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Viscoelastic Behavior of Lightly Sulfonated Polystyrene Ionomers

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ABSTRACT: Ionomers prepared by lightly sulfonating polystyrene exhibit a pseudorubbery plateau above the glass transition and a second mechanical loss process at elevated temperatures. The origin of these features in the linear viscoelastic properties is due to the formation of a second, microphase-separated phase, i.e., *ionic clusters*, that increases the longer time relaxation processes of the ionomer. For relatively low sulfonation levels (<6 mol %) the terminal region of linear viscoelastic behavior shifts to at least several decades longer in time or lower in frequency. These longer relaxation times are responsible for the higher viscosities and network-type mechanical behavior of the ionomer compared with the unfunctionalized parent material. The major effect of changing the counterion used is on the long-time processes.

Introduction

The use of ionic functional groups to modify the physical and mechanical properties of polymers is being used with increasing frequency. This class of materials, called ionomers, generally has much higher melt viscosities and solution viscosities than the analogous unfunctionalized polymer, which is due to interchain associations of the ionic groups. At elevated temperatures, i.e., above T_g , the associations persist and improved mechanical properties can be obtained. Ionic interactions also persist in non-polar solutions and in some cases have yielded unusual solution behavior.

The impact on the viscoelastic behavior of even a few ionic groups per chain can be formidable. Tant and Wilkes¹ recently reviewed the viscoelastic behavior of ionomers. The primary effects of ionic functionalization of a polymer are to increase T_g , the melt viscosity, and the characteristic relaxation times. The polymer microstructure is also affected, and it is generally agreed that in most ionomers, microphase separated, ion-rich aggregates, called *ionic clusters*, form as a result of strong ion-dipole attractions. As a consequence of this new phase, additional relaxation processes are often observed in the viscoelastic behavior of ionomers.

One ionomer that has been studied in numerous laboratories is lightly sulfonated polystyrene (SPS),² and in this paper, the viscoelastic behavior of SPS is described.

Experimental Details

Materials. Atactic polystyrene (Dow Chemical Co.; $M_n = 103\,000$, $M_w = 288\,000$) was randomly sulfonated according to the procedure of Makowski et al.³ The sulfonating reagent, acetyl sulfate, was prepared by slowly adding sulfuric acid to a solution of acetic anhydride in 1,2-dichloroethane (DCE) at 0 °C. The freshly prepared acetyl sulfate was then added to a well-stirred solution of the polymer in DCE at 50 °C. After 1 h the reaction was terminated by the addition of ethanol. The sulfonated polymer was isolated by steam distillation, washed with methanol, dried at room temperature for 3 days, and dried under vacuum above the T_g for another 3 days. The sulfonic acid content was determined by elemental sulfur analysis.

The sulfonated polymers were converted to either the sodium or the zinc salt by adding a 10% excess of either sodium hydroxide or zinc acetate. The polymer was dissolved in a mixture of toluene and methanol (90/10 v/v), and the base, dissolved in methanol or methanol with a minimal quantity of water, was added dropwise to the agitated solution. The solution was stirred for 30 min after all the neutralizing agent was added, and the neutralized polymer was recovered, washed, and dried as described above. Tant and Wilkes¹ have reported for telechelic poly(isobutylene

sulfonates) that significant improvement of the mechanical properties can be obtained by the addition of excess neutralizing agent. Similar effects have not been observed for SPS ionomers, and in this study it was assumed that the excess neutralizing agent was removed by the washes with boiling water and methanol.

The sample notation used for the ionomers is $x.xM$ -SPS, where $x.x$ is the degree of sulfonation expressed as mole percent of styrene sulfonate and M denotes the cation ($M = H, Na, \text{ and } Zn$ in the case of the free acid, sodium, and zinc salts, respectively). The neat ionomers were compression molded into films at 200 °C.

Viscoelastic Properties. Dynamic mechanical analyses (DMA) were performed with a Rheometrics System-4 mechanical spectrometer equipped with a 2000 g cm transducer and a computer system for control and data analysis. Cooling was accomplished with liquid nitrogen. Isochronal dynamic shear moduli measurements were made from -150 to 250 °C at five different frequencies between 0.03 and 3 Hz. Rectangular samples ($10 \times 63.5 \times 0.7$ mm) were used with the rectangular torsion mode for the high-modulus region ($>5 \times 10^7$ dyn/cm²) and disk samples (25.4-mm diameters \times 1 mm thick) were used for the low-modulus measurements ($<5 \times 10^7$ dyn/cm²). Isothermal dynamic shear data were obtained on thin-film specimens over the frequency range 0.003-3 Hz by using a modified rectangular torsion test fixture⁴ with a 10 g cm transducer. All measurements were made within the linear viscoelastic limit, which was determined from strain sweeps.

Moduli-frequency master curves, shift factors, and relaxation time distributions were calculated from the isothermal data by using computer programs that are described elsewhere.⁵ Vertical corrections were made by multiplying the moduli by T_g/T . Horizontal shifts involved an iterative scheme to determine the least-squares fit of a cubic equation to each shifted isothermal data set with respect to the accumulated master curve.

Results and Discussion

Effect of Sulfonation. Dynamic mechanical results for atactic PS, 1.82H-SPS, and 1.82Na-SPS are compared in Figure 1. The dynamic moduli curves for the 1.82 mol % acid derivative were qualitatively similar to those of PS, but the curves were shifted to higher temperature. In contrast, although the 1.82Na-SPS had the same T_g as the acid derivative, G' exhibited a much more gradual decline above T_g and a second loss peak was observed in G'' . The temperature shifts of the moduli of 1.82H-SPS were due to a pseudo-cross-linked network that resulted from hydrogen-bond interchain associations. The primary effect of these associations was to increase T_g , and the persistence of the hydrogen-bond associations above T_g increased the melt viscosity relative to the unmodified PS. While it is clear that hydrogen bonding in H-SPS

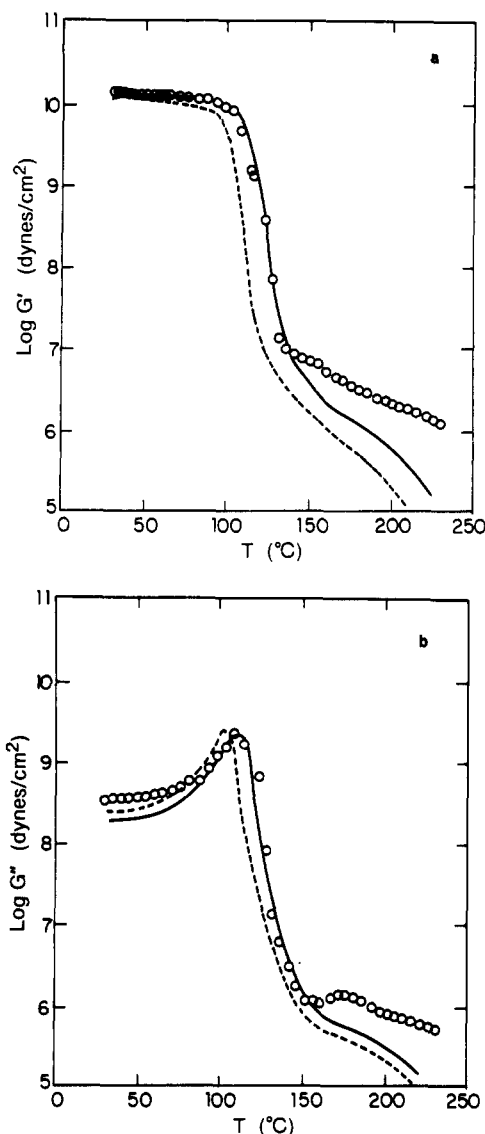


Figure 1. G' and G'' vs temperature for (---) PS, (—) 1.82H-SPS, and (O) 1.82Na-SPS ($f = 1$ Hz).

yielded transient cross-links, these were considerably weaker than those formed from ionic associations in the neutralized ionomers.

The two loss peaks in G'' for 1.82H-SPS indicated that the materials were biphasic, consisting of ion-rich microphase separated domains or clusters within a predominantly hydrocarbon matrix. These clusters functioned as multifunctional cross-links, which, like the hydrogen bonds in the acid, increased T_g . As shown by SAXS,⁶ however, at elevated temperature the ionic clusters persisted and a pseudorubbery plateau was observed in G' even at very low sulfonation levels.

Although microphase separation does not occur in the acid derivative of carboxylate ionomers, the situation for sulfonic acid ionomers is less clear. Because of the greater acid strength, hydrogen bonds between sulfonic acid groups are stronger than comparable interactions in carboxylic acid ionomers. Thus, the driving force for microphase separation in sulfonic acid ionomers is also greater. The primary evidence for microphase separation in ionomers is the observation of a scattering peak in SAXS that results from electron density differences between ion-rich and ion-poor phases.⁴ Characterizing microphase separation in acid derivatives is more difficult in that the electron density contrast needed to observe a SAXS peak is much

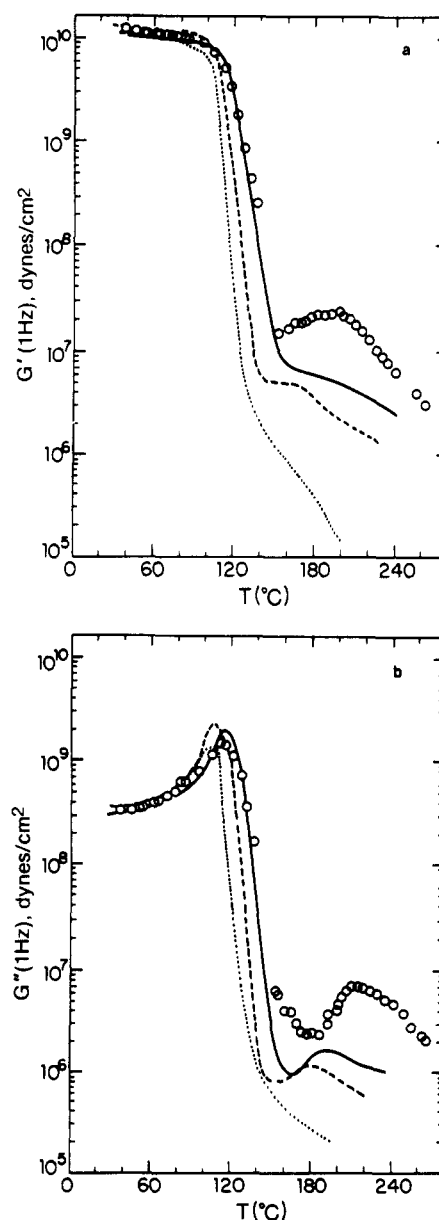


Figure 2. G' and G'' vs temperature for (···) PS, (---) 1.82Na-SPS, (—) 3.44Na-SPS, and (O) 5.81Na-SPS ($f = 1$ Hz).

lower than in the salts. As a result, interpretation of SAXS profiles of the acid derivatives is more ambiguous in that absence of an ionic peak does not preclude the possibility of two phases of similar electron density.

Dynamic mechanical confirmation of microphase separation, i.e., the observation of a relaxation process associated with a second phase, does not require the electron density contrast needed in SAXS. In fact, since DMA is sensitive to very local molecular motions, the presence of a second phase in acid ionomers should be no more difficult to detect than for a metal salt ionomer. Thus, the data in Figure 1 indicate that cluster formation did not occur in 1.82H-SPS, though DMA data of Weiss and Lefelar⁶ and Rigdahl and Eisenberg⁸ showed that a second phase was present at acid concentrations of 3 and 10 mol %, respectively. In those studies, the high-temperature peaks in G'' and $\tan \delta$ for the acid derivatives were smaller in magnitude and at lower temperatures than for the analogous sodium salts. This indicated that the clusters in the acids were much less developed and the intermolecular forces were weaker.

Figure 2 shows the effect of sulfonation level on G' and

G'' for the sodium salts of SPS. Three differences are notable when the data are compared for the ionomers and the unmodified polystyrene: (1) T_g increased with increasing sulfonation, (2) a plateau or inflection was present in the G' data above T_g for the ionomers, but not for PS, and (3) a peak in G'' occurred at elevated temperatures for the ionomers. Data for the zinc salts of SPS were qualitatively similar. The modulus of the rubbery plateau or inflection, which was due to the network formed by the physical, ionic cross-links, increased with increasing sulfonation level. This result was consistent with the theory of rubber elasticity that predicts that the rubbery modulus is proportional to the cross-link density. As the sulfonation level increased, the number of ionic cross-links per chain also increased, though the thermomechanically reversible nature of the ionic cross-link was demonstrated by the decrease in G' at elevated temperatures. Although the viscosities of the ionomers were significantly higher than that of the unfunctionalized PS, the ionomers did exhibit melt flow at elevated temperatures.

The temperature of the post- T_g peak in G'' increased with increasing sulfonation level. Post- T_g mechanical relaxations in ionomers have previously been attributed to a glass transition, T_c , of the microphase-separated ion-rich phase,⁵ and the G'' data in Figure 2 are consistent with this interpretation. Segmental motion within the ionic domains requires the dissociation of the ion-dipole interactions that form the physical cross-links. The energy required for this and, hence, the cluster T_g , should increase as the size and/or perfection of the associations increase. SAXS data of Weiss and Lefelar⁶ showed that reorganization of the cluster structure occurred at temperatures coinciding with those of the G'' peak. That result supports the conclusion that this loss process may be considered the glass transition of the ionic phase—at least within the context of equating the temperature at which the onset of segmental motion of the chains and their associated salt groups within the clusters first occurs with a glass transition.

Sulfonation of polystyrene increased the matrix T_g ca. 3 °C/mol % substitution. The increase of T_g was due to restriction of the chain segmental motion by the ionic network, which was relatively insensitive to the anion used as judged from data on SPS, carboxylated polystyrene,⁹ and poly(styrene-*co*-methacrylic acid) (PSMA) ionomers.¹⁰ The magnitude of T_c , however, did depend on whether a carboxylate or sulfonate group was used for polystyrene-based ionomers. Although T_c increased linearly with salt concentration for Na-SPS, the transition for Na-PSMA was independent of ion concentration up to about 6 mol %, above which a linear dependence was followed. For the latter system, the authors concluded that ionic clusters did not significantly influence the viscoelastic behavior above T_g until an ion concentration of 6 mol % was reached, whereas studies of SPS by several authors indicated that the microphase-separated clusters dominated the ionomer properties at much lower salt concentrations. This again may be a consequence of the stronger acid strength of a sulfonate versus a carboxylate group and a greater driving force for microphase separation in the sulfonate ionomers.

Frequency-Temperature Superposition. Master curves of G' and G'' for the different Na-SPS ionomers are shown in Figure 3. The effect of T_g on the viscoelastic behavior was removed by using T_g as the reference temperature. Excellent frequency-temperature superposition was obtained for all of the samples; in some cases over 20 decades of reduced frequency were covered. An

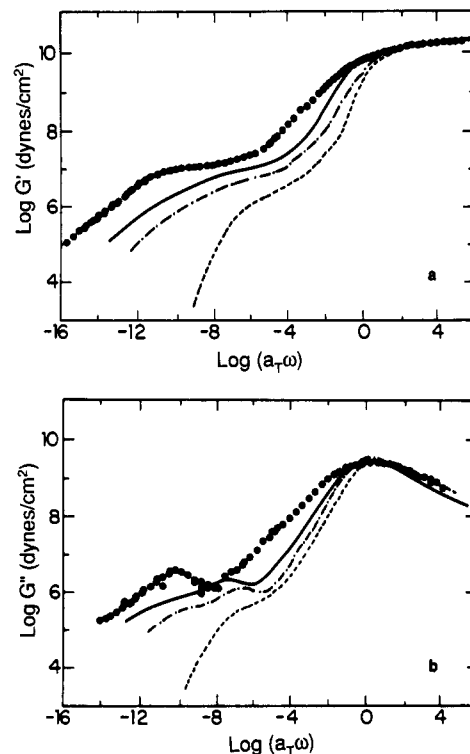


Figure 3. G' and G'' master curves of (---) PS, (- · -) 1.82Na-SPS, (—) 3.44Na-SPS, and (●) 5.81Na-SPS ($T_{\text{ref}} = T_g$).

extended rubbery plateau in G' and two relaxation peaks in G'' were observed, which were consistent with the concept that microphase-separated ionic clusters acted as physical cross-links in these materials. The peak at low frequency shifted to lower frequency with increasing sulfonate concentration, which supported the assignment of this relaxation to motion in the ion-rich phase. The peak position is related to the strength of the forces holding together the ionic clusters, and the results indicated that the strength increased as the sulfonate concentration increased.

Time (frequency)-temperature superposition has been reported for other ionomers. Shohamy and Eisenberg¹¹ attained frequency-temperature superposition for the acid, sodium salt, and methyl ester of PSMA ionomers, and they were also able to superimpose the three master curves of the acid, sodium salt, and methyl ester derivatives by selecting different reference temperatures for each. Eisenberg and Navratil,¹⁰ however, found that time-temperature superposition failed for the Na-PSMA ionomers containing more than 6 mol % salts groups. Agarwal et al.¹² and Broze et al.¹³ also achieved good frequency-temperature superposition for sulfonated EPDM and halato telechelic α, ω -dicarboxylated polybutadiene, respectively. Earnest and MacKnight¹⁴ reported that although G' for the sodium salt of a poly(ethylene-*co*-methacrylic acid) ionomer could be superposed to construct a master curve, G'' did not superpose. They reasoned that the elastic nature of the polymer, measured by G' , was dominated by the matrix polymer and, therefore, only the magnitude of G' in the time (or frequency) domain and not the shape of the curve was affected by the presence of the ions. Failure of superposition of G'' , however, was attributed to a second dissipative mechanism involving motion in the ionic domains.

The temperature dependence of the experimental shift factors, a_T , used to construct Figure 3 obeyed the WLF

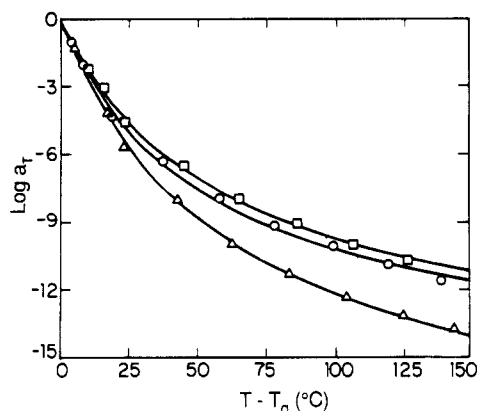


Figure 4. Temperature dependence of shift factors for (□) 1.82Na-SPS, (○) 3.44Na-SPS, and (Δ) 5.81Na-SPS. The reference temperature was T_g .

Table I
WLF Constants for SPS Ionomers

mater	T_g^a , °C	c_1	c_2 , °C	E , kcal/mol
PS ^b	100	13.7	50.0	49.6
PS ^c	102	12.9 (0.05)	52.5 (2.50)	49.6
1.82Na-SPS	105	15.6 (0.14)	56.5 (1.56)	55.1
3.44Na-SPS	112	15.8 (0.09)	58.1 (1.60)	57.1
5.81Na-SPS	115	20.3 (0.33)	67.3 (3.02)	65.7
1.82Zn-SPS	107	15.2 (0.28)	52.3 (4.76)	52.6
3.44Zn-SPS	112	16.8 (0.33)	53.7 (0.61)	59.7
5.81Zn-SPS	116	21.7 (0.28)	88.3 (2.88)	65.1

^a Measured by DSC using a 10 °C/min heating rate. ^b From: Ferry, J. D. *Viscoelastic Properties of Polymers*, 2nd ed.; Wiley: New York, 1970. ^c This study (numbers in parentheses are the standard deviation calculated from three sets of experimental data).

relation¹⁵

$$\log a_T = -c_1(T - T_g)/(c_2 + T - T_g) \quad (1)$$

as shown in Figure 4 for the Na salts. The solid lines in Figure 4 are the least-squares fit of eq 1 to the data, and the values of c_1 and c_2 are given in Table I. c_1 and c_2 increased with increasing sulfonate concentration, but the increase was much more significant for the highest sulfonate concentration. This result was similar to what was found by Navratil and Eisenberg¹⁰ for PSMA ionomers. The WLF equation is a representation of the free volume theory of the glass transition.¹⁶ In this context, c_1 is inversely proportional to the fractional free volume at T_g , f_g . The increase of c_1 with sulfonation shown in Table I, then, indicates that f_g decreases on the order of 40% when polystyrene is sulfonated to ca. 6 mol %. This trend is consistent with the idea of strong intermolecular associations, which would be expected to result in densification of the polymer. The other constant, $c_2 = f_g/\alpha_f$, where α_f is the free volume coefficient of expansion above T_g and $\alpha_f \approx c_1 c_2$. Thus, α_f increases 2–3-fold by sulfonation up to 6 mol %. The large increase for α_f may be a consequence of the sensitivity of the intermolecular interactions to temperature, though the nature of these changes cannot be quantified without a better understanding of the intermolecular forces and structures that occur in ionomers.

Activation energies for viscous flow were calculated for the ionomers and PS by fitting the shift factors to an Arrhenius-type equation. Plots of $\log a_T$ vs $1/T$ were linear, and the activation energies, E , calculated from the slopes (slope = $-E/RT$) are listed in Table I. The activation energy increased linearly with increasing ion content at a rate of ca. 2.8 kcal/mol % sulfonation. Within the experimental uncertainty, the activation energy was independent of the cation used.

Table II
Model Parameters from Eq 3 for the Master Curves of SPS Ionomers

mater	$\log G_g$	$\log G_e$	K	h
PS	10.11	6.38	-0.97	0.48
1.82Na-SPS	10.26	6.77	-1.45	0.38
3.44Na-SPS	10.27	7.01	-1.75	0.40
5.81Na-SPS	10.23	7.12	-2.36	0.29
1.82Zn-SPS	10.26	6.71	-1.37	0.39
3.44Zn-SPS	10.25	7.00	-2.55	0.41
5.81Zn-SPS	10.25	7.14	-3.23	0.27

Table III
Cross-Link Densities for Na-SPS Ionomers^a

mater	$10^4 \nu_e$, mol/cm ³	$10^4 \nu_c$, mol/cm ³	$10^4 \nu_i$, mol/cm ³
1.82Na-SPS	1.88	1.03	1.08
3.44Na-SPS	3.27	1.91	2.47
5.81Na-SPS	4.32	3.16	3.52

^a ν_e was calculated from eq 4. ν_c was calculated from sulfonate concentration. $\nu_i = \nu_e - \nu_c$.

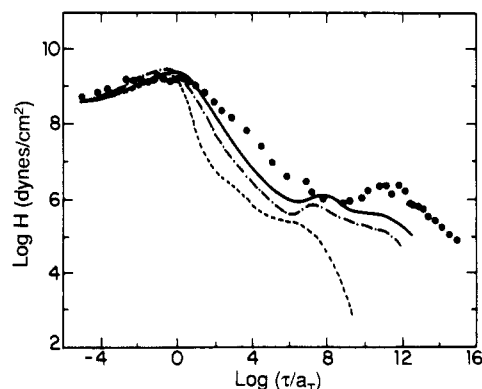


Figure 5. Relaxation time spectra for (---) PS, (---) 1.82Na-SPS, (---) 3.44Na-SPS, and (●) 5.81Na-SPS. The reference temperature was T_g .

Tobolsky¹⁷ proposed an empirical expression for describing the relaxation modulus, $G(t)$, in the transition region:

$$\log G(t) = (\log G_g + \log G_e)/2 - [(\log G_g - \log G_e)/2] \operatorname{erf}(h \log(t/K)) \quad (2)$$

where G_g is the glassy modulus, G_e is the rubbery modulus, h and K are adjustable parameters, and erf is the error function. Equation 3 is the comparable expression for

$$\log G'(\omega) = (\log G_g + \log G_e)/2 - [(\log G_g - \log G_e)/2] \operatorname{erf}(h \log(t/K)) \quad (3)$$

$G'(\omega)$. The parameter h is the slope of $\log G'(\omega)$ vs $\log \omega$ at the midpoint of the transition region, i.e., when $\log G'(\omega) = (\log G_g + \log G_e)/2$. Thus, h measures the breadth of the transition. K is the frequency at the midpoint of the transition region. For an analogous series of polymers, K is a relative measure of the mobility of the chain segments, i.e., K increases with increasing chain mobility. Nonlinear regression calculations of G_g , G_e , h , and K are given in Table II for PS and the Na- and Zn-SPS ionomers.

Sulfonation decreased the chain mobility and increased the breadth of the transition region. The glassy moduli, G_g , were independent of sulfonate concentration and counterion but were about 40% higher than that of the starting polystyrene. G_e increased linearly with increasing ion content at a rate of ca. 1.97×10^5 dyn/cm² % sulfonation but was insensitive to the cation used. Thus, a degree of

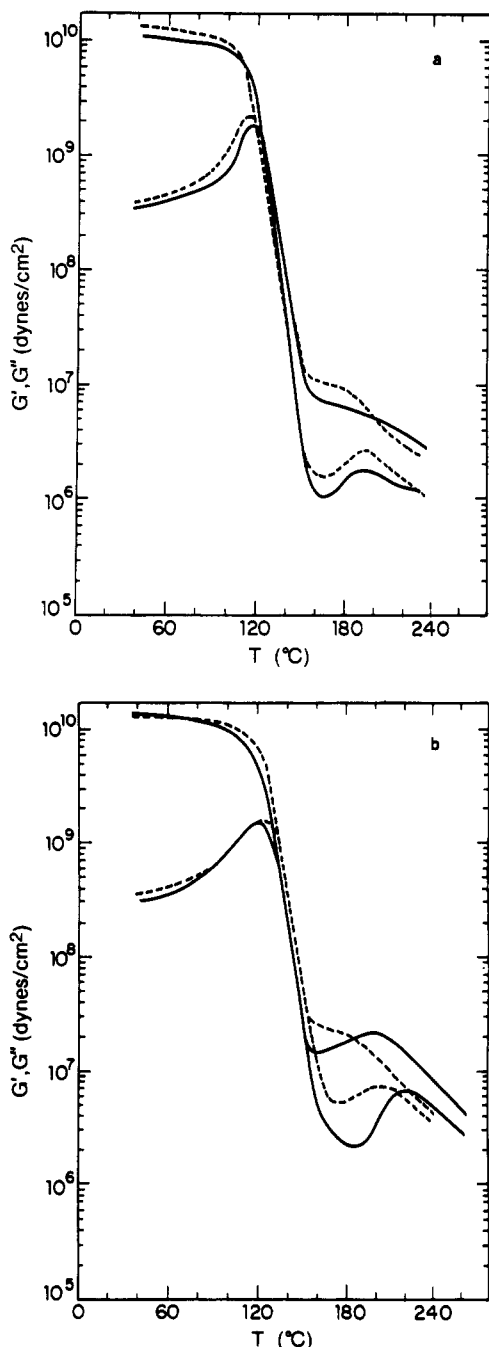


Figure 6. G' and G'' vs temperature for (—) Na and (---) Zn salts of (a) 3.44M-SPS and (b) 5.81M-SPS.

substitution of 5.81 mol % increased the rubbery modulus by almost an order of magnitude. An effective cross-link density was calculated from the theory of rubber elasticity:

$$G_e = \nu RT \quad (4)$$

where ν represents the density of network chains, R is the gas constant, and T is absolute temperature.¹⁹ The densities of network chains for the Na-SPS ionomers calculated from eq 4, ν_e , are compared in Table III with the values, ν_c , calculated by assuming that each pair of sodium sulfonate groups formed a cross-link. The experimental values were consistently higher than those calculated on the basis of simple ion-dipole cross-links. The difference may be accounted for, at least in part, by molecular entanglements of the polystyrene chain. The entanglement density of the chain, ν_{ps} , was calculated from the value of G_e for polystyrene in Table III, and when this

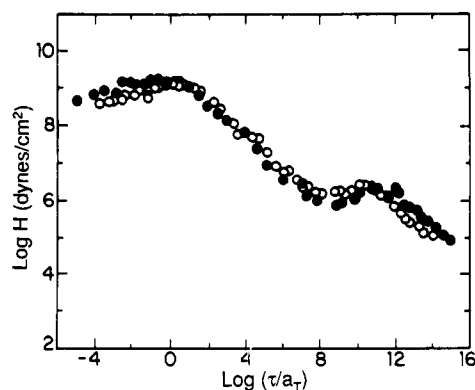


Figure 7. Relaxation time spectra for (O) 5.81Zn-SPS and (●) 5.81Na-SPS.

contribution was subtracted from ν_e for the Na-SPS ionomers, the corrected experimental network chain densities, ν_i , and the calculated values still disagreed by about 20%. The corrected experimental values were consistently higher, and the disparity may be even larger if not all the ionic groups participate in effective cross-links. For example, *intrachain* associations give rise to loops or dangling chain ends that do not contribute to the network.

One possible origin of the higher than expected values of ν is a synergism between the ionic cross-links and molecular entanglements that yielded a higher effective cross-link density than that based on a linear combination of the two effects alone. One explanation for this is that the *interchain* ionic interactions may trap molecular chains such that the effective molecular entanglement density is enhanced. As shown in the discussion that follows, the networklike behavior arose from exceedingly long relaxation times and not covalent cross-links. Trapped entanglements may, therefore, persist much longer than entanglements in unmodified polystyrene. As a result, they contribute to the network characteristics of the ionomer in the same way as the ionic associations.

An alternative explanation is that the supramolecular structure of the cross-links, i.e., the ionic clusters, yielded a much lower molar mass between cross-links than that calculated from the average chain length between simple contact ion-pair associations. This hypothesis implies that the segments of the backbone chain containing the sulfonate group, which are contained within the cluster, relax at a different rate than the ion-free segments of the polymer chain. A longer relaxation time for the cluster chains is consistent with a second phase and the glass transition argument for the high-temperature G'' peak discussed earlier. This *hard-phase cross-link* might be analogous, though on a smaller length scale, to the cross-linking effect of crystallites in semicrystalline polymers.

Relaxation time distributions for the ionomers were calculated from the master curves of G' and G'' by using the second approximation formula of Tschoegel:¹⁹

$$H(\tau) = G' \left[\frac{(\frac{d \log G'}{d \log \omega})}{(\frac{d \log \omega}{d \log \omega})} - \frac{1}{2} \left(\frac{d \log G'}{d \log \omega} \right)^2 - \frac{1}{4.606} \left(\frac{d^2 \log G'}{d(\log \omega)^2} \right) \right]_{1/\omega = \tau/\sqrt{2}} \quad (5)$$

or

$$H(\tau) = \frac{2}{\pi} \left[G'' + \frac{4}{3} \left(\frac{d G''}{d \ln \omega} \right) + \frac{1}{3} \left(\frac{d^2 G''}{d(\ln \omega)^2} \right) \right]_{1/\omega = \tau/\sqrt{2}} \quad (6)$$

$H(\tau)$ calculated from G' and G'' were in good agreement, and the distributions calculated from G' for the Na-SPS

ionomers and PS are plotted in Figure 5. $H(\tau)$ for the PS had the general wedge and box shape described by Tobolsky¹⁷ for amorphous polymers, but the ionomers also exhibited a peak at longer times due to the relaxation of the ionic-rich phase. The relaxation time distribution broadened with increasing sulfonate content, which indicated that the ionic associations of the sodium sulfonate groups slowed down the diffusional relaxation processes. The peak due to the ionic groups shifted to longer time and increased in intensity with increasing sulfonate concentration. Thus, the relaxation of the ionic-rich regions becomes increasingly dominant with regard to the viscoelastic response of the ionomer as the level of functionalization increases.

Comparison of Na and Zn Salts. The viscoelastic behavior of the Zn-SPS ionomers was qualitatively the same as that of Na-SPS. An important difference between the two salts, however, is that the Zn salts generally had much lower melt viscosities. This can be seen in comparisons of the DMA data of matched ionomers, i.e., the Zn and Na salts formed from the same H-SPS.

Comparisons of the DMA behavior of the two salts for 3.44M-SPS and 5.81M-SPS are given in Figure 6. The transition region was independent of the cation. Above the glass transition, G' of Zn-SPS was higher than that of Na-SPS. However, the decrease of G' with increasing temperature was also greater for the zinc salts, and the G' curves for the two derivatives crossed at higher temperature.

Melt flow of ionomers is believed to be characterized by the repetitious breaking and reforming of cross-links, a process that has been termed *ion-hopping*,²⁰ and the viscosity of the melt is determined by the kinetics of this process. The more rapid decline of G' for the Zn salts suggest that the ion-hopping kinetics are more temperature sensitive for the Zn salts than the Na salts. This difference should be visible in the relaxation time distributions. $H(\tau)$ vs τ for 5.81Na-SPS and 5.81Zn-SPS are compared in Figure 7. The peak due to relaxations in the ionic phase occurred at shorter time for the Zn salt. Since viscosity is more sensitive to the longer relaxation times, these data are in agreement with the observed lower melt viscosity for the Zn-SPS.

Conclusions

Sulfonation of polystyrene increases T_g and gives rise to two new features in the viscoelastic behavior: (1) a rubbery plateau above T_g and (2) a second loss process at elevated temperatures (or at low frequencies). The rubbery plateau was due to the formation of a physical

network that can persist over a range of 100 °C. The high-temperature loss process resulted from the presence of an ion-rich microphase, i.e., ionic clusters, that acted as multifunctional cross-links. The major effect of the ionic cluster was to increase the longer time relaxation processes. This, in turn, increases the melt viscosity and is responsible for the networklike behavior of ionomers above T_g . The viscoelastic behaviors of the Na and Zn salts were similar, although at a given ionic content, the cluster relaxation processes for the Na salts extended to longer times.

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References and Notes

- (1) Tant, M. R.; Wilkes, G. L. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, C28, 1.
- (2) Fitzgerald, J. J.; Weiss, R. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, C28, 99.
- (3) Makowski, H. S.; Lundberg, R. D.; Singhal, G. H. U.S. Patent 3,870,841, 1975.
- (4) Foss, P. H. Ph.D. Dissertation University of Connecticut, 1985.
- (5) Kim, D. S. Ph.D. Dissertation University of Connecticut, 1987.
- (6) Weiss, R. A.; Lefelar, J. A. *Polymer* **1986**, 7, 3.
- (7) Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic Press: New York, 1977.
- (8) Rigdahl, M.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, 19, 1641.
- (9) Brockman, N. L.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, 23, 1145.
- (10) Navratil, M.; Eisenberg, A. *Macromolecules* **1974**, 7, 84.
- (11) Shohamy, E.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, 14, 1211.
- (12) Agarwal, P. K.; Makowski, H. S.; Lundberg, R. D. *Macromolecules* **1980**, 13, 1679.
- (13) Broze, G.; Jerome, R.; Teyssie, P.; Marco, C. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, 21, 2205.
- (14) Earnest, T. R.; MacKnight, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, 16, 143.
- (15) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, 77, 3701.
- (16) Eisenberg, A. In *Physical Properties of Polymers*; Mark, J. E., Eisenberg, A., Graessley, W. W., Mandelkern, L., Koenig, J. L., Eds.; American Chemical Society: Washington, D.C., 1984; p 67.
- (17) Tobolsky, A. V. *J. Appl. Phys.* **1956**, 27, 673.
- (18) Treloar, L. R. G. *The Physics of Rubber Elasticity*, 3rd ed.; Oxford University Press: Oxford, 1975.
- (19) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley-Interscience: New York, 1970.
- (20) Hara, M.; Eisenberg, A.; Storey, R. F.; Kennedy, J. P. In *Coulombic Interactions in Macromolecular Systems*; Eisenberg, A., Bailey, F. E., Eds.; ACS Symp. Ser.; American Chemical Society: Washington, D.C., 1986; No. 302, p 176.