Preparation, Characterization, and Some Properties of Ionomers from a Sulfonated Styrene–Butadiene–Styrene Triblock Copolymer without Gelation

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ABSTRACT: The conditions for the sulfonation of a highly unsaturated styrene–butadiene–styrene triblock copolymer (SBS) in cyclohexane containing a small amount of acetone with acetyl sulfate made by sulfuric acid and acetic anhydride without gelation were studied. After neutralization with metallic ions, the ionomers were characterized with IR spectrophotometry, dynamic mechanical analysis, and transmission electron microscopy. The melt flow, solution properties, and mechanical properties of the ionomers were studied. The results showed that gelation occurred during the sulfonation of SBS in cyclohexane at a 5–10% concentration without acetone, whereas in the presence of 5–10 vol % acetone, sulfonation proceeded smoothly without gelation. Transmission electron microphotographs of the lead ionomer indicated the presence of ionic domains. A dynamic mechanical spectrum showed the presence of three transition temperatures: -82.9, 68, and 96.5°C. The melt viscosity of the ionomer increased with the sulfonate content. The melt viscosity of the different ionomers neutralized with different cations seemed to decrease with decreasing ionic potential for both monovalent cations and divalent cations The solution viscosity of the sodium-sulfonated ionomer increased with increasing sulfonate content. The ionomer still behaved as a thermoplastic elastomer and showed better mechanical properties than the original SBS. The tensile strength of the different ionomers decreased as follows. For the monovalent cations, it decreased with decreasing ionic potentials: $Li^+ > Na^+ > K^+$. For the divalent cations, it decreased with increasing ionic potentials: $Pb^{2+} > Zn^{2+} > Mg^{2+}$. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1398–1404, 2005

Key words: ionomers; triblock copolymers; sulfonation; elastomers

INTRODUCTION

MacKnight and Lundberg[1] indicated in their review that sulfonated rubber ionomers could be used as thermoplastic elastomers. Makowski et al.[2] prepared ethylene–propylene–diene monomer (EPDM) ionomers through the sulfonation of EPDM in hexane with acetyl sulfate, followed by neutralization with zinc acetate. They stated that it was necessary to use zinc stearate as an ionic plasticizer during the processing of the sulfonated EPDM ionomer.[3] Canter[4] obtained butyl rubber ionomers through the sulfonation of butyl rubber with a 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 iono-

mers,[6,7] both of which were obtained by sulfonation with acetyl sulfate in petroleum ether and neutralization with metallic salts or alkylamine. They pointed out that it was not necessary to use zinc stearate during the processing of alkylamine-neutralized ionomers of sulfonated butyl rubber. Xie and coworkers also studied blends of sulfonated EPDM[8] and butyl rubber ionomers[9] with several kinds of polymers and found that some blends exhibited synergistic effects with respect to the tensile strength. Weiss et al.[10] prepared ionomers from a sulfonated hydrogenated styrene–butadiene–styrene triblock copolymer (SEBS) with acetyl sulfate in 1,2-dichloroethane and studied their dilute solution properties, water absorbency, and thermal properties. Storey et al.[11] synthesized ionomers of a styrene–isobutylene–styrene triblock copolymer by sulfonation with acetyl sulfate, followed by neutralization with an alcoholic solution of metallic acetate, and studied the dynamic mechanical properties of the ionomers.

However, the aforementioned ionomers were derived from rubbers with a low degree of unsaturation. Fitzgerald and Weiss[12] in their review pointed out that rubbers with a high degree of unsaturation, such as

polybutadiene and polyisoprene, cannot be sulfonated in concentrated solutions because they gel easily during sulfonation. Weiss et al.[13] prepared sulfonated styrene–butadiene rubber (SBR) ionomers through the emulsion polymerization of sodium styrene sulfonate and butadiene. Xie et al.[14] found that in the presence of a small portion of methyl ethyl ketone, SBR, which can be obtained through the emulsion polymerization of styrene and butadiene, can be sulfonated in petroleum ether with sulfuric acid and acetic anhydride (Ac$_2$O) as a sulfonating agent without gel formation, and they reported the melt flow and mechanical properties of the ionomers of the sulfonated SBR.

This article deals with the sulfonation conditions of SBS in concentrated solutions, with acetyl sulfate as the sulfonating agent, its neutralization with metallic ions to form ionomers, and the characterization of the ionomers by IR spectrophotometry, dynamic mechanical spectroscopy, and transmission electron microscopy (TEM). The melt flow, solution viscosity, and mechanical properties of the ionomers were also studied to obtain polar-functionalized SBS, which is attracting increasing interest for many applications, such as adhesives for polar substances and compatibilizers for blends of polar and nonpolar substances.

EXPERIMENTAL

Materials

SBS 801 with a styrene concentration of 30% was supplied by the Yue-Yang Synthetic Rubber Factory (Yue-Yang, China). Ac$_2$O, sulfuric acid, zinc stearate, metallic acetates, ethyl alcohol, cyclohexane, and acetone were all chemically pure and were used as received.

Sulfonation of SBS and neutralization of the sulfonated styrene–butadiene–styrene triblock copolymer (SSBS) for the formation of the ionomer

The SBS ionomer was obtained through the sulfonation of SBS in cyclohexane containing a small amount of acetone with acetyl sulfate as the sulfonating agent (made from sulfuric acid and Ac$_2$O). SBS (100 g) was dissolved in a mixed solvent of 900 mL of cyclohexane and 100 mL of acetone with stirring at room temperature. A mixture of 5 mL or 8.5 g of concentrated sulfuric acid with Ac$_2$O with a molar ratio of sulfuric acid to Ac$_2$O of 1/1.5–2.0 was added at a constant temperature for 10 min. The reaction was carried out at a constant temperature for 0.5–1 h. An aliquot of the sulfonation solution was taken out and terminated with ethyl alcohol containing 0.2% antioxidant 264 (2,6-di-*tert*-butyl-4-methylphenol). The sample was purified by three precipitations in ethyl alcohol and redissolution in cyclohexane/acetone so that it could be used for determining the sulfonate content of the sulfonated product. The concentration of the sulfonate groups, in milliequivalents (mequiv)/100 g of SSBS, was measured through the titration of a weighed amount of a sulfonated sample (*W*) with an alcoholic solution of KOH, with phenolphthalein used as an indicator. The sulfonate group concentration or sulfonation degree was calculated as follows:

Sulfonate group content

$$(\text{mequiv}/100 \text{ g of SSBS}) = 100 \times N_{\text{KOH}}(V_1 - V_0)/W$$

where N_{KOH} is the normality of the alcoholic KOH solution and V_1 and V_0 represent the volumes of the alcoholic KOH solution used in the determination of the sample and blank, respectively.

The chief amount of the sulfonated product was used to prepare the ionomer as follows. The sulfonation solution was neutralized through the addition of alkali hydroxide, metallic acetate, or ethylamine at a neutralization degree of 1.2 in an ethyl alcohol/water mixture with stirring at room temperature for 1 h. The solvent was removed through flashing in hot water, and the ionomer was dried

Characterization

An IR spectrum of the SSBS ionomer was taken with a Bruker Equinox 55 Fourier transform infrared spectrophotometer (Ettlingen, Germany); a KBr disc was coated with a solution of the sample, and this was followed by the evaporation of the solvent. The dynamic mechanical spectrum of the sodium ionomer with a sulfonate content of 29.1 mequiv of SO$_3$H/100 g was taken with a Netzsch DMA 242 dynamic mechanical spectroscope (Burlington, MA) at a frequency of 33.3 Hz and a heating rate of 2°C/min under a nitrogen atmosphere. A TEM micrograph of the lead-ion-neutralized SBS ionomer was obtained with a Phillips CM300 transmission electron microscope (England).

Melt flow of the ionomer

The ionomer was mixed with 10 wt % zinc stearate at 160°C at a shear rate of 30 rpm in a mixer of a Brabender plasticorder (Berlin, Germany), and the mixing torque (Nm) was recorded. The melt viscosity of the ionomer was represented by the torque value because the torque value was proportional to the melt viscosity of the ionomer when the shear rate of the mixer and the amount of the sample were kept constant. After the torque value reached equilibrium, it was recorded as the characteristic torque value or melt viscosity.

Solution viscosity of the ionomer

The solution viscosity of the sodium-sulfonated SBS ionomer was measured with an NDJ-1 rotary viscosimeter at room temperature.
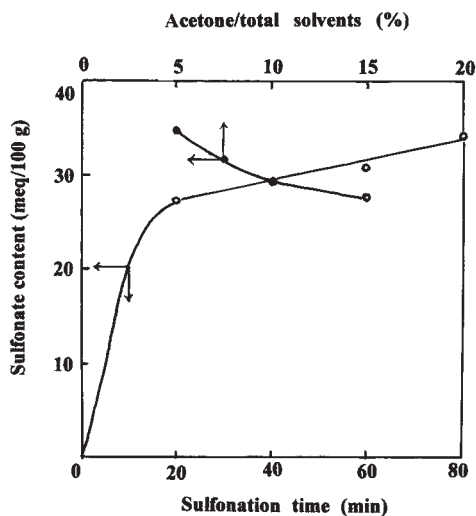
Figure 1 Effects of the acetone/total-solvent volume percentage and the sulfonation time on the sulfonate content of SSBS.

Mechanical properties of the ionomer

The ionomer was mixed with zinc stearate and antioxidant 264 on a hot mill at 160°C for 15 min and was compression-molded at 160°C and 10–15 MPa. The tensile strength and ultimate elongation were measured on an XL-2500 tensile tester at a stretching rate of 250 mm/min. The permanent set was measured as the elongation percentage 3 min after the specimen was broken and reunited.

RESULTS AND DISCUSSION

Sulfonation conditions of SBS

When SBS was sulfonated in cyclohexane by acetyl sulfate at a 5–10% concentration, gelation occurred. We found that if a small portion of acetone was added to cyclohexane and a mixture of sulfuric acid and Ac_2O was dropped into the SBS solution, the sulfonation of SBS could be carried out smoothly without gelation.

The addition of moderately polar acetone to cyclohexane could solvate the sulfonate groups formed on SBS and weaken their association between the SSBS molecules, thus lowering the viscosity of the sulfonation solution and avoiding the gelation caused by the association of the sulfonate groups. With an increasing amount of acetone, the sulfonate content of SSBS decreased, as shown in Figure 1. This was probably due to the water and other impurities present in acetone, which consumed acetyl sulfate Thus, it was preferable to use the mixed solvent with an acetone/cyclohexane–acetone volume ratio of 5–10%. The general sulfonation conditions were as follows: an acetone/mixed-solvent ratio of 10% (v/v), an SBS concentra-

tion of 10% (w/v), an H_2SO_4/SBS ratio of 8.5 wt %, an Ac_2O/H_2SO_4 molar ratio of 1.5 molar ratio, a temperature of 25°C, and a reaction time of 40 min. Only one condition was varied, and the other conditions were kept unchanged. Figure 1 also shows the sulfonation rate of SBS. The sulfonate content of SSBS increased rapidly at first for 20 min and then gradually.

Figure 2 illustrates the effect of the Ac_2O/H_2SO_4 molar ratio on the sulfonate content. The maximum sulfonate content occurred at an Ac_2O/H_2SO_4 molar ratio of approximately 1.75. Theoretically, the Ac_2O/H_2SO_4 molar ratio for forming acetyl sulfate was 1. The excess Ac_2O was wasted in a reaction with water and other impurities in the solvent and SBS. Too much Ac_2O could induce side reactions.

The effect of the amount of the sulfonating agent on the sulfonate content is also shown in Figure 2. The more sulfonating agent was used, the higher the sulfonate content was.

Figure 3 shows the effect of the sulfonation temperature on the sulfonate content of SSBS. The sulfonate content increased with the temperature below 25°C. An optimum sulfonation temperature existed at 25°C. Too high a temperature caused side reactions and gelation.

Figure 3 also illustrates the effect of the SBS concentration on the sulfonate content of SBS. The higher the concentration was, the higher the sulfonate content was. However, if the SBS concentration was too high, the sulfonation solution became too viscous and difficult to stir. In general, a 12–15% (g/mL) SBS concentration was suitable.

Characterization of the SSBS ionomer

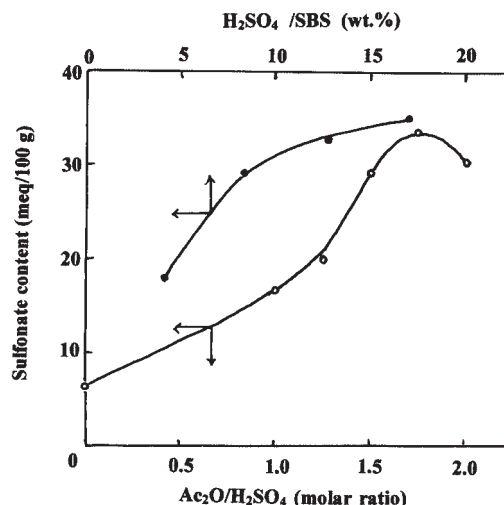Figure 4 illustrates the IR spectra of the zinc-sulfonated SBS ionomer. The absorption peaks at 1042, 1180,

Figure 2 Effects of the Ac_2O/sulfuric acid molar ratio and the amount of sulfuric acid on the sulfonate content of SSBS.
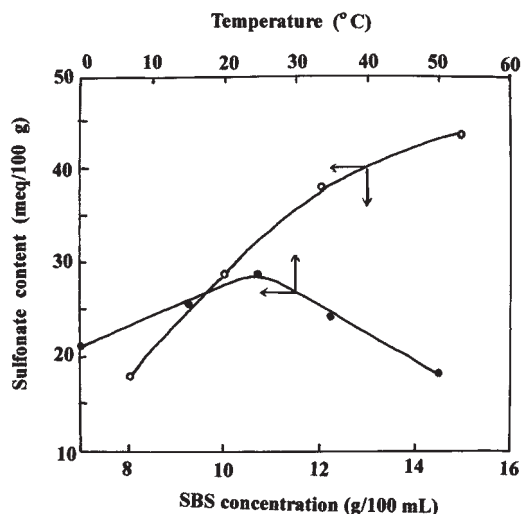
Figure 3 Effects of the sulfonation temperature and SBS concentration on the sulfonate content of SSBS.

Figure 5 TEM micrograph of the lead-sulfonated SBS ionomer.

and 1215 cm^{-1} are due to the vibration of the sulfonate group. The absorption peak at about 800 cm^{-1} indicates the existence of disubstituted phenyl groups and implies that the sulfonation occurred not only at polybutadiene segments but also at polystyrene segments. The characteristic absorption peaks at 960, 1640, and 3000 cm^{-1} are due to the double bonds of polybutadiene units, and those at 905 and 700 cm^{-1} and at 750 and 905 cm^{-1} are due to the phenyl rings of polystyrene units.

Figure 5 shows a TEM micrograph of the lead-sulfonated SBS ionomer without the addition of zinc stearate. Because lead ions belong to a heavy metal, they can absorb electrons and appear black in micrographs. The black spots seem to be the ionic domains or ionic clusters in SBS.
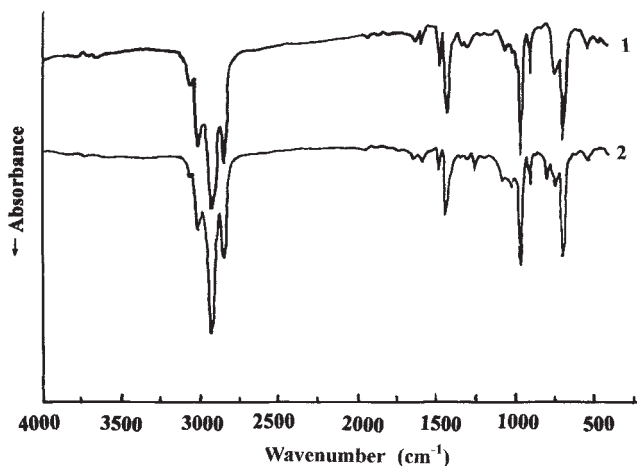
The dynamic mechanical spectrum of the zinc-sulfonated SBS ionomer is shown in Figure 6. In the curve of tan δ versus the temperature, there are three peaks at −82.9, 68.0, and 96.5°C. The peak at the lowest temperature represents the glass-transition temperature (T_g) of the polybutadiene block matrix containing a small number of ion pairs or multiplets, the peak at the medium temperature represents T_g of the polystyrene block domains, and the peak at the highest temperature is the transition temperature or dissociation temperature of the ionic domains.

Melt flow of the SSBS ionomer

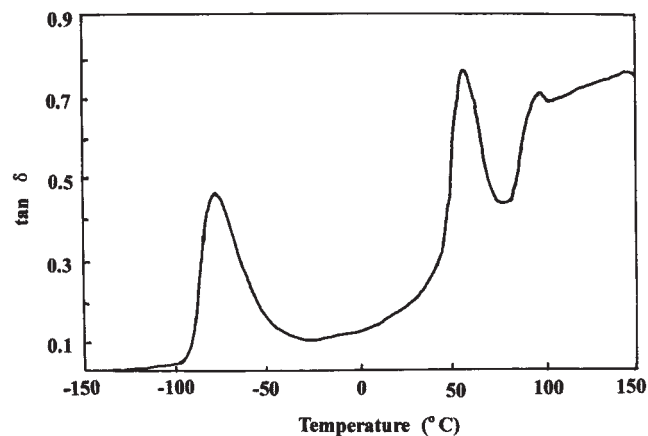The metallic-ion-neutralized SSBS ionomer could hardly be kneaded uniformly at 160°C or be compres-

Figure 4 IR spectra of (1) SBS and (2) the sodium-sulfonated SBS ionomer.

Figure 6 Dynamic mechanical spectrum of the sodium-sulfonated SBS ionomer.
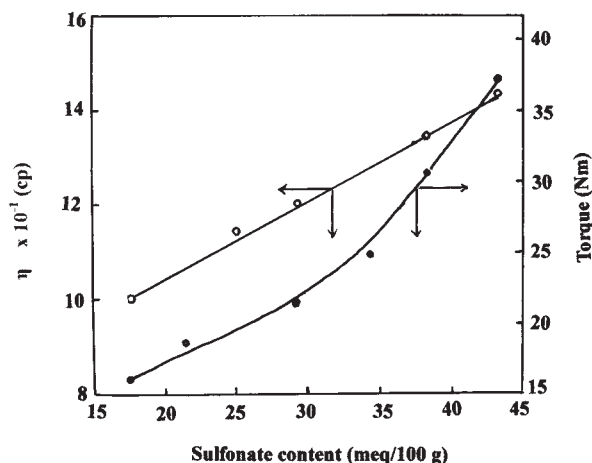
Figure 7 Effects of the sulfonate content of the sodium SBS ionomer with 10 wt % zinc stearate on the melting torque at 160°C and on the 5% solution viscosity (η) of the ionomer in a mixed solvent of toluene and methanol (9/1 v/v).

sion-molded well because of the strong association between the sulfonate groups on the different ionomer chains. However, when zinc stearate as an ionic plasticizer was added, the sample was plasticized and could be kneaded together easily.

Figure 7 indicates the effect of the sulfonate content on the equilibrium melt torque or melt viscosity of the sodium ionomer with 10% zinc stearate at 160°C with a Brabender plasticorder. The equilibrium torque increased gradually at first and then more rapidly with an increasing sulfonate content in the ionomer. It could be concluded that an increase in the sulfonate content caused an increase in the ionic association and thus increased the viscosity.

The effects of different types of cations on the melt viscosity of the ionomer are listed in Table I. The melt viscosity of the ionomer decreased in the following order of cations used in the neutralization: for the ionomers with monovalent cations, $Li^+ > Na^+ > K^+$,

TABLE I
Effects of the Types of Cations Used in the Neutralization on the Torque Values of the Ionomers at 160°C

Cation	Ionic potential	Torque (Nm)
Li^+	1.47	28
Na^+	1.03	24
K^+	0.75	21
Pb^{2+}	1.65	44
Zn^{2+}	2.70	36
Mg^{2+}	3.03	33
Ca^{2+}	2.02	23
$(C_2H_5)_3NH^+$	—	18

For the SBS ionomer, sulfonate content = 29.1 mequiv of $SO_3H/100$ g, neutralization degree = 1.2, and zinc stearate/ionomer = 10 wt %.

TABLE II
Effect of the Amount of Added Zinc Stearate on the Mechanical Properties of the Sodium SBS Ionomer

Zinc stearate (wt %)	TS (MPa)	UE (%)	PS (%)
0	14.1	787	24
5	15.7	798	26
10	17.2	823	24
15	—	—	—

For the SBS ionomer, sulfonate content = 29.1 mequiv of $SO_3H/100$ g and neutralization degree = 1.2. TS = tensile strength; UE = ultimate elongation; PS = permanent set.

and for the ionomers with divalent cations, $Pb^{2+} > Zn^{2+} > Mg^{2+} > Ca^{2+}$. In the former case, the melt viscosity decreased with decreasing ionic potential; this is also shown in the Table. This occurred because the higher the ionic potential was of the cation, the larger the repulsion force was between the neighboring sulfonate groups in the macromolecules, and this resulted in more straightening of the macromolecules in the melt and hence higher melt viscosity. For ionomers with divalent cations, the melt viscosity also decreased with decreasing ionic potential, except for the more covalent Pb^{2+} and Zn^{2+}.

However, for the ionomer neutralized with ethylamine, the melt viscosity was the lowest, even without ionic plasticizer. This result was similar to that for the ionomers of sulfonated butyl rubber.[6]

Solution viscosity of the sodium-sulfonated SBS ionomer

The sodium-sulfonated SBS ionomer with a higher sulfonate content could not be dissolved completely in toluene but could be dissolved completely in a mixed solvent of toluene and methanol (9/1 v/v). Figure 7 also illustrates the solution viscosities of the ionomers with different sulfonate contents in a mixed solvent of toluene and methanol (9/1 v/v) at a 5% concentration and at room temperature. The solution viscosity increased almost linearly with increasing sulfonate content in the ionomer, and this implied that the greater the sulfonate content was, the more ion association there was between the macromolecules; this resulted in higher resistance to flow or higher viscosity.

Mechanical properties of the sulfonated SBR ionomer

Table II shows the tensile strength, ultimate elongation, and permanent set of the ionomer in the presence of various amounts of zinc stearate. The tensile strength and ultimate elongation increased with increasing amounts of zinc stearate as a plasticizer up to 10%, whereas the ionomer containing 15% zinc stear-

TABLE III
Effect of the Sulfonate Content on the Mechanical Properties of the Sodium SBS Ionomer

Sulfonate content (mequiv/100g)	TS (MPa)	UE (%)	PS (%)
17.7	12.2	657	20
21.3	13.4	666	24
25.1	14.1	687	24
29.1	17.2	823	24
34.8	18.7	867	26
36.6	20.8	858	28
43.4	22.3	923	32

Neutralization degree = 1.2; zinc stearate/ionomer = 10 wt %. TS = tensile strength; UE = ultimate elongation; PS = permanent set.

ate flowed as a liquid during melt mixing and could not be molded. The effect of zinc stearate on the mechanical properties of the ionomer could be interpreted as follows. With an increasing amount of zinc stearate, more zinc stearate was distributed in the ionic domains of the ionomer. This reduced the size of the domains and the number of domains, or the number of physical crosslinks increased; this resulted in increased tensile strength. However, excess zinc stearate separated. A uniform distribution of ionic domains in the presence of zinc stearate also made the exchange of ionic bonds easier, thus increasing the ultimate elongation of the ionomer.

Table III indicates that with increasing sulfonate content, both the tensile strength and ultimate elongation increased because of the increased number of ionic domains formed in the ionomers with higher sulfonate content. In the presence of zinc stearate, a uniform distribution of ionic domains also made the exchange of ionic bonds easier, thus increasing the ultimate elongation of the ionomer.

The ionomer still behaved as a thermoplastic elastomer and showed better mechanical properties than the original SBS because it contained two kinds of physical crosslinks, one from glassy polystyrene domains and the other from ionic domains.

The types of cations used in the neutralization also showed different influences on the mechanical properties of the ionomer, as summarized in Table IV. The tensile strength of the ionomers was arranged in the following order: $Pb^{2+} > Zn^{2+} > Li^+ > Mg^{2+} > Na^+ > (C_2H_5)NH_3^+ > K^+$.

For the monovalent cations, the tensile strength of the ionomers seemed to decrease with decreasing ionic potential: $Li^+ > . Na^+ > K^+$. The higher the ionic potential was, the more dispersed the ionic domains were and, therefore, the greater the ionomer tensile strength was. The SSBS ionomer neutralized with triethylamine had a lower tensile strength, perhaps because of its larger steric hindrance, which retarded the

strong association of ions and the formation of ionic domains.

For the divalent cations, the tensile strength of the ionomers decreased with increasing ionic potential: $Pb^{2+} > Zn^{2+} > Mg^{2+}$. This case was quite contrary to the case of the monovalent cations. The reason may be the different natures of the monovalent and divalent cations in the formation of crosslinks. The former formed weak crosslinkages through the association of oppositely charged ions, whereas the latter formed ionic bridging crosslinks.

CONCLUSIONS

Gelation occurred during the sulfonation of SBS in cyclohexane at a 5–10% concentration, whereas in the presence of a portion of acetone, sulfonation proceeded smoothly without gelation. The optimum conditions were a sulfuric acid/Ac_2O molar ratio of 1/1.75, an SBR concentration of 12–15% (w/v), a reaction temperature of 25°C, and a reaction time of 60–80 min. TEM microphotographs of the lead ionomer indicated the presence of ionic domains. A dynamic mechanical spectrum showed the presence of three transition temperatures, and this indicated that the ionomer was a multiphase polymer. The melt viscosity of the ionomer increased with the sulfonate content. The melt viscosities of the different ionomers neutralized with different cations seemed to decrease with decreasing ionic potential with both monovalent cations and divalent cations. The solution viscosity of the sodium-sulfonated ionomer increased with increasing sulfonate content, and this indicated ionic association between the macromolecules in the solution. The ionomer still behaved as a thermoplastic elastomer and showed better mechanical properties than the original SBS because it contained two kinds of physical crosslinks, one from glassy polystyrene domains and the other from ionic domains. The tensile strength and ultimate elongation of the ionomer in-

TABLE IV
Effects of the Types of Cations Used in the Neutralization on the Mechanical Properties of the Ionomer

Cation	TS (MPa)	UE (%)	PS (%)
Li^+	20.2	892	32
Na^+	17.2	823	24
K^+	16.1	788	26
Pb^{2+}	21.9	798	32
Zn^{2+}	21.5	806	36
Mg^{2+}	18.5	823	30
$(C_2H_5)NH_3^+$	16.5	958	24

Sulfonate content = 29.1 mequiv of SO_3H/100 g; neutralization degree = 1.2; zinc stearate/ionomer = 10 wt %. TS = tensile strength; UE = ultimate elongation; PS = permanent set.

creased with an increasing amount of zinc stearate up to 10% zinc stearate and with an increasing sulfonate content, whereas the permanent set remained below 35%. The tensile strength of the ionomers decreased in the following order of cations used in the neutralization: $Pb^{2+} > Zn^{2+} > Li^{+} > Mg^{2+} > Na^{+} > (C_2H_5)NH_3^{+} > K^{+}$.

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