Physicomechanical and Dielectric Properties of Magnesium and Barium Ionomers Based on Sulfonated Maleated Styrene-Ethylene/Butylene-Styrene Block Copolymer

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ABSTRACT: Ionomers, containing both carboxylate and sulfonate anions on the polymer backbone, based on metal cations like Mg^{+2} and Ba^{+2} were prepared by sulfonating maleated styrene-ethylene/butylene-styrene block copolymer, hereafter referred to as m-SEBS, followed by its neutralization by metal acetates. Infrared spectroscopic studies reveal that sulfonation reaction takes place in the *para* position of the benzene rings of polystyrene blocks and metal salts are formed on neutralization of the precursor acids. Dynamic mechanical thermal analyses show that sulfonation causes increase in T_g of the rubbery phase of m-SEBS and decrease in tan δ at T_g of the hard phase, along with formation of a rubbery plateau. The changes become more pronounced on neutralization of the sulfonated maleated SEBS, and the effect is greater in the case of Ba salt. Dielectric thermal analyses (DETA) show that incorporation of ionic groups causes profound changes in the dielectric constant (ϵ') of m-SEBS. In addition to the low temperature glass–rubber transition, the plot of ϵ' vs. temperature shows occurrence of a high-temperature transition, also known as the ionic transition. Activation energy for the dielectric relaxation could be determined on the basis of frequency dependence of the ionic transition temperature. Two values of the activation energy for the dielectric relaxation refer to the presence of two types of ionic aggregates, namely multiplets and clusters. Incorporation of the ionic groups causes enhancement in stress–strain properties as well as retention of the properties at elevated temperatures (50° and 75°C), and the effect is more pronounced in the case of Ba ionomer. Although sulfonated ionomers show greater strength than the carboxylated ionomers, the sulfonated maleated ionomers show higher stress–strain properties in comparison to both sulfonated and carboxylated ionomers. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 816–825, 2000

Key words: sulfonated SEBS; maleated SEBS; sulfonated maleated SEBS; ionomer; DMTA; DETA; multiplets and clusters; stress–strain properties

INTRODUCTION

Thermoplastic block copolymers like styrene–ethylene/butylene–styrene (SEBS) suffer from the inherent disadvantage in high-temperature applications. One way to improve the high-temperature property might be to incorporate pendant ionic groups in the polymer backbone to form ionomers or ionic polymers. Dramatic changes in the properties of the polymer take place when the concentration of the pendant salt groups reaches 10 to 15 mol %.[1–5] There are two convenient routes for the preparation of ionomers: (a) copolymerization of a low level of functionalized monomer with an olefinic unsaturated monomer,[6] and (b) direct functionalization of a preformed polymer.[7,8] Ionomers are generally based on either carboxylated or sulfonated salts.[3,6,9–11] Weiss et al. has reported the properties of ionomers based on sulfonated SEBS.[12] But ionomers having both carboxylated and sulfonated groups on the same polymer backbone have not been studied. The

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present investigation deals with formation of an ionomer based on SEBS containing both carboxylated and sulfonated groups. It has been reported that ionic interactions are stronger in sulfonated salts than the corresponding carboxylated salts in a low polarity polymer matrix, because of the higher degree of polarity inherent in the sulfonate system and a consequent increase in the strength of the ion-pair associations.[3,5,13,14] However, properties of ionomers deteriorate due to gel formation, if the level of sulfonation is increased.[15,16] An alternate way to increase the extent of ionic associations might be incorporation of both carboxylated and sulfonated groups at optimum levels. In the present investigation, maleated SEBS, abbreviated as m-SEBS, was sulfonated, and then neutralized to form an ionomer containing both carboxylate and sulfonate anions on the same backbone and magnesium or barium as the cation. Permittivity was chosen as the dielectric parameter because preliminary experiments reveal that different relaxations could be easily differentiated in the plots of permittivity vs. temperature.[17] To understand the effect of coexistence of sulfonated and carboxylated groups in the base polymer, the physical properties of sulfonated SEBS and carboxylated SEBS have been compared with sulfonated maleated SEBS, abbreviated as s-m-SEBS.

EXPERIMENTAL

Materials

The polymers used were styrene–ethylene/butylene–styrene block copolymer (SEBS), and its maleated derivative, Kraton FG1901X, obtained from Shell Chemical Company, USA. The polymer has a styrene content of 30% (by wt), ethylene–butylene content of 70% and the maleic acid/maleic anhydride level of 19.2 mEq/100 g of polymer.

Sulfonation

The method is similar to that described by Makowski and Lundberg.[18] The polymer (that is, SEBS or m-SEBS) was taken in 1,2-dichloroethane. After complete disolution the solution was heated to 50°C and purged with nitrogen for 1 h. Then an appropriate amount of acetyl sulfate [1:4 mixture of conc. H_2SO_4 (98.5%) and acetic anhydride] was added and stirred for 2 h at this temperature. Next isopropanol was added to arrest the sulfonation reaction. The product was steam stripped, washed with boiling water for 2 h, and dried under vacuum for 15 days at 50°C. The product was termed either sulfonated SEBS, abbreviated as s-SEBS, or sulfonated maleated SEBS, abbreviated as s-m-SEBS, as the case may be. The sulfonation level was determined by titration with standard NaOH solution (standardised by *p*-toluene sulfonic acid solution) and was found to be 41 mEq for s-SEBS and 43 mEq for s-m-SEBS per 100 g of polymer.

Preparation of Sulfonated Ionomers

The sulfonated products, namely s-SEBS or s-m-SEBS, was taken in toluene/methanol (90/10, v/v) mixture and neutralized stoichiometrically by either magnesium acetate in methanol or barium acetate in methanol, along with a few drops of water. Then a sufficient amount of either magnesium or barium acetate was added to completely neutralize the sulfonic acid groups. The product was steam stripped, washed thoroughly with water, and dried under vacuum at 70°C for 7 days. While the magnesium salts were designated as Mg-s-SEBS and Mg-s-m-SEBS, the barium salts were designated as Ba-s-SEBS and Ba-s-m-SEBS, respectively.

Preparation of Carboxylated Ionomers

The magnesium and barium salts of m-SEBS, namely Mg-m-SEBS and Ba-m-SEBS, were prepared by neutralizing m-SEBS in 1,2-dichloroethane by magnesium and barium acetate, respectively. The products were steam stripped, washed with water, and dried at 70°C in vacuum for 15 days. The carboxyl acid content in Mg-m-SEBS and Ba-m-SEBS was 19.2 mEq/100 g of polymer, according to the specifications of the base polymer, m-SEBS, as supplied by the manufacturer.

TESTING

Infrared Spectroscopic Studies

Infrared spectra of compression moulded thin films of the polymers were obtained in a Perkin-Elmer spectrophotometer, model 843, at a resolution of 3.2 cm^{-1}.

Dynamic Mechanical Thermal Analyses (DMTA)

The dynamic mechanical thermal analyses of the polymers were evaluated using a dynamic mechanical thermal analyser (model MK-II, Polymer Laboratories, UK) in shear mode at a frequency of 1 Hz and at a 64-μm peak-to-peak strain in the temperature range from −150°C to +150°C, with a 2°C min^{-1} temperature rise.

Dielectric Thermal Analyses (DETA)

A dielectric analyser DEA 2970 from TA Instruments Inc., USA, coupled with a 2000 Thermal Analyser, was used to measure the dielectric properties of the samples. The experiment was carried out at variable frequencies ranging from 10 to 3×10^5 Hz, using the temperature range of −150°C to +225°C at a heating rate of 3°C min^{-1} in nitrogen atmosphere.

Stress–Strain Properties

The stress–strain properties of the polymers were measured in a ZWICK UTM 1445 according to ASTM-D-412-80. The samples were kept for 5 min in a hot chamber prior to the high temperature testing.

Thermogravimetric Analyses

The thermogravimetric experiments were carried out on a Du Pont 9000 Thermal Analyser (model 951) at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Infrared Spectroscopic Studies

The representative infrared spectra of the polymers are shown in Figure 1. The spectrum of m-SEBS shows a sharp band at 1716 cm^{-1}, which characterizes the carbonyl stretching (>C═O) of a five-membered cyclic anhydride group in hydrogen-bonded maleic acid form.[19] The absorbance at 1602 cm^{-1} is due to monosubstituted benzene ring vibration, whereas the absorbance band at 700 cm^{-1} indicates the C—H stretching of the benzene ring.[20] The carboxylate salt (Mg-m-SEBS) shows the occurrence of two new bands at 1583 and 1558 cm^{-1} as a doublet, which is ascribed to the asymmetric carboxylate stretching vibration. Ba-m-SEBS also shows the presence of a doublet at 1583 and 1558 cm^{-1} for the carboxylate asymmetric stretching vibration.

Mg-s-m-SEBS is characterized by several bands and shoulders in the region of 700–1400 cm^{-1}. The band at 1199 cm^{-1} is due to the asymmetric stretching of S═O, which clearly indicates the symmetric bonding of Mg^{+2} ions with SO_3^- anion, whereas the absorbance at 1261 cm^{-1} is due to the asymmetric stretching vibration of S═O in $—SO_3^-$ anion.[21,22] Again, the band at 1020 cm^{-1} results from the in-plane bending vibration of a phenyl ring substituted with a metal sulfonate group. The characteristic band at 805 cm^{-1} confirms the *para* substitution in the benzene ring, which clearly indicates that sulfonation preferentially occurs at the *para* position of the benzene ring in the polystyrene block.[19] Moreover, the bands at 1583 and 1558 cm^{-1} in the high-frequency region indicate the symmetric stretching vibration of the carboxylate anion.[23]

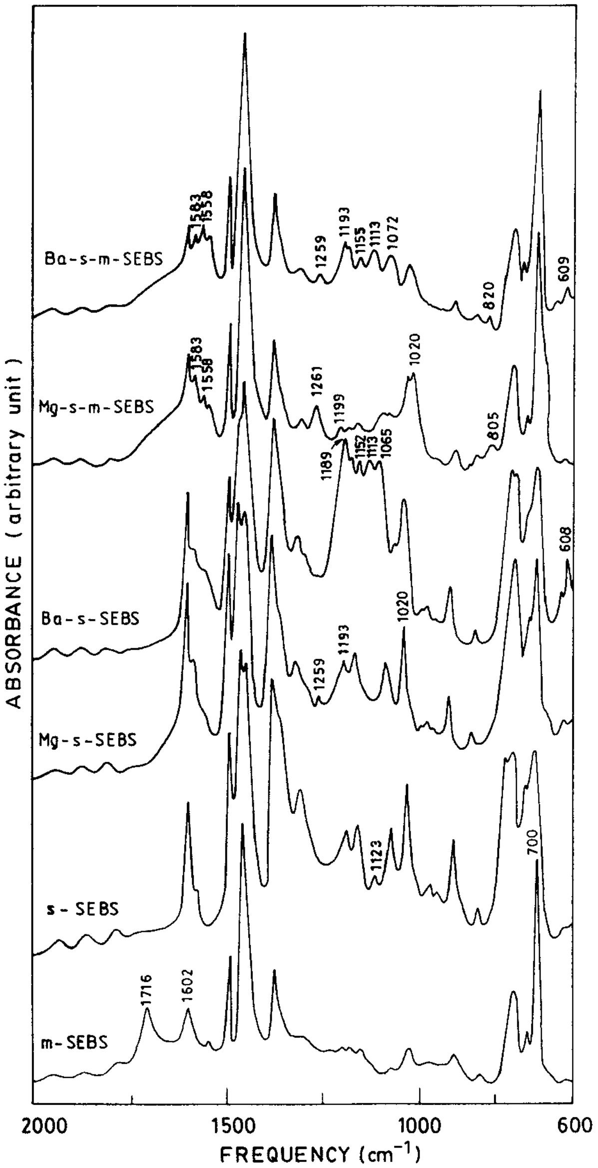

Figure 1 Infrared Spectra of m-SEBS, s-SEBS, Mg-s-SEBS, Ba-s-SEBS, Mg-s-m-SEBS, and Ba-s-m-SEBS.

Infrared spectra of Ba-s-m-SEBS shows a pronounced splitting pattern due to strong intermolecular interaction. The absorbance at 1072 cm^{-1} is due to the symmetric stretching of the —SO_3^- anion, whereas the absorbance maxima at 1113, 1155, and 1193 cm^{-1} are due to the asymmetric stretching vibration of the S=O group. Furthermore, the peak at 1259 cm^{-1} is attributed to the asymmetric stretching of the sulfonate anion.[22] While the 820 cm^{-1} peak indicates the presence of the *para*-substituted benzene ring, the band at 609 cm^{-1} is due to C—S stretching of the $=\overset{|}{\mathrm{C}}\!-\!\mathrm{SO_3^-}$ anion. The doublet at 1583 and 1558 cm^{-1} is due to the asymmetric stretching vibration of carboxylate anions.[23] s-SEBS shows a new absorbance band at 1123 cm^{-1} due to a hydrated sulfonate anion attached to the benzene ring, thereby confirming that the benzene ring is disubstituted.[21] The other characteristic sulfonate stretching vibration of sulfonated SEBS in the region of 1000–1400 cm^{-1} could not be clearly identified due to the absorbance of the base polymer in the same region. However, it could be seen that the intensity of the peak changes upon sulfonation. Mg-s-SEBS shows the asymmetric stretching of S=O at 1193 cm^{-1}. It also shows the characteristic absorbance at 1259 cm^{-1} and 1020 cm^{-1}, which are due to asymmetric stretching of S=O in the sulfonate anion and the in-plane bending vibration of the sulfonate anion. Ba-s-SEBS shows the characteristic absorbance of 1065 cm^{-1}, which is due to the symmetric stretching of the SO_3^- anion. The other characteristic sulfonate bands for Ba-s-SEBS appear at 1113, 1152, and 1189 cm^{-1}, due to the asymmetric stretching vibration of sulfonate anions. It shows another band at 608 cm^{-1} due to the C—S stretching of the $=\overset{|}{\mathrm{C}}\!-\!\mathrm{SO_3^-}$ anion. The decrease in vibrational frequency for SEBS ionomers is due to the formation of less stronger ionic associations in comparison to s-m-SEBS ionomers.

Figure 2 represents the difference spectrum (that is, ionomer minus base polymer) in the case of Mg-s-m-SEBS and Ba-s-m-SEBS. The difference spectra were taken with respect to the 700 cm^{-1} peak as the standard one for thickness correction. The difference spectrum shows the disappearance of the hydrogen bonded cyclic anhydride group showing absorbance at 1716 cm^{-1} and the appearance of the carboxylate anion peaks (1583, 1558 cm^{-1}) in both salts. The change in intensity of the band at 1020 cm^{-1} is characteristic of symmetric stretching vibration of the sulfonate anion, and it is also observed in the difference spectrum.[20] Moreover, the C—S stretching of the $=\overset{|}{\mathrm{C}}\!-\!\mathrm{SO_3^-}$ anion at 609 cm^{-1} is also clearly observed in the difference spectrum. A schematic representation of the mechanism of sulfonation based on the spectral data is shown in Figure 3.

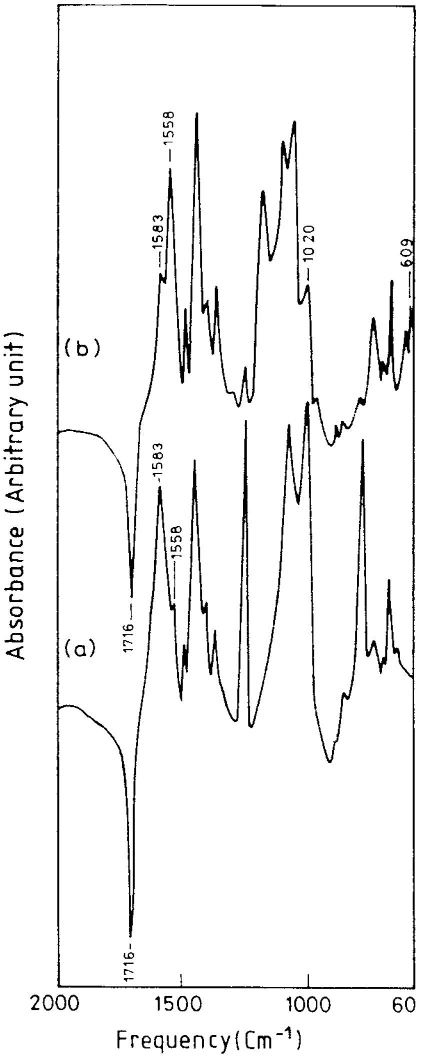

Figure 2 Difference spectra of (a) Mg-s-m-SEBS minus m-SEBS, and (b) Ba-s-m-SEBS minus m-SEBS.

Dynamic Mechanical Thermal Analyses

Figure 4 shows the plots of storage modulus (E') vs. temperature. Results of dynamic mechanical thermal analyses are summarized in Table I. The ionomers show lower E' than the parent polymer (that is, m-SEBS and s-m-SEBS) at lower temperatures (that is, up to 93°C, the glass–rubber transition temperature of the polystyrene phase). A

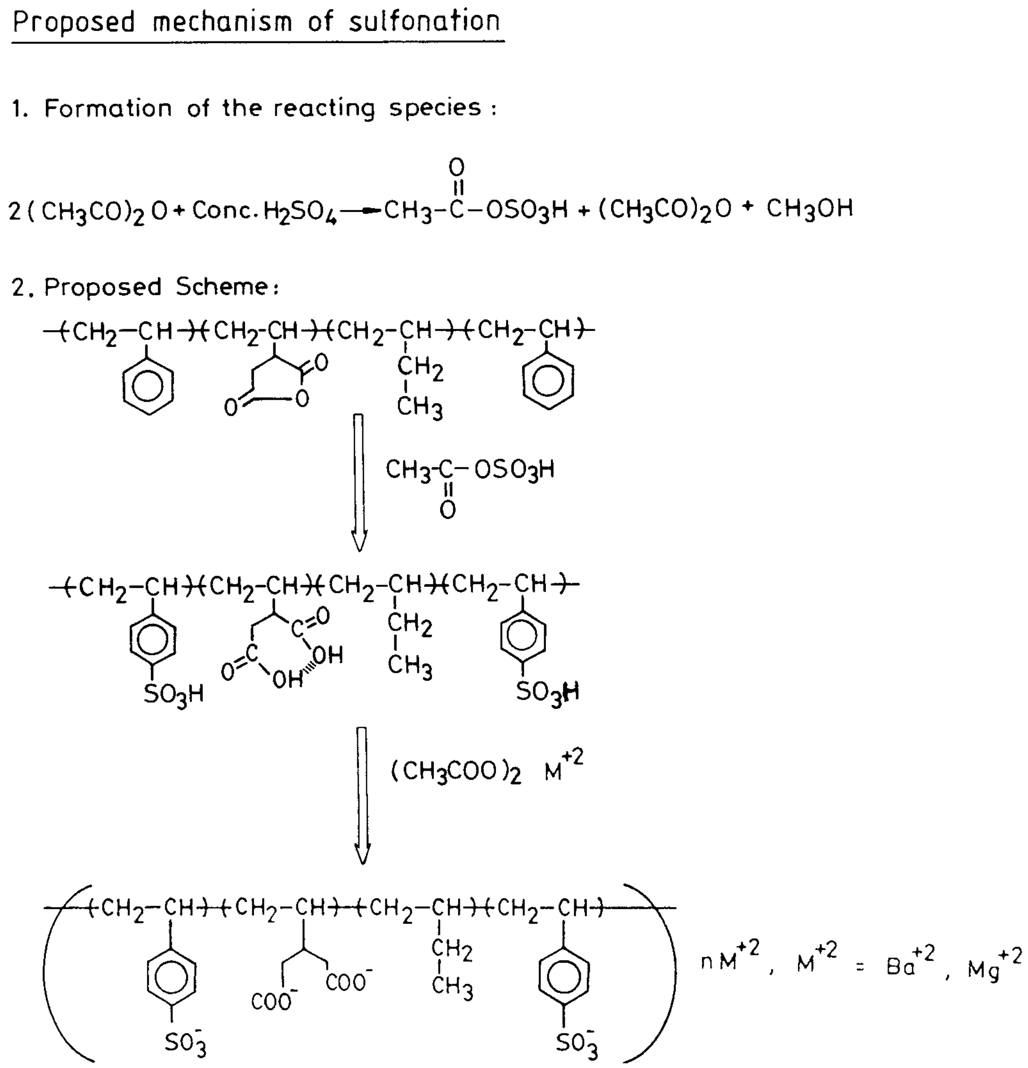

Figure 3 Schematic representation of the sulfonation of m-SEBS block copolymer.

drop in E' due to chemical modification of EPDM has also been reported earlier.[24] At higher temperature the modulus of the nonionomers (m-SEBS and s-m-SEBS) drop drastically due to plastic flow, while the ionomers resist the plastic flow due to network formation, and show a rubbery plateau with modulus in the range of 10^7 Pa at 150°C. It is obvious that the modulus of the ionomers remain constant in the high-temperature region, while the same for the nonionomers show a decreasing trend at elevated temperatures. Due to the instrumental limitations, the experiments could not be conducted beyond 150°C. Figure 4 also shows the plots of tan δ against temperature for the different polymers. The base polymer (m-SEBS) shows two transitions, one at -36°C due to $T_{g(\mathrm{EB})}$, and the second one at 93°C due to $T_{g(\mathrm{PS})}$. $T_{g(\mathrm{EB})}$ refers to the glass–rubber transition for the ethylene/butylene block and $T_{g(\mathrm{PS})}$ refers to the same for the polystyrene phase. At higher temperature (>100°C), the tan δ increases drastically due to matrix softening. Upon sulfonation, $T_{g(\mathrm{EB})}$ increases by 5°C, with an increase in tan δ value at $T_{g(\mathrm{EB})}$. However $T_{g(\mathrm{PS})}$ remains unchanged, along with a significant decrease in tan δ value at $T_{g(\mathrm{PS})}$. Because sulfonation occurs at the polystyrene segments, as indicated by IR spectra, increase in E', with a consequent decrease in loss modulus (E'') of the polystyrene segments cause a reduction in tan δ value at $T_{g(\mathrm{PS})}$. Formation of ionomers (that is, by neutralization of the sulfonated derivative by metal acetates) causes a further increase in $T_{g(\mathrm{EB})}$ along with a marginal increase in tan δ at $T_{g(\mathrm{EB})}$, but with a significant decrease in tan δ value of $T_{g(\mathrm{PS})}$ (Table I). Formation of the ionomer lowers

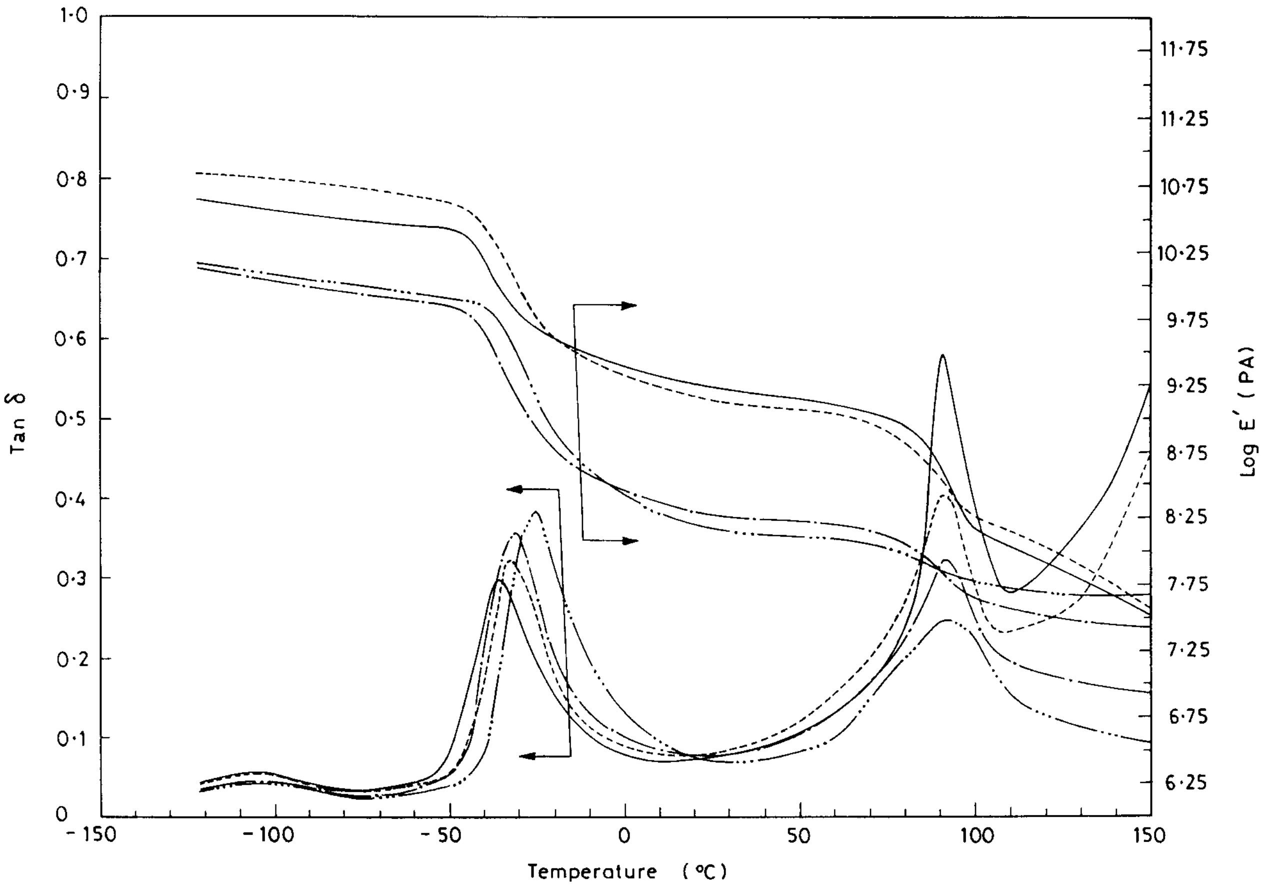

Figure 4 Plots of mechanical loss (tan δ) and storage modulus (E') versus temperature for m-SEBS (—), s-m-SEBS (– – –), Mg-s-m-SEBS (– · – · –) and Ba-s-m-SEBS (– · · · –).

the E' value in the low-temperature region, thereby increasing tan δ at $T_{g(\mathrm{EB})}$. Neutralization reaction causes enhancement in E' of the polystyrene phase along with lowering of E'', thereby lowering the tan δ value at $T_{g(\mathrm{PS})}$, which follows the order m-SEBS > s-m-SEBS > Mg-s-m-SEBS > Ba-s-m-SEBS. Furthermore, formation of ionomer provides a rubber-like network for the soft phase,[16] shifting the $T_{g(\mathrm{EB})}$ to a higher temperature. The effect is more pronounced in the case of a barium ionomer, compared to the magnesium ionomer. At higher temperature (>100°C) tan δ for the ionomers, unlike m-SEBS and s-m-SEBS, does not increase due to matrix softening, but remains constant due to formation of a rubbery network.

Dielectric Measurements

The variation of a dielectric constant or permittivity (ϵ') with temperature at a frequency of 10

Table I Results of Dynamic Mechanical Thermal Analyses

	T_g (°C)		Tan δ at T_g		$E'' \times 10^{-7}$ (Pa) at T_g		$E' \times 10^{-7}$ (Pa) at T_g	
Polymer	EB	PS	EB	PS	EB	PS	EB	PS
m-SEBS	−36	93	0.30	0.58	261	16.1	1059	28.7
s-m-SEBS	−31	93	0.32	0.40	323	10.5	907	26.0
Mg-s-m-SEBS	−29	93	0.36	0.33	38	1.9	103	5.62
Ba-s-m-SEBS	−25	93	0.38	0.26	51	1.6	133	6.74

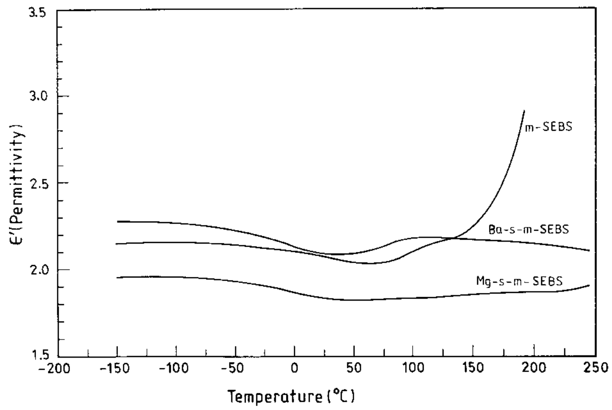

Figure 5 Plots for ϵ' versus temperature for m-SEBS, Mg-s-m-SEBS, and Ba-s-m-SEBS.

Hz for the base polymer and the ionomers are shown in Figure 5. In the case of m-SEBS, as the temperature increases, ϵ' decreases, and attains a minimum value. An increase in volume at a higher temperature causes a decrease in the number of dipoles per unit volume (dipole density). Accordingly, ϵ' decreases marginally with an increase in temperature up to 0°C, as is observed in the case of many nonpolar and slightly polar polymers.[25–28] A further increase in temperature, particularly beyond 100°C, may cause thermal softening of the polymer, which facilitates dipole rotations, thereby causing a sharp increase in ϵ'. In the case of ionomers, the dependence of ϵ' on temperature is similar in the low-temperature region but the behavior changes at higher temperature. For the Mg ionomer, for example, ϵ' remains almost constant with an increase in temperature, in contrast to the base polymer, which shows a sharp increase in ϵ'. However, barium ionomer shows gradual decrease in ϵ' in the high-temperature region due to increased ionic aggregation, presumably arising out of the greater ease of ion hopping,[29] which restricts the chain mobility and hinders the process of dipole orientation under an electric field.

Figure 6 shows the plots of $d\epsilon'/dT$ vs. temperature obtained from the dielectric thermal analyses of the base polymer, that is, m-SEBS, and the ionomers (that is, Mg-s-m-SEBS and Ba-s-m-SEBS) at the frequency of 10 Hz. All the polymers mentioned above contain three main dipolar relaxations. For m-SEBS, these transitions occur at −100°, 42°, and 91°C, whereas for the magnesium ionomer, the transitions occur at −100°, 72°, and 123°C, respectively, and for the barium ionomer, the corresponding transition temperatures are −100°, 75°, and 135°C, respectively. The lowest temperature relaxation (γ is associated with crank shaft movement of the —CH_2 groups. The intermediate temperature relaxation (β) is due to restricted movements of main chain ethylene/butylene segments, and the higher temperature relaxation (α) is associated with the polystyrene hard-segmental associations. In the case of the metal salts, the α and β relaxations occur at higher temperatures compared to the base polymer, with the γ-relaxation temperature remaining unchanged. This may be due to the physical crosslinks arising out of the ionic aggregates, which restrict the motion of the chain segments requiring higher energy for the molecular motion. Furthermore, both ionomers exhibit a new high-temperature transition that occurs at 166°C for Mg-salt and 172°C for Ba-salt. This high-temperature relaxation, which is absent in the case of the base polymer, is associated with the polymeric chain segments in the vicinity of the ionic clusters present in the ionomer, and may be termed as the ionic relaxation, and the corresponding temperature is designated as Ti. Weiss et al. observed a high-temperature (180°C) rubbery plateau in the dynamic mechanical spectra of the sulfonated SEBS ionomer.[16] It is observed that Ti is shifted to a higher temperature side with the increase in frequency. The thermal activation of dipolar relaxation often follows the well-known Arrhenius law,[30] where the activation energy (E_{act}) can be calculated from the slope in the plot of log f vs. $1/T_{max}$, where f represents the measurement fre-

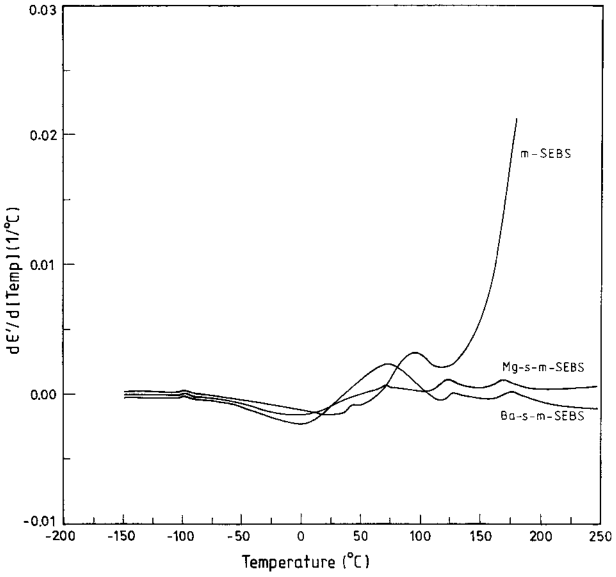

Figure 6 Derivative plots of ϵ' (that is, $d\epsilon'/dT$ vs. temperature) of m-SEBS, Mg-s-m-SEBS, and Ba-s-m-SEBS.

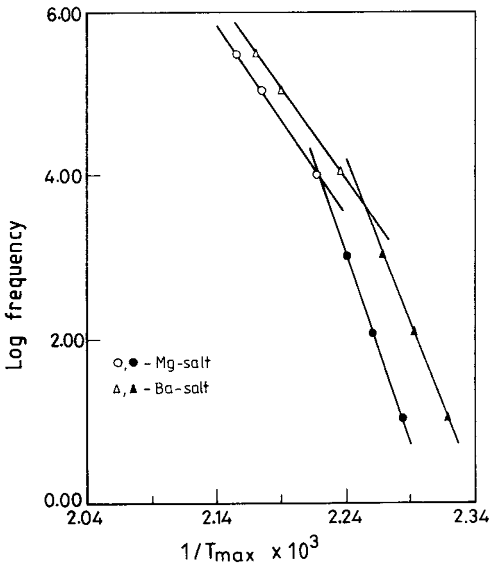

Figure 7 Plots of log (frequency) versus $1/T_{\max}$ at the frequency range of $10–10^3$ Hz (●, ▲) and $10^4–3 \times 10^5$ Hz (○, △) for Mg-s-m-SEBS (○, ●) and Ba-s-m-SEBS (△, ▲).

quency and $T_{\max}$, the temperature corresponding to the maximum in the plot of $d\epsilon'/dT$ vs. temperature at Ti, at that frequency.[17,30] Figure 7 shows the Arrhenius plots of log (frequency) vs. $1/T_{\max}$. These plots show two slopes—one in the high-frequency region (10^4—3×10^5 Hz), and the other in the low frequency region ($1–10^3$ Hz). The results lead to two activation energy values for the dielectric relaxation. While the activation energy values in the high-frequency region for magnesium and barium ionomers are 92 and 110 KJ/mol, respectively, the same in the low-frequency region are 171 and 239 KJ/mol, respectively.

The ionic comonomer concentration in most ionomers vary from 10 to 15 mol %, and in such compositions the low dielectric constant of the major component (e.g., ethylene, butylene or styrene) leads to the formation of ion pairs, which are believed to aggregate further into "multiplets" of a few ion pairs or "clusters" containing a much larger number of ion pairs.[31,32] Occurrence of two activation energy values for both magnesium and barium ionomers is presumably due to occurrence of two types of ionic aggregates, namely multiplets and clusters.[17,33,34] The transition at lower frequencies shows higher activation energy than that at higher frequencies. The low-frequency transition, which occurs at the lower temperature, might be attributed to smaller ionic groups present in the matrix (i.e., multiplets), whereas the high-frequency transition occurring at rela-

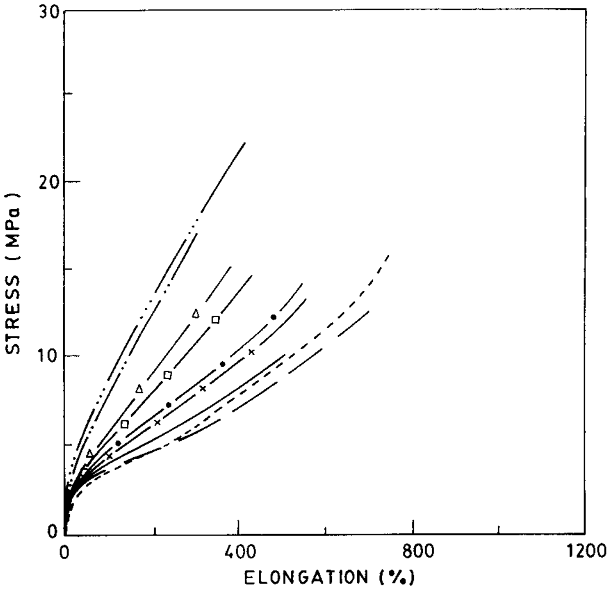

Figure 8 Stress–strain plots at 25°C of m-SEBS (——), s-SEBS (— —), Mg-s-SEBS (—□—), Ba-s-SEBS (—△—), Mg-m-SEBS (—x—), Ba-m-SEBS (—●—), s-m-SEBS (– – –), Mg-s-m-SEBS (– · – · –), and Ba-s-m-SEBS (– · · · –).

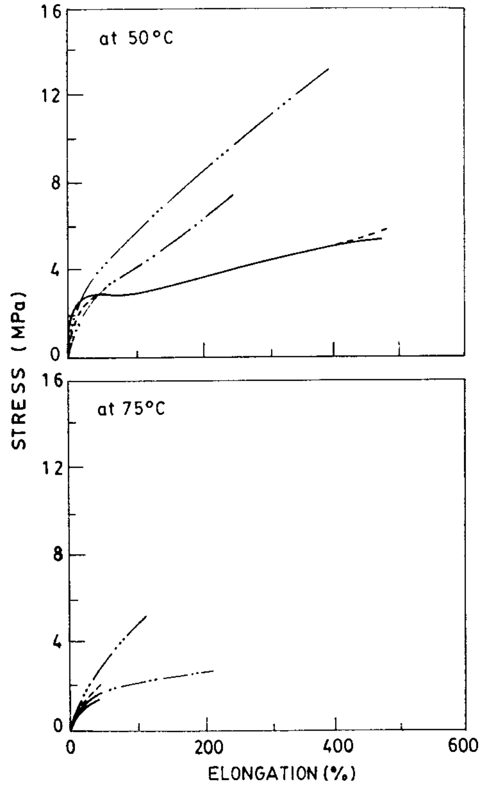

Figure 9 Stress–strain plots of m-SEBS (——), s-m-SEBS (– – –), Mg-s-m-SEBS (– · – · –), and Ba-s-m-SEBS (– · · · –) at 50° and 75°C.

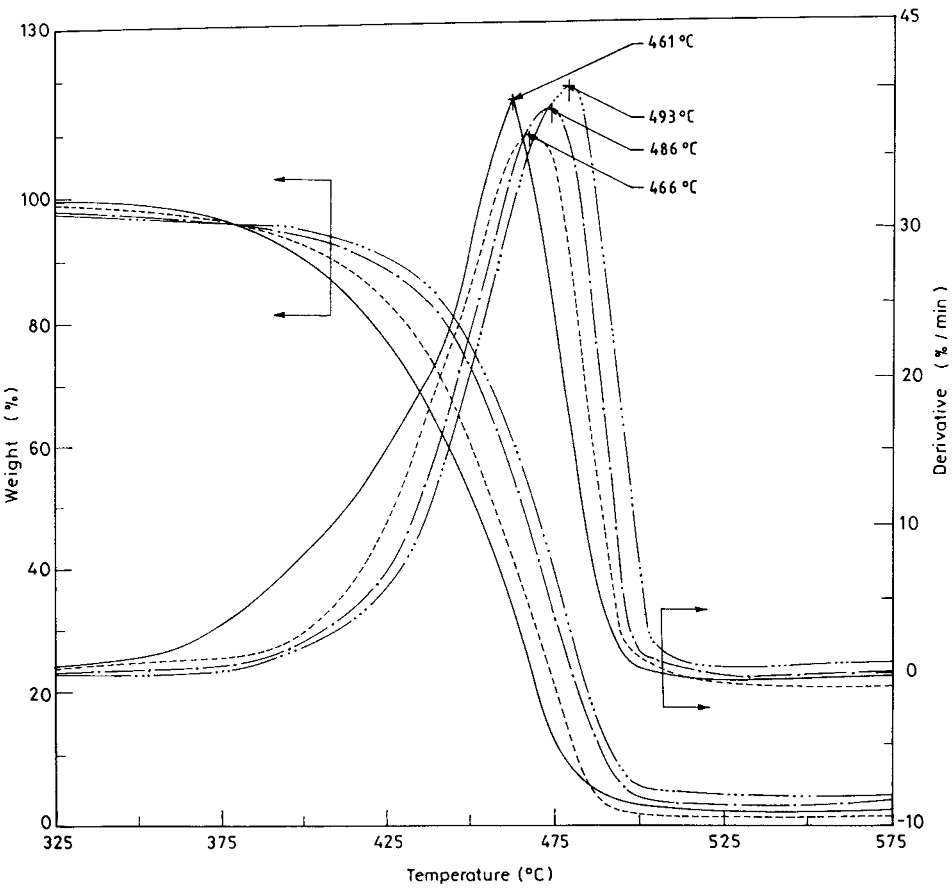

Figure 10 Thermograms of m-SEBS (——), s-m-SEBS (– – –), Mg-s-m-SEBS (– • – • –), and Ba-s-m-SEBS (– • • • –).

tively higher temperature might be originating from the region of restricted mobility chain segments adjacent to the larger ionic aggregates (i.e., clusters).[34,35] The barium ionomer shows higher activation energy than the magnesium ionomer, presumably due to the formation of stronger ionic associations in the former.

Physical Properties

The stress–strain behavior of the polymers at 25°C are shown in Figure 8. Incorporation of ionic groups causes an increase in modulus and tensile strength, but a decrease in elongation at break and the behavior is more pronounced in the case of barium ionomer. Although sulfonated ionomers show greater strength than the carboxylated ionomers, the sulfonated maleated ionomers show higher stress–strain properties in comparison to both sulfonated ionomers and carboxylated ionomers. This is due to the formation of stronger ionic associations in the case of the sulfonated maleated ionomers.

Figure 9 shows that incorporation of ionic groups is responsible for greater retention of properties at elevated temperature, and the Ba ionomer shows higher strength than the Mg ionomer at all temperatures. Results of thermogravimetric analyses (Fig. 10) reveal that thermal stability of the polymers increase in the order, m-SEBS < s-m-SEBS < Mg-s-m-SEBS < Ba-s-m-SEBS.

CONCLUSIONS

Maleated SEBS can be sulfonated, and neutralization of the resulting sulfonated maleated SEBS by magnesium or barium acetates results in formation of ionomers containing both carboxylate and sulfonate groups on the same polymer backbone. Dynamic mechanical thermal analyses reveal formation of a rubbery network in the case of ionomers, as is evident from the formation of rubbery plateau in the dynamical mechanical spectra. Dielectric thermal analyses also reveal formation of a rubbery network arising out of the ionic aggregates in the polymer matrix. DETA results also show occurrence of a high-temperature transition due to the relaxation of the restricted mobility segments of the polymer chains in the neighborhood of the ionic domains. Frequency dependence of the high-temperature relaxation provides two activation energy values due to the occurrence of two types of ionic aggregates, namely multiplets and clusters. Enhanced physical properties and their retention at elevated temperatures are due to the formation of physical crosslinks through ionic associations. The Ba ionomer displays a greater extent of ionic associations compared to the Mg ionomer. Although sulfonated ionomers show greater strength than the carboxylated ionomers, the sulfonated maleated ionomers show higher stress–strain properties in comparison to the both sulfonated ionomers and carboxylated ionomers.

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