

Control of Ionic Interactions in Sulfonated Polystyrene Ionomers by the Use of Alkyl-Substituted Ammonium Counterions

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Synopsis

Polystyrenes containing up to about 20 mol % sulfonic acid are reproducibly and readily prepared by the sulfonation of polystyrene at 50°C with acetyl sulfate in 1,2-dichloroethane solution. The metal salts of sulfonated polystyrene possess extremely high melt viscosities and are soluble in single solvents such as toluene and THF only at very low sulfonate levels. Such properties are the result of the very strong ion-dipole interactions among the metal sulfonate groups. Such strong interactions can be substantially reduced through the neutralization of the sulfonic acid with ammonia and, most especially, relatively simple low molecular weight amines. Sulfonated polystyrenes varying in sulfonic acid content from about 1 mol % to about 20 mol % were neutralized with various mono-, di-, and tri-substituted alkyl amines ranging in alkyl chain length from H (ammonia) to C₂₀, and their rheological and thermal properties were measured. As the number of substituents on the nitrogen increased, the glass transition temperature and the melt viscosity decreased. The tributylamine sulfonates possessed viscosities almost as low as unsulfonated polystyrene and the longer chain amines behaved as if internally plasticized. The properties of amine neutralized sulfonated polystyrenes are concluded to be primarily a function of amine size. Increasing the size of the amine reduces the strength of the ion-dipole interaction by preventing close approach of the amine sulfonate groups.

INTRODUCTION

Within the past decade there has appeared in the literature a large number of papers concerned with the properties and structure of ionomers based on sulfonate groups.^{1,2} A common observation in each of these studies is the occurrence of intermolecular aggregation of the sulfonate groups that results in physical crosslinks that markedly affect the properties of the polymer. These ionic interactions can be subdued, however, by the application of heat or by the introduction of polar plasticizers,³ and, therefore, one can achieve with these ionomers the melt processability characteristics of a thermoplastic and the mechanical and viscoelastic properties analogous to a crosslinked polymer.⁴

One detail common to most of the previous studies of sulfonate ionomers, and ionomers in general, is the use of metal salt counterions. Although changes in the intensity of the ionic interactions can be achieved by using different metal salts, these changes are not substantial. For example, the

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neutralization of a sulfonated ethylene-propylene-diene terpolymer with a metal salt counterion results in an increase of several orders of magnitude in such molecular weight dependent properties as viscosity, yet less than an order of magnitude variation in the melt viscosity was observed for eight different metal salt cations.⁴ Larger variations in the properties of ionomers can be accomplished, however, by using counterions other than metal salts, and this paper is concerned with the properties of sulfonated polystyrenes neutralized with various aliphatic amines.

The use of amine counterions in an ionomer is not without precedent, though no systematic study has been made of the effects of the amine structure on the properties of the resultant ionomer. Brown^{5,6} prepared hexamethylene diamine salts of elastomers containing carboxylic acid groups, but he was primarily interested in them as intermediates in the vulcanization of these elastomers. Thus, while the diamine salt was stable at 80°C it converted to a diamide crosslink when the polymer was heated above 121°C. Brown did, however, recognize that the diamine salt could behave as an ionic crosslink.⁶

Rees⁷ considered aliphatic diamines as ionic crosslinks in ethylene-methacrylic acid ionomers. The tensile modulus and yield point of these materials increased with increasing diamine salt content, but the ultimate strength did not change. In marked contrast to the effect of metal salt cations on the melt viscosity of ionomers, the diamine cation did not significantly affect the viscosity at 190°C. This result led Rees to conclude that the ionic interactions in the diamine salt were weaker than those attained with metal cations.

Weiss and Agarwal⁸ studied the melt viscosity of various salts of a propylene-acrylic acid graft copolymer. While metal salts dramatically increased the melt viscosity, an ionomer neutralized with tributylamine exhibited a lower viscosity than that of the unneutralized copolymer. Similarly, the activation energy for flow for the tributylamine salt was identical to that of polypropylene and lower than those of the metal salts and unneutralized copolymer. These authors postulated that the bulky amine salt effectively shielded the ionic groups from each other, thus minimizing the ionic interactions.

In this paper, we describe the effects of various aliphatic amine counterions on the thermal, thermomechanical, and rheological behavior of sulfonated polystyrene ionomers (SPS). We consider the influences of short vs. long-chain alkyl substituents and the number of alkyl substituents on the amine. These comparisons clearly show that the structure of the amine counterion has a strong influence on the properties of the ionomer.

EXPERIMENTAL

Materials. The starting homopolymer was a commercial polystyrene (PS), Styron 666 (Dow Chemical Co.), that had the following molecular weights as determined by gel permeation chromatography: $M_n = 104,000$, $M_w = 261,000$, $M_z = 522,000$, and $M_{z+1} = 829,000$. Sulfonated polystyrenes (SPS) varying in sulfonic acid concentration from 1 to 21 mol % were prepared by the reaction of PS with acetyl sulfate in 1,2-dichloroethane at 50°C.⁹ The

sulfonic acid derivatives were isolated by steam distillation of the reaction solution, and the various zinc and amine salts were prepared by titrating a solution of the acid derivative (H-SPS) with either zinc acetate or the appropriate amine. Fully sulfonated SPS were obtained from Polysciences. The various amines used are summarized in Table I.

Measurements. Glass transition temperatures, T_g , were measured with a Perkin-Elmer Model 2 Differential Scanning Calorimeter (DSC) using a heating rate of 20°C/min and a nitrogen atmosphere. The samples were encapsulated in aluminum pans, and, in order to remove any prior thermal history,¹⁰ the samples were heated to 170°C and quenched to room temperature in the DSC prior to testing. The T_g 's reported represent the temperature at which the change in specific heat at T_g reached one-half of its ultimate value.

The softening behavior of the ionomers was measured with a Perkin-Elmer Model TMS-2 Thermomechanical Analyzer (TMA) using a quartz compression probe with a hemispherical tip (1.52 mm radius), a helium atmosphere, and a heating rate of 10°C/min. Samples approximately 1 mm thick were prepared by compression molding and were conditioned at room temperature for at least 24 h prior to testing.

Melt index was determined at 190°C and 250 psi following the procedure outlined in ASTM Standard D-1238. Melt viscosity vs. shear rate data were obtained at 200°C with an Instron Capillary Rheometer. A die with an aspect ratio of $L/D = 20$ was used, for which entrance errors are small, and the data reported were not corrected for the non-Newtonian nature of the polymer.

Dynamic mechanical measurements were made with a Rheometrics Mechanical Spectrometer (RMS-7200), using a frequency of 1 Hz and covering

TABLE I
Alkyl Amines Used in This Study

Amine	Formula	Molecular weight
Ammonia	NH ₃	17.03
Methylamine	CH ₃ NH ₂	31.06
Dimethylamine	(CH ₃) ₂ NH	45.09
Trimethylamine	(CH ₃) ₃ N	59.11
Butylamine	C ₄ H ₉ NH ₂	73.12
Dibutylamine	(C ₄ H ₉) ₂ NH	129.24
Tributylamine	(C ₄ H ₉) ₃ N	185.36
Octylamine	C ₈ H ₁₇ NH ₂	129.24
Triocetylamine	(C ₈ H ₁₇) ₃ N	353.68
Triisodecylamine	((CH ₃) ₂ C ₈ H ₁₅) ₃ N	437.84
Laurylamine	C ₁₂ H ₂₅ NH ₂	185.35
Trilaurylamine	(C ₁₂ H ₂₅) ₃ N	522.01
Stearylamine	C ₁₈ H ₃₇ NH ₂	185.35
Dimethyloctylamine	(C ₈ H ₁₇)N(CH ₃) ₂	157.29
Dimethyl laurylamine	(C ₁₂ H ₂₅)N(CH ₃) ₂	213.40
Dimethylstearylamine	(C ₁₈ H ₃₇)N(CH ₃) ₂	297.55
C ₂₀ -C ₂₂ amine		
Di-C ₂₀ -C ₂₂ amine		
Dimethyl C ₂₀ -C ₂₂ amine		

the temperature range from 50°C to 250°C. Measurements of G' and G'' were made on compression molded bars, 0.125 in. \times 0.5 in. \times 2 in., in a nitrogen atmosphere using an oscillatory deformatron.

RESULTS AND DISCUSSION

Previous studies¹¹ of ion-containing polymers have shown that the presence of a metal salt species usually raises the T_g ; this phenomenon is believed to be due to restrictions of the molecular mobility of the chains as a consequence of the ionic crosslink. The effect of the sulfonate concentration on the T_g for the sulfonic acid, zinc salt, and ammonium salt derivatives of SPS is shown in Figure 1. The data for all three materials lie on a straight line with a slope, dT_g/dc , of 3°C/mol % sulfonate group. This result is consistent with that reported by Eisenberg and Navratil^{12,13} for styrene-sodium methacrylate ionomers, except that for that system dT_g/dc was ca. 2°C/mol % ionic groups. This indicates that the ionic interactions between sulfonate groups are stronger than those between carboxylate groups, which is consistent with the conclusion of Lundberg and Makowski³ from rheological experiments. In a more recent paper, Eisenberg¹⁴ reported a non-linear dependence of T_g on composition for polystyrene ionomers, though T_g still increased with increasing ionic concentration.

When the counterion is formed from an aliphatic amine of the general type $\text{NR}'\text{R}''\text{R}'''$, where the substituents may be either hydrogen or an al-

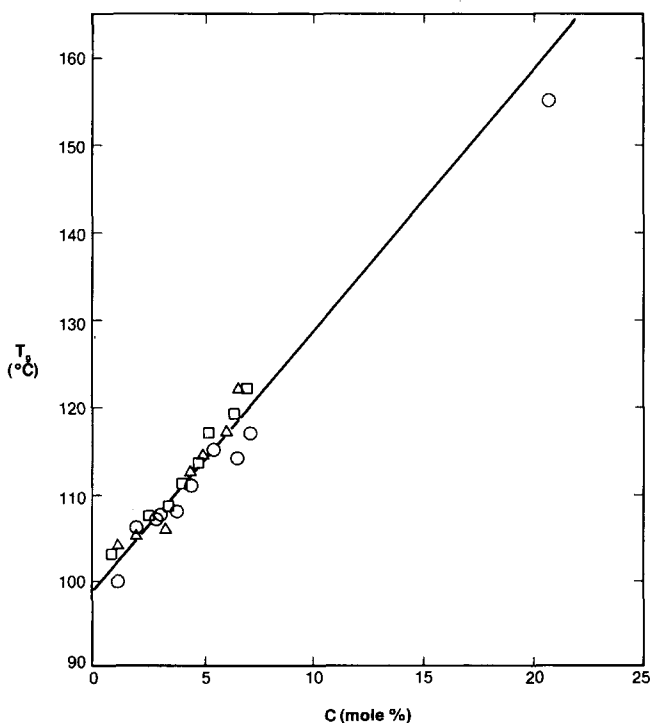


Fig. 1. T_g vs. sulfonate concentration for the free acid, zinc salt, and ammonium salts. (○) SO_3H ; (□) Zn; (△) NH_3 . $T_g = 98.4 \pm 3.0^\circ\text{C}$.

iphatic group, the T_g of SPS does not always increase with increasing sulfonate concentration (see cf. Figs. 2-6). In the case of monosubstituted ammonium salts, NRH_3^+ , where R is a linear alkyl group ranging from C_1 to C_{22} , the linear relationship between T_g and C shown in Figure 1 for the acid, zinc salt, and ammonium salt holds true only up to the octylammonium salt (C_8) (see Fig. 2). For the laurylammonium salt (C_{12}) no change in T_g from that of PS was observed at a sulfonate concentration of ca. 2.5 mol %, while for the stearylammonium salt (C_{18}) and for the C_{20-22} salt, T_g actually decreases with increasing ionic composition.

These results can be explained in terms of a competition between the tendency of the ionic species to form ionic crosslinks that reduce mobility and, hence, increase the T_g and the bulky nature of the pendent group that increases the free volume of the polymer, which acts to decrease T_g . For short aliphatic substituents the ionic interactions predominate, while for longer substituents the steric hindrance of the cation becomes more important. In fact, as the counterion becomes sufficiently bulky, the anion centers are effectively shielded and no intermolecular ionic interactions occur. As demonstrated here, the cation can be chosen so as to either increase T_g or act as an internal plasticizer and decrease T_g .

Similar results are shown in Figures 3-5 for aliphatic ammonium salts with the following structures: NR_2H_2^+ , NR_3H^+ , and $\text{NR}(\text{CH}_3)_2\text{H}^+$. In each case some critical chain length for the alkyl group, R, is reached where the

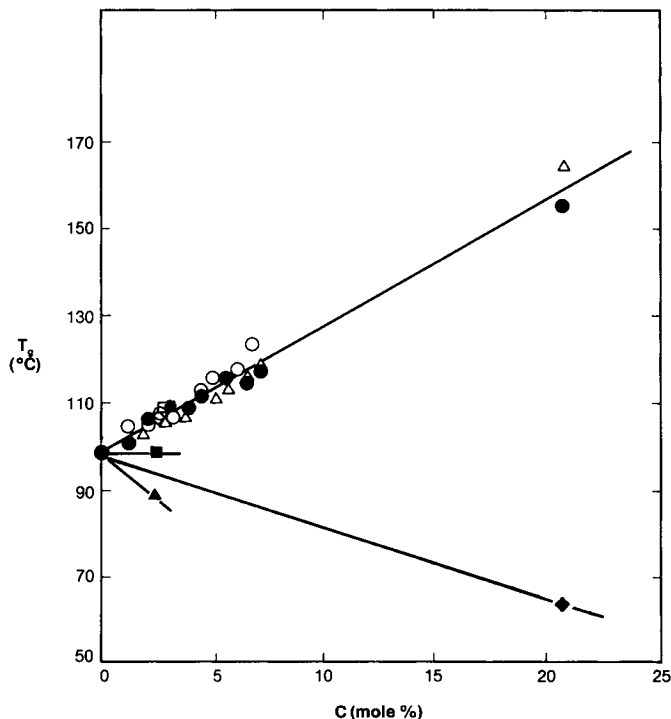


Fig. 2. T_g vs. sulfonate concentration for alkyl ammonium salts of the form NRH_3^+ . (●) SO_3H ; (○) NH_3 ; (□) CH_3 ; (△) C_4H_9 ; (◇) C_8H_{17} ; (■) $\text{C}_{12}\text{H}_{25}$; (▲) $\text{C}_{18}\text{H}_{37}$; (◆) C_{20-22} .

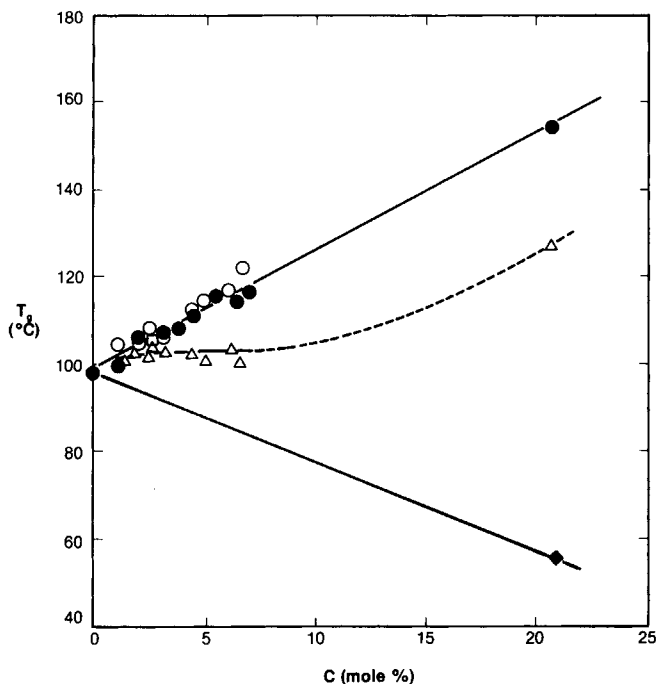


Fig. 3. T_g vs. sulfonate concentration for alkyl ammonium salts of the form NR_2H_2^+ . (●) SO_3H ; (○) NH_3 ; (□) CH_3 ; (△) C_4H_9 ; (◆) C_{20-22} .

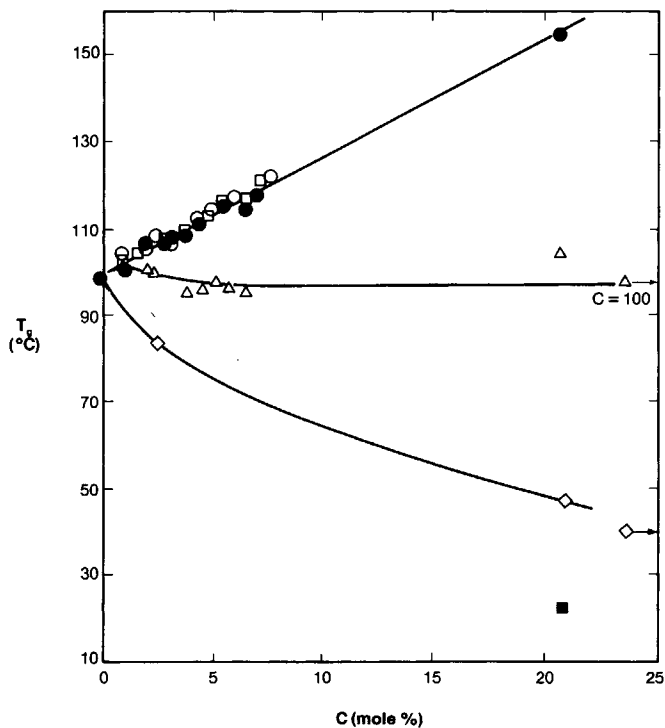


Fig. 4. T_g vs. sulfonate concentration for alkyl ammonium salts of the form NR_3H^+ . (●) SO_3H ; (○) NH_3 ; (□) CH_3 ; (△) C_4H_9 ; (◆) C_8H_{17} ; (■) $\text{C}_{12}\text{H}_{25}$.

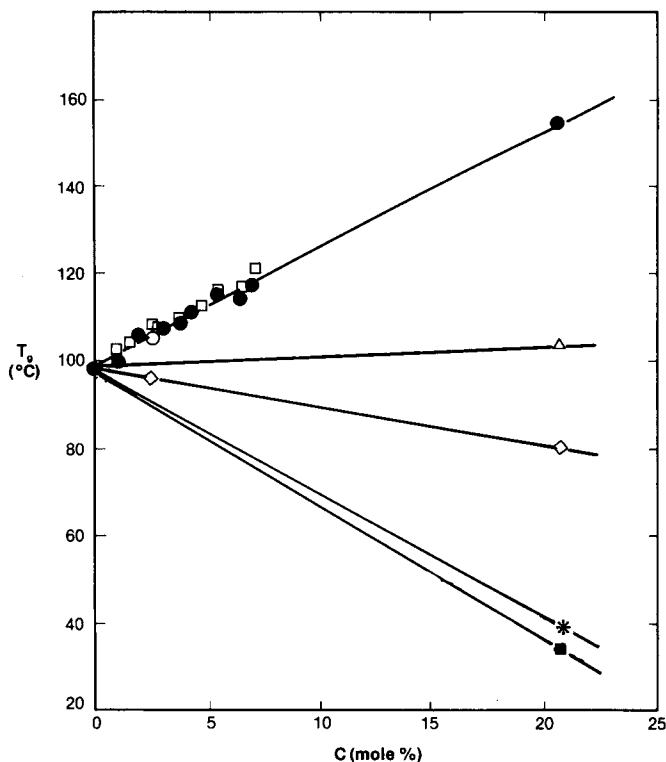


Fig. 5. T_g vs. sulfonate concentration for alkyl ammonium salts of the form $\text{NHR}(\text{CH}_3)_2^+$. (●) SO_3H ; (○) H; (□) CH_3 ; (△) C_8H_{17} ; (◆) $\text{C}_{12}\text{H}_{25}$; (*) $\text{C}_{18}\text{H}_{37}$; (■) C_{20-22} .

ammonium salt is sufficiently bulky so that the T_g remains either constant or decreases with increasing sulfonate concentration. As the number of alkyl substituents on the amine increases, this critical chain length becomes shorter.

Figure 6 demonstrates how the T_g varies with composition of the ionomer as ammonium hydrogens are replaced by *n*-butyl groups. The effect of a single butyl group is inconsequential; however, substitution of a second and third butyl group results in a decrease in T_g . In the case of tributylammonium salt the T_g is essentially the same as PS over the entire range of sulfonate concentrations.

Melt index (MI) and T_g are plotted against the number of carbon atoms in the alkyl chain length in Figure 7 for SPS containing 2.7 mol % sulfonate groups and neutralized with primary and tertiary aliphatic amines. Here, the plasticization effect of increasing the alkyl chain length and increasing the number of alkyl substituents is clearly shown. For the primary amines T_g remains constant until the number of carbon atoms in the chain is between 5 and 10, after which point the T_g decreases with increasing alkyl chain length. One might expect that the melt viscosity of these ionomers should also be sensitive to the ability of the ionic groups to interact. This is demonstrated in Figure 7 by the behavior of the MI, which is inversely related to viscosity. The MI increases with increasing chain length indicating a plasticization phenomenon. Note that the changes in MI with changing alkyl chain length are dramatic; the MI data are plotted in Figure

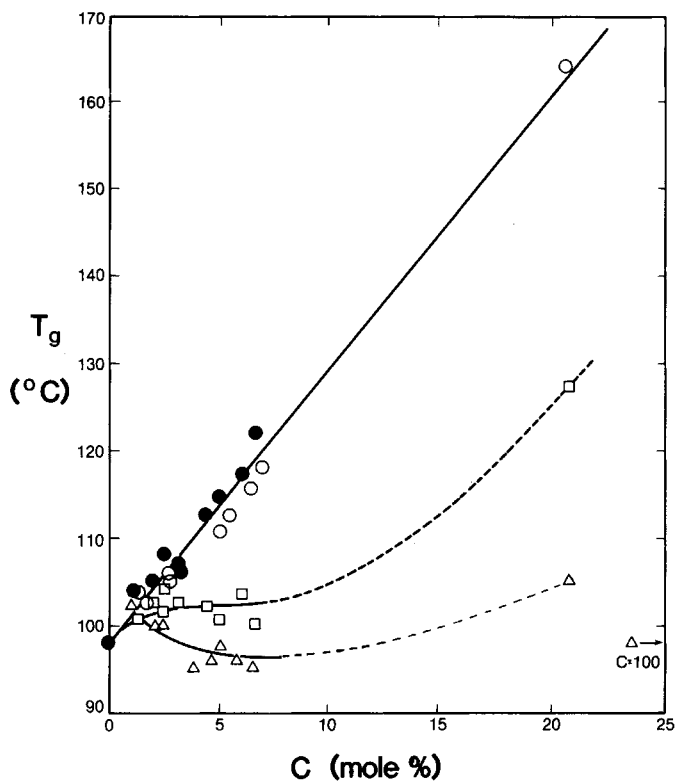


Fig. 6. T_g vs. sulfonate concentration for alkyl ammonium salts with varying numbers of butyl substituents. (●) NH_4^+ ; (○) $\text{NH}_3(\text{C}_4\text{H}_9)^+$; (□) $\text{NH}_2(\text{C}_4\text{H}_9)_2^+$; (△) $\text{NH}(\text{C}_4\text{H}_9)_3^+$.

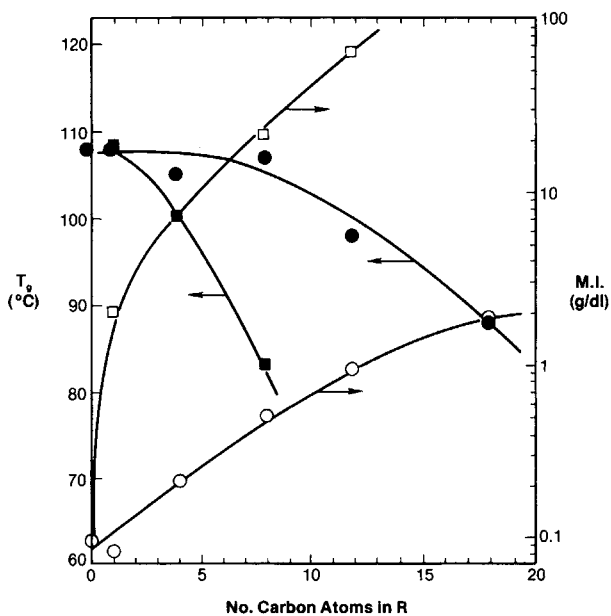


Fig. 7. T_g and melt index vs. the number of carbon atoms in the alkyl group for aliphatic ammonium salts derived from primary and tertiary amines. Sulfonate content = ~ 2.7 mol % (○) NH_3R^+ ; (□) NHR_3^+ .

7 on a logarithmic scale in order to fit all the data onto a single graph. The critical alkyl chain length at which plasticization occurs, as determined by a decrease in T_g , is shorter for the tertiary ammonium salts than for the primary ammonium salts. Similarly, the changes in T_g and MI are much greater for the tertiary ammonium salts than for the primary ammonium salts. This result is consistent with the conclusion that an increase in the bulkiness and the hydrocarbon nature of the counterion increases the free volume and diminishes the intermolecular associations.

The ionomers described in this paper are derived from a common polystyrene, and, because the sulfonation/neutralization reactions employed here do not affect the backbone molecular weight,³ these materials have molecular weights that vary only due to that of the different cations employed. As a consequence, in the absence of intermolecular interactions, the rheological behavior of these ionomers should be identical. Intermolecular forces of attraction such as occur with metal sulfonate groups increase the effective polymer molecular weight, which is manifested by an increase in viscosity. On the other hand, shielding of the ionic groups with a bulky counterion that increases the steric hindrance of the pendant group should lower the melt viscosity. Therefore, the melt viscosity or MI should be a sensitive measure of the relative interactions attained with the different cations.

Viscosity-shear rate curves at 200°C for SPS with different cations are given for ionomers containing 2 and 5 mol % ionic groups in Figures 8 and 9, respectively. The viscosity at 200°C and apparent shear rate of 0.88 s⁻¹ and the MI at 190°C are given as a function of sulfonate concentration in Figures 10 and 11, respectively. In all cases, the differences in the viscosity

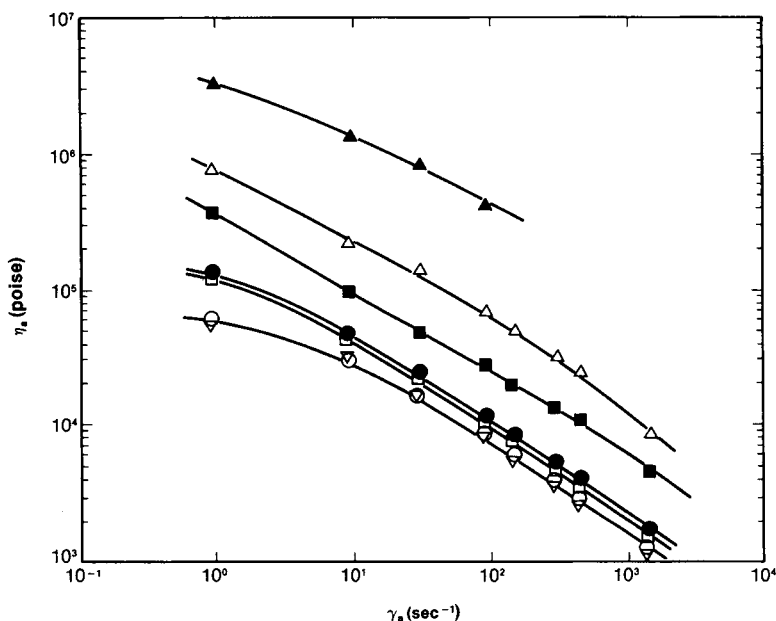


Fig. 8. Apparent viscosity vs. shear rate for SPS ionomers containing 2 mol % ionic groups neutralized with various alkyl amines ($T = 200^\circ\text{C}$). (\blacklozenge) Zn salt; (\triangle) NH_4 salt; (\blacksquare) $(\text{Bu})\text{NH}_2$ salt; (\blacklozenge) $(\text{Me})_3\text{N}$ salt; (\square) free acid; (\bullet) $(\text{Bu})_2\text{NH}$ salt; (\circ) $(\text{Bu})_3\text{N}$ salt.

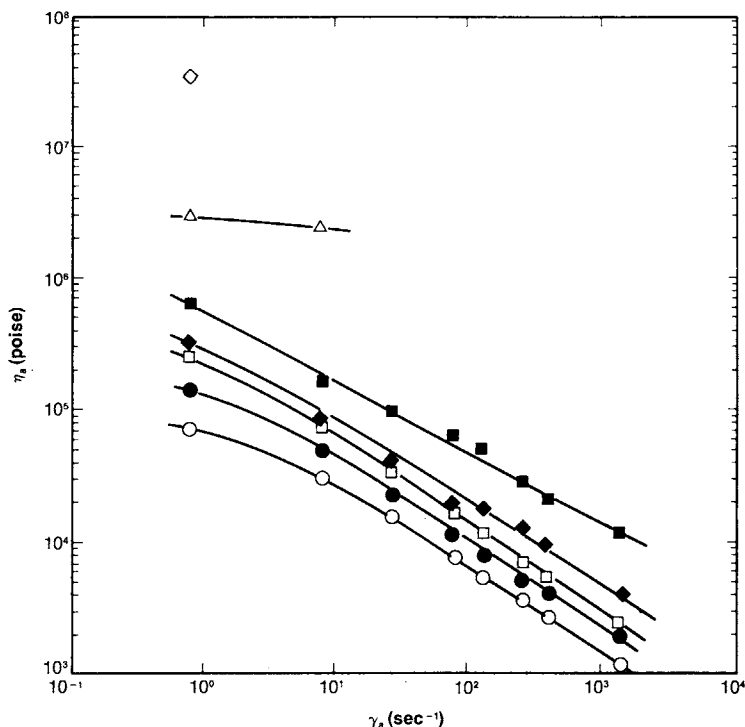


Fig. 9. Apparent viscosity vs. shear rate for SPS ionomers containing 5 mol % ionic groups neutralized with various alkyl amines ($T = 200^{\circ}\text{C}$). (▲) Zn salt; (△) NH_4 salt; (■) BuNH_2 salt; (●) $(\text{Bu})_2\text{NH}$ salt; (□) free acid; (○) $(\text{Bu})_3\text{N}$ salt; (▽) polystyrene.

can be attributed to differences in the interchain interactions. The relative degree of ionic interaction in these materials can be summarized as follows: $\text{Zn}^{++} > \text{NH}_4^+ > \text{BuNH}_3^+ > \text{Me}_3\text{NH}^+ > \text{SO}_3\text{H} > \text{Bu}_2\text{NH}_2^+ \sim \text{Bu}_4\text{N}^+ > \text{Bu}_3\text{NH}^+ \sim \text{PS}$, where $\text{Bu} = \text{C}_4\text{H}_9$ and $\text{ME} = \text{CH}_3$. This result is consistent with those obtained from thermal analysis and clearly shows that the strength of the ionic interactions that occur in a sulfonated polymer can be varied over a wide range simply by varying the cation substituent. With a metal salt, such as zinc, the interchain interactions are so intense that the material behaves as if it were crosslinked. A similar result is realized with an ammonium cation, though the melt viscosity is lower than that of the zinc salt by an order of magnitude. More significant decreases in the ionic interactions are achieved by substituting alkyl groups for hydrogen atoms on the ammonium ion. In fact, the viscosity data for the tributylammonium salts and the unmodified PS are nearly identical, which indicates that with this counterion the intermolecular interactions are completely negated by the steric hindrance of the bulky amine salt. This result is in agreement with the conclusion of Weiss and Agarwal⁸ for polypropylene ionomers.

The temperature resistance of the ionic crosslink was determined from the softening characteristics of the ionomers using TMA. Thermograms for various salts of SPS containing 6.5 mol % sulfonate are shown in Figure 12. A relative ranking of the temperature resistance of the intermolecular

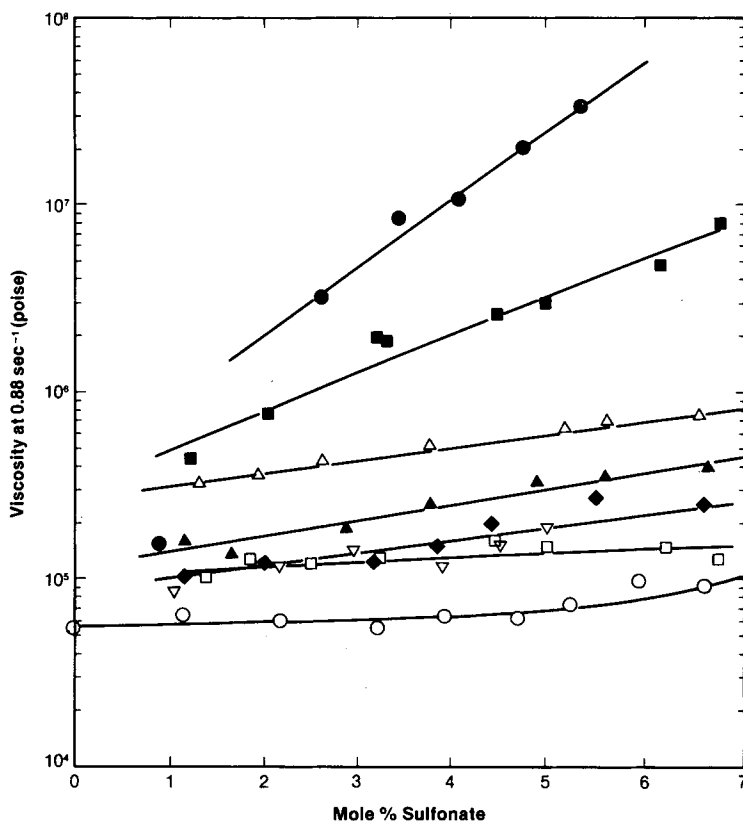


Fig. 10. Apparent viscosity at a shear rate of 0.88 s^{-1} vs. sulfonate concentration for SPS ionomers neutralized with various alkyl amines ($T = 200^\circ\text{C}$). (●) Zn salt; (■) NH_4 salt; (Δ) BuNH_2 salt; (\blacktriangle) $(\text{Me})_3\text{N}$ salt; (\blacklozenge) free acid; (\square) $(\text{Bu})_2\text{NH}$ salt; (∇) $(\text{Bu})_4\text{NOH}$ salt; (\circ) $(\text{Bu})_3\text{N}$ salt.

interaction was determined from the temperatures at which the probe penetrated halfway into the sample (cf. Table II). This result is very similar to that found for the melt viscosities of the different SPS.

A surprising result of the TMA experiments was that the temperature resistance of the intermolecular interactions in the sulfonic acid derivative appear to be greater than that of many of the aliphatic amine salts. In case of the sulfonic acid, the interactions result from hydrogen bonding. Similar hydrogen bonding effects from carboxylic acid groups were noted by Brown.⁶

The viscoelastic behavior of the SPS ionomers is described by Figures 13–15. The in-phase modulus data for three salts: zinc, ammonium, and tributylammonium, are shown in Figure 13; the salts were prepared from the same SPS containing 2.2 mol % sulfonate groups. Although the tributylammonium salt exhibits the same qualitative features as PS, the dynamic mechanical curve of this material does indicate some degree of ionic association as evidenced by the somewhat elevated rubbery plateau. Similarly, there appears to be a slight increase in T_g vs. PS for the tributylammonium salt containing 2.2 mol % sulfonate groups. This agrees with the DSC data shown in Figure 4.

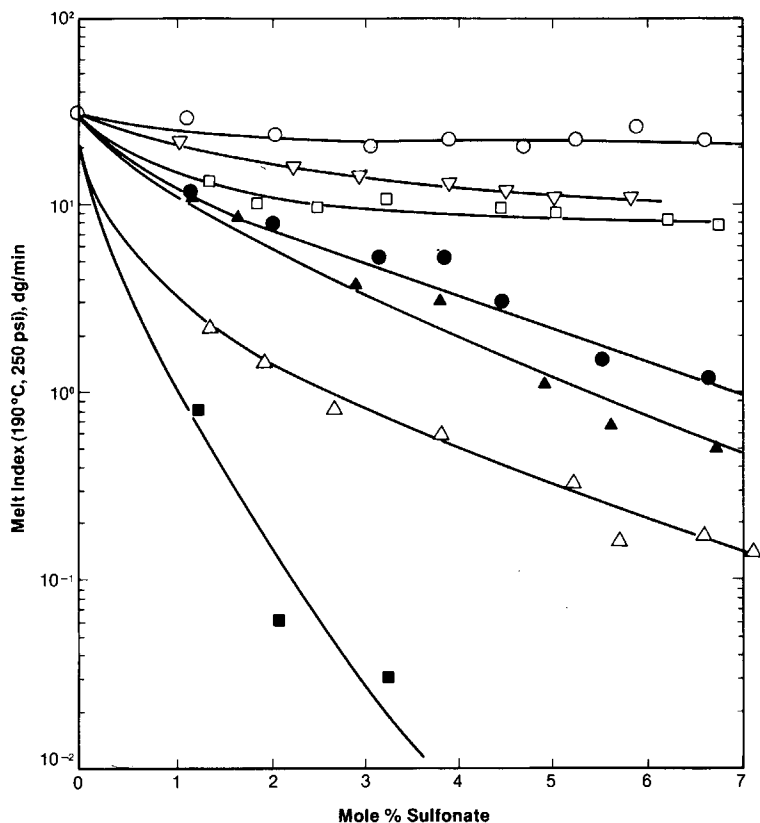


Fig. 11. Melt index vs. sulfonate concentration for SPS ionomers neutralized with various alkyl amines. (○) (Bu)₃N salt; (▽) (Bu)₄NOH salt; (□) (Bu)₂NH salt (●) Zn salt; (▲) (Me)₃N salt; (△) BuNH₂ salt; (■) NH₄ salt.

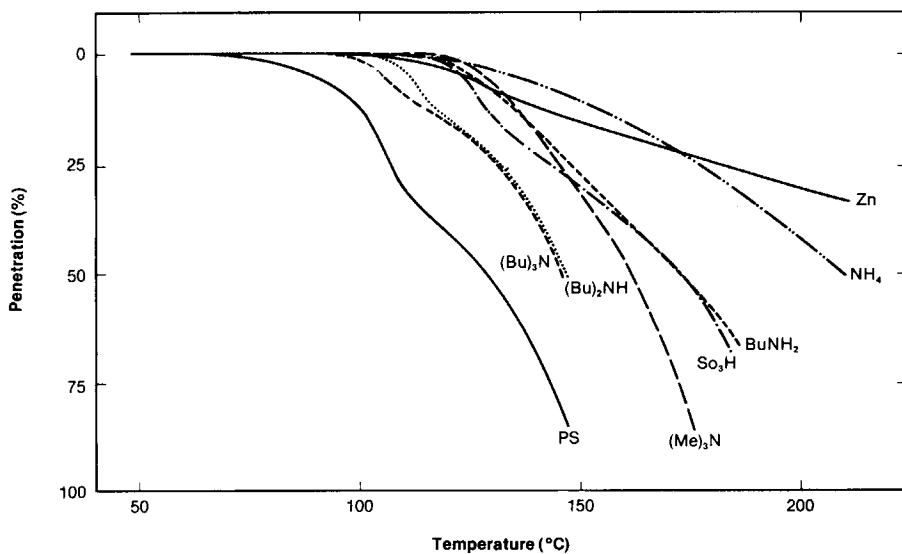


Fig. 12. TMA thermograms for SPS ionomers containing ca. 6.5 mol % sulfonate groups and neutralized with various alkyl amines.

TABLE II
Temperature at Which TMA Penetration Is 50% of Sample Thickness

Cation	T_{50} (°C)
PS	128
(Bu) ₃ N	145
(Bu) ₂ NH	146
(Me) ₃ N	161
BuNH ₂	172
SO ₃ H	172
NH ₄	210
Zn	260 (est.)

Significant differences are seen in the dynamic mechanical behavior of the ammonium and zinc salts. In agreement with the DSC data, T_g shows a larger increase than for tributylammonium salt at this sulfonate concentration. What is even more significant is the well-developed rubbery plateau observed in these ionomers, indicating the occurrence of strong ionic associations. The moduli of these salts are more than an order of magnitude higher than for PS above T_g . The rubbery plateau of the zinc salt persists to much higher temperature than for the ammonium salt and the decrease in modulus with increasing temperature is more rapid for the latter. This indicates that the zinc forms a more temperature stable and stronger network than does the ammonium cation.

The temperature dependence of G' and $\tan \delta$ for the ammonium salts of

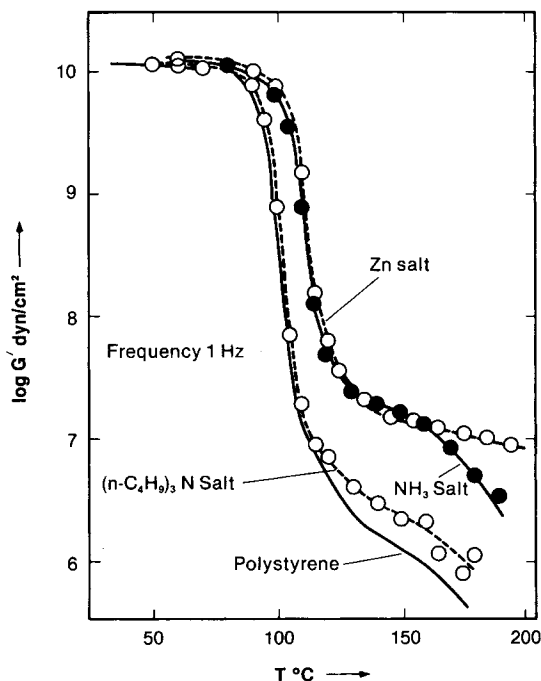


Fig. 13. Storage shear modulus vs. temperature for SPS ionomers containing ca. 2.2 mol % sulfonate groups with various metal and ammonium counterions.

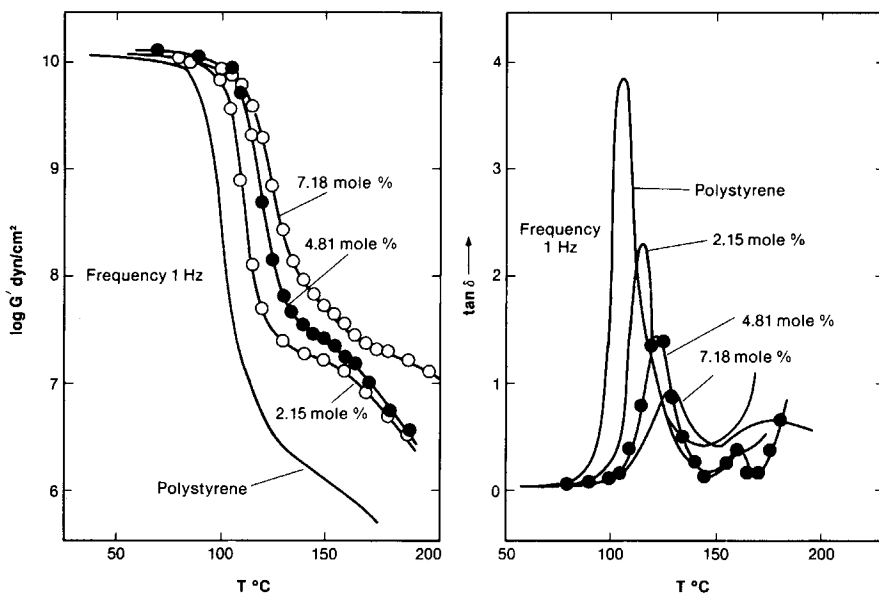


Fig. 14. Storage modulus and $\tan \delta$ vs. temperature for various ionic concentrations of SPS containing the ammonium counterion.

SPS at various sulfonate concentrations is shown in Figure 14. As discussed earlier, increasing the sulfonate concentration with this counterion results in an increase in T_g . In addition, the rubbery modulus increases with increasing sulfonate concentration, indicating that the crosslink density increases with increasing sulfonation. The loss dispersion associated with T_g decreases in intensity and broadens with increasing sulfonate concentration, indicating a reduction in the primary relaxation rates of the ionomer. Similar results were observed for the zinc salts.

In addition to the $\tan \delta$ maximum at T_g , a second $\tan \delta$ maximum is observed above 150°C for the ammonium salts. This loss dispersion probably represents the relaxation of an ion-rich phase, which is consistent with the data reported by Eisenberg¹⁵ for the sodium salt of SPS.

G' is plotted versus temperature for the tributylammonium salts of SPS in Figure 15. T_g increases slightly above that of PS at a concentration of ca. 2 mol %, but then decreases and remains invariant with sulfonate concentration between 2 and 7 mol %, which is consistent with the DSC data shown in Figure 4. The rubbery modulus decreases with increasing sulfonate concentration and the rubbery plateau persists only over a small temperature interval in contrast to the ammonium salt data of Figure 14. These data agree with the earlier stated conclusion that the bulky trialkylammonium salts inhibit strong intermolecular ionic interactions, presumably due to steric hindrance of the counterions.

CONCLUSIONS

It has been demonstrated that the ionic interactions which are characteristic of sulfonated polymers can be controlled by using aliphatic ammonium counterions. By varying the number and the alkyl chain length

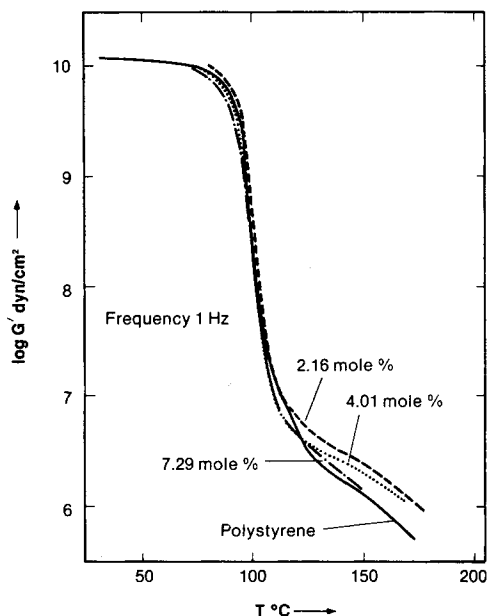


Fig. 15. Storage modulus vs. temperature for various ionic concentrations of SPS neutralized with tributyl amine.

of the ammonium substituents, one may obtain a broad spectrum of thermal, mechanical, and rheological behavior. While properties such as T_g , melt viscosity, and modulus increase compared to those properties of the unsulfonated polymer when a metal or ammonium cation is used, bulky aliphatic amine-based cations tend to either decrease these properties or lead to less significant increases. For example, tristearylammonium sulfonate acts as an internal plasticizer and a polystyrene ionomer containing 21 mol % of this substituent is essentially a rubber at room temperature.

The potential implications of this work are evident. A primary goal of the polymer chemist is to "tailor" polymers to achieve specific property requirements. Historically, this has been accomplished by either synthesizing new polymers or copolymers or by preparing blends of different polymers. It has been demonstrated by this work, however, that one can achieve a wide range of polymer properties from a single functionalized polymer simply by changing the counterion.

In addition, manipulation of the degree of ionic interactions in sulfonated polymers may provide some insight into the structure and morphology of ionomers. Thus, small angle scattering experiments as well as additional rheological analyses may provide new information on the ionic-microstructure in this class of materials.

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