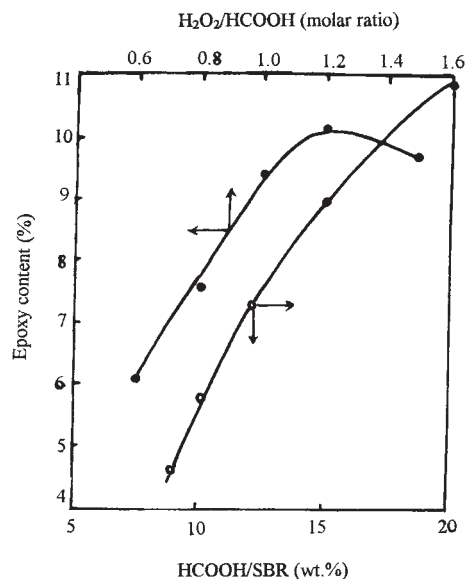
Figure 2 Effects of the formic acid amount and molar ratio of H$_2$O$_2$ to HCOOH on the epoxy content of the epoxidized product.
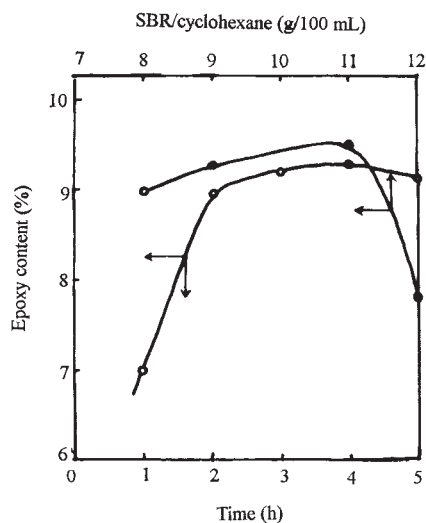
Figure 3 Effects of the reaction time and SBR concentration on the epoxy content of the epoxidized product.

somewhat slowly over 12 wt %. This is due to the fact that the more performic acid or peroxidation agent is used, the more epoxy groups form and the fewer double bonds remain to be epoxidized.

Figure 2 also shows that the epoxy group content increases with an increasing molar ratio of H_2O_2 to HCOOH. When the molar ratio of H_2O_2 to HCOOH exceeds 1–1.2, the epoxy group content decreases. This implies that performic acid rather than H_2O_2 plays the real role in epoxidation.

Figure 3 shows the effect of the reaction time on the epoxidation reaction of SBR. With an increase in the epoxidation time, the epoxy content of the product (ESBR) increases quickly at first and gradually after 2 h and then decreases gradually after about 4 h. This can be attributed to the side reaction of ester formation when more epoxy groups formed at longer reaction times will be opened by the acid.

The epoxy group content increases gradually with the SBR concentration in cyclohexane when the concentration is less than 11% (w/v) and then falls, as shown in Figure 3. This fact can be explained by the higher viscosity of the more concentrated SBR solution, which hinders the epoxidation of double bonds.

**Synthesis conditions for the sodium sulfonate ionomer of SBR**

The effect of the molar ratio of $NaHSO_3$ to epoxy groups on the conversion of epoxy groups of ESBR is shown in Figure 4. The conversion increases with an increase in the molar ratio of $NaHSO_3$ to epoxy groups. The optimum molar ratio is 1.5/1, over which the conversion increases slowly. However, even at the optimum molar ratio, the epoxy conversion is as low as 26%.

Because the reaction is carried out in both an aqueous solution of $NaHSO_3$ and a toluene solution of ESBR, the ring-opening reaction of ESBR with $NaHSO_3$ to form the sulfonated ionomer is difficult and may be accelerated by the addition of a phase-transfer catalyst. Figure 4 also shows the effect of TEAB as a phase-transfer catalyst on the conversion of epoxy groups to sodium sulfonate groups. The conversion of epoxy groups increases with an increasing amount of TEAB. The optimum concentration is 5 wt % TEAB with respect to ESBR as the conversion gradually increases over 5 wt % TEAB. PEG 600, used as a phase-transfer catalyst, seems somewhat poorer than TEAB because 5 wt % PEG can raise the conversion of epoxy groups only about 2%.

Figure 5 indicates that in the presence of 5% TEAB, with increasing ESBR concentration, the conversion of epoxy groups into sodium sulfonate groups increases rapidly at first and then gradually. However, the reaction solution becomes too viscous and difficult to stir when the ESBR concentration is over 13 g/100 mL. Hence, the optimum ESBR concentration is 13 g/100 mL.

DMA can be used as a catalyst for the ring-opening reaction of epoxy groups with carboxylic acid, so it has been tested as a catalyst for the ring-opening reaction of epoxy groups of ESBR with $NaHSO_3$ to form the sulfonated ionomer of SBR. The addition of 5 wt % DMA can increase the conversion about 2 times. Over 5 wt % DMA, the increase in the conversion seems slower, as shown in Figure 5.

As indicated previously, even in the presence of DMA and a phase-transfer catalyst, the conversion is still not high. After the addition of Na_2SO_3 to the reaction mixture to adjust the pH of the reaction, the conversion increases with an increasing amount of
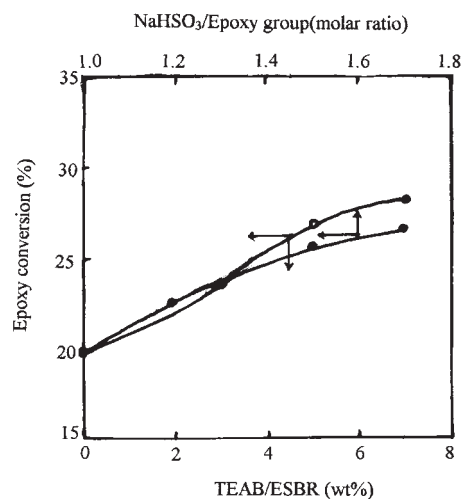
Figure 4 Effects of the molar ratio of $NaHSO_3$ to epoxy groups and phase-transfer catalyst (TEAB) amount on the epoxy conversion.
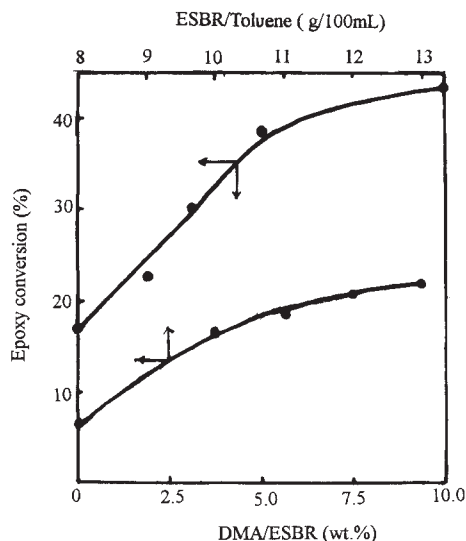
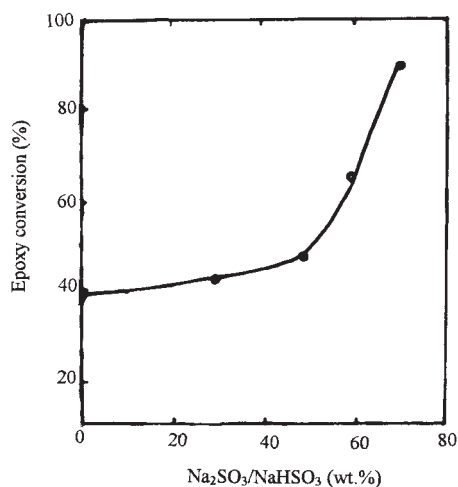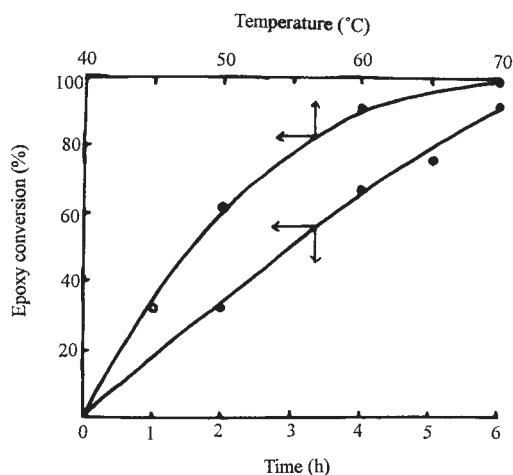**Figure 5** Effects of the ESBR concentration and DMA amount on the epoxy conversion.

Figure 7 Effects of the reaction temperature and time on the epoxy conversion.

Na_2SO_3, especially at a $Na_2SO_3/NaHSO_3$ weight ratio of 70 wt %, as shown in Figure 6. It seems that a slightly alkaline medium is beneficial to this ring-opening reaction.

Figure 7 shows that the epoxy group conversion increases with the reaction time almost linearly. It reaches over 94% at 60°C in 6 h. To obtain a higher conversion of epoxy groups, a long reaction time seems necessary.

Figure 7 also shows the effect of the reaction temperature on the conversion of epoxy groups to sulfonate groups. The reaction rate increases rapidly below 60°C and then gradually to 70°C. The conversion under the optimum conditions reaches 100% at 70°C.

Characterization of ESBR and the sulfonate ionomer of SBR

Because the characteristic absorption peaks for epoxy groups are not strong in the FTIR spectrum, the ^{1}H-NMR spectrum of ESBR is used, as shown in Figure 8. The peaks at 1.45, 2.05, 2.71, 2.95, 4.98, 5.41, and 7.3 ppm represent the protons for methylene, methine, *cis*-epoxy, *trans*-epoxy, 1,2-double bonds, 1,4-double bonds, and phenyl groups. This demonstrates the structure of ESBR.

The FTIR spectrum of the sodium sulfonate groups containing SBR (Fig. 9) shows that the absorption peaks at 810 and 880 cm^{-1} for the epoxy groups disappear. There exist absorption peaks at 910, 968, and 730 cm^{-1} for the double bonds of polybutadiene segments and at 699 and 1450 cm^{-1} for the phenyl groups. The broad absorption peak at 3450 cm^{-1} exists for the OH group, which is formed during the ring-opening reaction of epoxy groups with $NaHSO_3$. The existence of absorption peaks at 1059 and 1145 cm^{-1} can be attributed to the S=O and sulfonate groups. Thus, the IR spectrum indicates the functional groups of the sulfonated SBR ionomer.

A TEM microphotograph (Fig. 10) shows black spots in a specimen of the sodium sulfonate SBR iono-

Figure 6 Effect of the weight ratio of Na_2SO_3 to $NaHSO_3$ on the epoxy conversion.
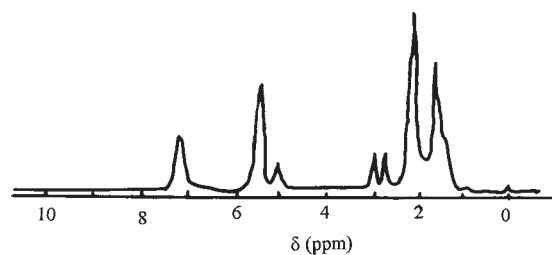
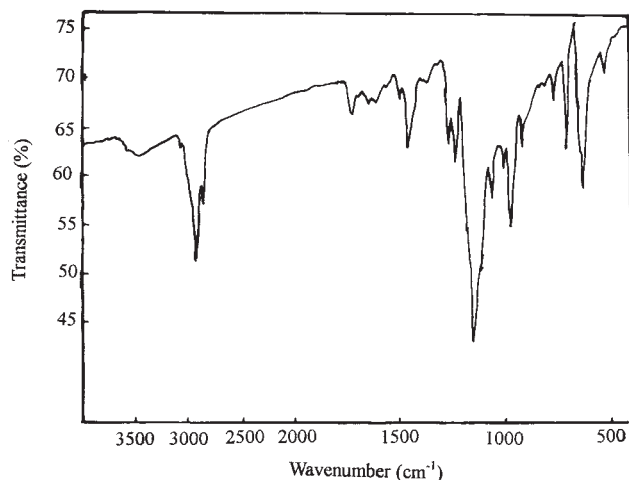**Figure 8** ^{1}H-NMR spectrum of ESBR.

Figure 9   FTIR spectrum of the sulfonate ionomer of SBR.

mer after exchange with lead acetate in solution for 24 h, followed by washing. Because the lead ions can absorb the electrons and the ions associate into ionic domains, the latter appear as dark spots. Thus, TEM demonstrates that the product is an ionomer.

Figure 11 illustrates the DSC curve of the sodium sulfonate ionomer, which shows two transition temperatures: one at −35.1°C for the glass-transition temperature of the styrene–butadiene random copolymer segments of SBR and the other at 110.6°C for the dissociation temperature of ionic domains.

Some properties of the sodium sulfonate ionomer of SBR

The ionomer can absorb water because it contains hydrophilic ionic groups. Table I indicates that with increasing ion groups, the water absorbency increases, more obviously over 2.1 mmol of ionic groups/g.
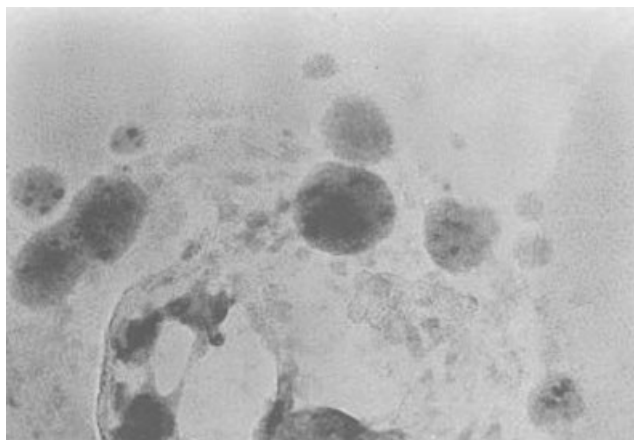

Figure 10   TEM microphotograph of the sulfonate ionomer of SBR (with a magnification of 61,000).
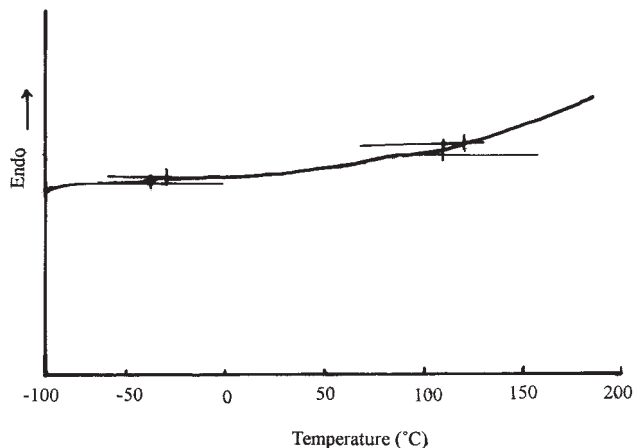

Figure 11   DSC curve of the sulfonate ionomer of SBR.

Table I also shows that the ionomer offers some oil-resistant properties. SBR is completely dissolved in diesel oil after 48 h at room temperature, whereas the SBR ionomer containing a certain number of sodium sulfonate groups does not dissolve but absorbs oil. The oil absorbency of the ionomer containing 1.0 mmol of sulfonate groups/g is less than the oil absorbency of that containing 1.6 mmol of sulfonate groups/g, probably because some of the sample still dissolves in diesel oil. Then, the oil absorbency of the ionomer decreases with increasing sodium sulfonate groups from 1.6 mmol of sulfonate groups/g. This fact can be attributed to the association of the ionic groups in the nonpolar oil, which results in oil resistance.

η_r/c of the ionomers in a mixed solvent of toluene and methanol (9/1) increases with increasing sodium sulfonate groups, as shown in Figure 12. It increases more sharply over 1.6 mmol of sulfonate groups/g. This phenomenon can be explained by the fact that the more ionic groups there are, the more association there is between the macromolecules of the ionomer, resulting in higher resistance to flow or higher viscosity.

CONCLUSIONS

A novel method for the preparation of the sodium sulfonate ionomer of SBR has been developed through

TABLE I
Water Absorbency and Oil Absorbency of the Sulfonated Ionomer of SBS

Sulfonate groups (mmol/g)	Water absorbency (%)	Oil absorbency (%)	η_r/c (mL/g)
0	—	Dissolved	
1.06	10.9	104.4	209.5
1.61	46.9	232.8	221.9
2.07	82.5	174.9	258.2
2.59	165.9	45.9	274.7
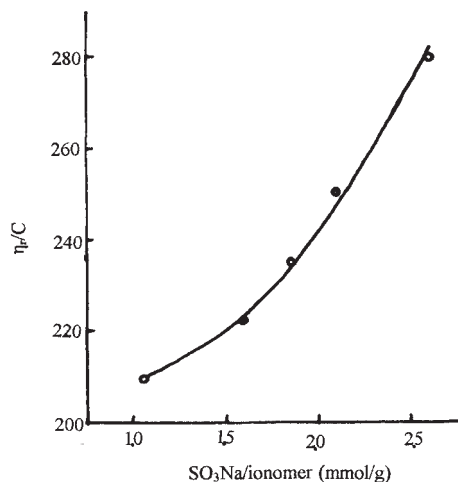
Figure 12 Relationship between η_r/c and the ionic group content of the SBR ionomer.

the ring-opening reaction of ESBR with $NaHSO_3$. During the epoxidation of SBR, a phase-transfer catalyst enhances the conversion of double bonds to epoxy groups. During the ring-opening reaction of ESBR with $NaHSO_3$, both a phase-transfer catalyst and a ring-opening catalyst are necessary to enhance the conversion of epoxy groups to ionic groups, whereas the addition of Na_2SO_3 is important to obtain 100% conversion. The optimum conditions are an ESBR concentration of 130 g/L, a molar ratio of $NaHSO_3$ to epoxy groups of 1.5, a weight ratio of TEAB to ESBR of 5%, a weight ratio of DMA to ESBR of 5%, a temperature of 70°C, and a period of 6 h. The FTIR spectrum

demonstrates the characteristic groups of the sulfonated SBR ionomer. The DSC curve shows the presence of the dissociation temperature of ionic domains at 110°C, whereas TEM of the lead sulfonate ionomer demonstrates the presence of ionic domains as dark spots. With increasing ionic group content, the water absorbency of the ionomer increases, whereas its oil absorbency decreases. η_r/c of the ionomer increases abruptly with increasing ionic group content because of the association of ionic groups between ionomer molecules.

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