Viscoelastic Behavior of Plasticized Sulfonated Polystyrene Ionomers

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ABSTRACT: Two different approaches for modifying the linear viscoelastic behavior of an ionomer, lightly sulfonated polystyrene (SPS), are described. Adding a *backbone* plasticizer, such as dioctyl phthalate (DOP), affects that part of the relaxation behavior due to the backbone polymer. Thus, DOP lowered the primary glass transition temperature without affecting the relaxation time spectrum associated with the ionic clusters. However, an *ionic domain* plasticizer, such as glycerol, affects the relaxation of the ionic clusters and has little or no effect on the viscoelastic response of the nonpolar phase. For SPS, the addition of glycerol shifted the long-time relaxations associated with the ionic clusters to shorter times, thus decreasing the melt viscosity and reducing the networklike response due to physical associations of the ionic groups.

Introduction

Strong intermolecular ionic associations and the relatively high stability of the ionic clusters are responsible for unusually high melt viscosities and long relaxation times of ionomers. These characteristics make melt processing of ionomers difficult, which limits their applications. As with conventional polymers, the addition of low molecular weight diluents, i.e., *plasticizers*, affects the viscoelastic behavior of ionomers and can improve their processability. The two-phase morphology and the large difference in the polarity of the two phases (hydrocarbon vs ionic) offers two distinctly different possibilities for plasticization: (1) plasticization of the continuous nonionic phase or (2) plasticization of the ionic clusters. This paper discusses the consequences of these two possibilities on the microstructure and viscoelastic behavior of lightly sulfonated polystyrene ionomers, SPS. A previous paper[1] described the viscoelastic behavior of SPS.

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.[2] 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 T_g for another 3 days. The sulfonic acid content was determined by elemental sulfur analysis.

The sulfonated polymers were converted to the sodium, zinc, or manganese salt by adding a 10% excess of sodium hydroxide, zinc acetate, or manganese 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. The sample notation used for the ionomers is *x.y*M–SPS, where *x.y* is the degree of sulfonation expressed as mole percent of styrenesulfonate and M denotes the cation (M = H, Na, Zn, and Mn in the case of the free acid and the sodium, zinc, and manganese salts, respectively). The neat ionomers were compression molded into films at 200 °C.

The properties of the two plasticizers used, dioctyl phthalate and glycerol, are listed in Table I. These were selected to provide a large difference in polarity and low volatility. Both were liquids at room temperature. Plasticized compositions were prepared by solution blending in a 90/10 toluene/methanol solvent mixture. The compounds were isolated by evaporating the solvent in air for 2 days at room temperature, followed by vacuum drying at 80 °C for 15 h. The plasticizer content was determined gravimetrically. The plasticized samples were twice melt pressed at 150 °C between flat steel plates and then compression molded into the test specimens.

Table I
Plasticizers

plasticizer	bp,[a] °C	solubility param,[b] (cal/cm^3)$^{1/2}$	dielectric const[c]
dioctyl phthalate	384	7.9	6.4
glycerol	180/20 mmHg[d]	16.5	42.5

[a] From: Aldrich catalog, 1987. [b] From: *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975. [c] From: *CRC Handbook of Chemistry and Physics*, 59th ed.; CRC Press: Cleveland, 1978. [d] Boiling at 180 °C in vacuum (20 mmHg).

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 × 63.5 × 0.7 mm) were used with the rectangular torsion mode for the high-modulus region (>5 × 10^7 dyn/cm^2) and disk samples (25.4 mm diameter × 1 mm thick) were used for the low-modulus measurements (<5 × 10^7 dyn/cm^2). Isothermal dynamic shear data were obtained on thin-film specimens over the frequency range 0.003–3 Hz. A modified rectangular torsion test fixture[3] was used 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.[4] 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.

Small Angle X-ray Scattering (SAXS). SAXS experiments were made at the National Center for Small Angle Scattering Research (NCSASR) at Oak Ridge National Laboratory using the 10-m camera. This instrument uses a rotating anode X-ray generator source (λ = 1.542 Å, Cu Kα), crystal monochromatization of the incident beam, pinhole collimation, and a two-dimensional position-sensitive detector. The sample-to-detector distance used was either 1.12 or 2.24 m.

Electron Spin Resonance Spectroscopy (ESR). ESR measurements were made at X-band frequency with a custom-

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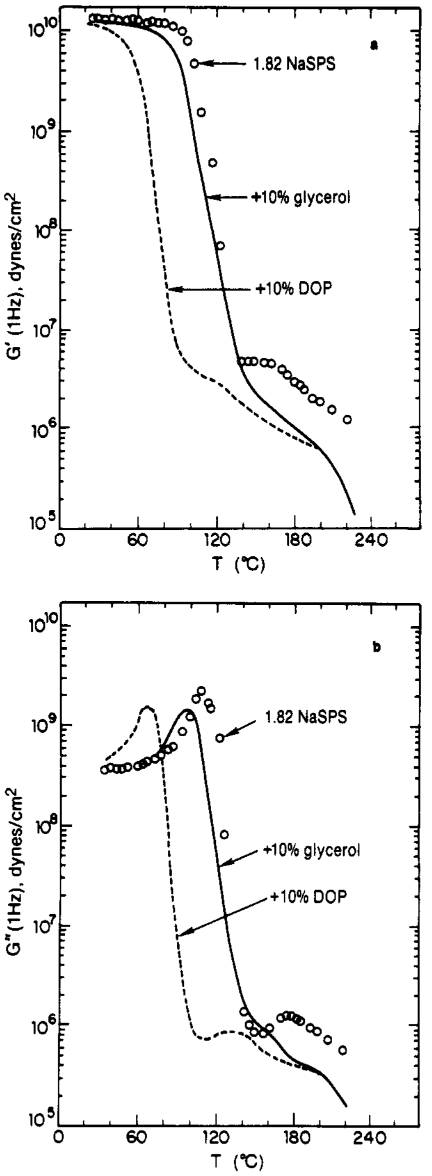

Figure 1. Dynamic mechanical behavior of 1.82Na-SPS, 1.82Na-SPS + 10 wt % DOP and 1.82Na-SPS + 10 wt % glycerol (f = 1 Hz).

built spectrometer that used a Varian E-109 microwave bridge and a TE microwave cavity. The spectra were stored in a Nicolet LAS 12/70 signal averager.

Results and Discussion

Two plasticizers of different polarity (as measured by the dielectric constant, ϵ), glycerol ($\epsilon = 42.5$) and dioctyl phthalate (DOP, $\epsilon = 6.4$), were used to assess the effects of low molar mass diluents on the structure and viscoelastic behavior of the SPS ionomers. DOP is a conventional plasticizer for PS, while glycerol is immiscible with PS.

The dynamic mechanical behavior of 1.82Na-SPS and the same material plasticized with 10 wt% glycerol and 10 wt% DOP are shown in Figure 1. The neat ionomer exhibited a plateau region in G' and a new high temperature loss peak in G'' above T_g, denoted T_c. The addition of DOP lowered T_g and shifted the entire modulus vs temperature curve to lower temperature along the temperature axis. Although the plateau in G' and the loss peak in G'' moved to lower temperature, both of these features, which are characteristic of ionic aggregation, remained. For the case of the ionomer containing glycerol, however, only a small decrease in T_g occurred, and the rubbery plateau and the high-temperature loss peak disappeared. These results clearly demonstrated the dual plasticization mechanism of ionomers described by Lundberg et al.[5] The polar glycerol preferentially interacted with the ionic domains and solvated the ionic associations. This weakened the ionic cross-links and primarily influenced that part of the viscoelastic behavior due to the ionic aggregation. The relatively nonpolar DOP affected only the polystyrene matrix and left the ionic associations and clusters intact.

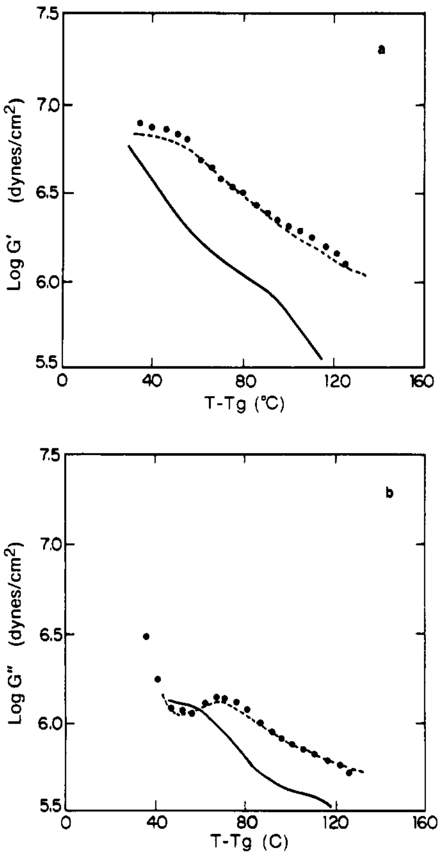

Figure 2. Dynamic mechanical data plotted against ($T - T_g$) for (●) 1.82Na-SPS, (- - -) 1.82Na-SPS + 10 wt % DOP, and (—) 1.82Na-SPS + 10 wt % glycerol (f = 1 Hz).

The different effects of DOP and glycerol on the viscoelastic behavior of SPS are more clearly seen in Figure 2, in which the dynamic mechanical moduli are plotted against ($T - T_g$). The viscoelastic response of the unplasticized SPS and the DOP-plasticized material were identical when the effect of T_g was removed. In contrast, the dynamic modulus above T_g of the glycerol-plasticized SPS fell considerably below that of the neat ionomer and the high-temperature G'' peak disappeared with the addition of 10% glycerol.

It was surprising that a *matrix plasticizer* like DOP shifted the ionic transition in a manner identical with that for T_g. One explanation is that the DOP swelled both the matrix and the clusters, though the SAXS data discussed below do not support that conclusion. An alternative explanation is that the decrease of T_c was a consequence of the connectivity of the two phases and the enhanced mobility of the plasticized polymer chains. As in block copolymers, the phases in ionomers are intimately connected due to the fact that individual chains pervade both the ionic domains and the hydrophobic continuous phase. Although DOP swelled only the hydrocarbon-rich portion of the ionomer, motion of the chain segments in the nonionic phase can create stresses at the boundary between

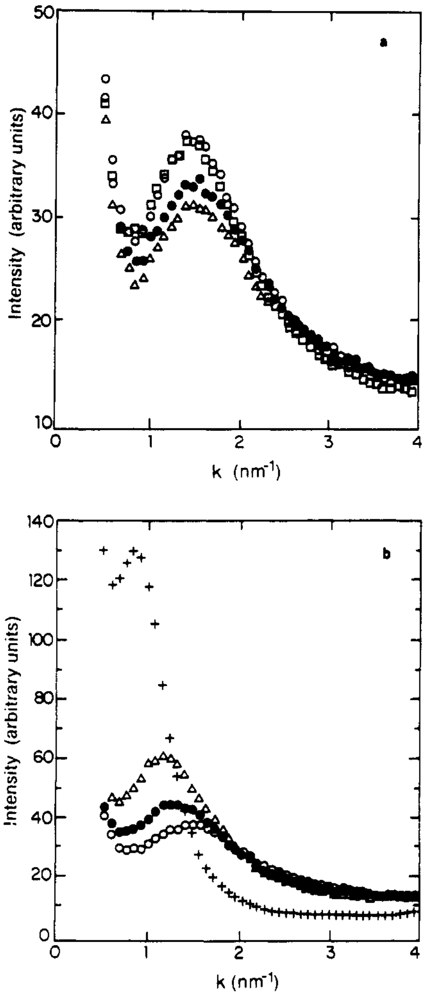

Figure 3. SAXS intensity vs scattering vector for 2.65Mn–SPS with plasticizers. a: (○) 0%, (□) 1%, (●) 5%, and (△) 10% DOP. b: (○) 0%, (●) 1%, (△) 5%, and (+) 10% glycerol.

phases that can influence the relaxation behavior in the clusters. Similar obsevations of dynamic interactions between phases were reported in styrene–butadiene block copolymers.[6] In that case, the authors proposed that the highly mobile butadiene segments induced premature molecular motions in the polystyrene microphase.

A more quantitative analysis of the interdependence of the two relaxation processes in microphase-associating polymers has recently been proposed. A model by Leibler et al.[7] suggests that the relaxation process intermediate between the glass transition and the terminal flow is due to the breaking of the associations and occurs on the time scale that ions break away from the cluster. The relaxation process is thermally activated with a characteristic relaxation time given by $t = t_0 \exp(E/kt)$ where E is the activation energy, k is Boltzmann's constant, T is the absolute temperature, and t_0 is proportional to a molecular friction factor. Therefore, if the plasticizer partitions into only the hydrocarbon phase, the activation energy of the process would be unaffected. However, the relaxation time t would be affected if t_0 decreased due to a reduction of T_g.

The selective solubilities of DOP and glycerol in the different phases was confirmed by SAXS characterization of the ionomer microstructure, and this was discussed in detail in a recent paper by Fitzgerald and Weiss.[8] The effect of DOP and glycerol on the SAXS of 2.65Mn–SPS is shown in Figure 3. For DOP the intensity of the ionic peak decreased with increasing plasticizer concentration,

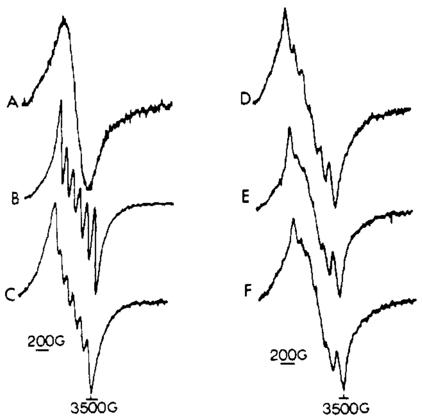

Figure 4. ESR spectra of 1% solutions of 1.65Mn–SPS in toluene and toluene/alcohol mixtures containing 0.01 mol of alcohol: (A) no alcohol, (B) methanol, (C) ethanol, (D) *n*-butanol, (E) *n*-amyl alcohol, (F) heptanol.

but the shape and position of the peak did not change. This indicated that the addition of DOP did not affect the clusters, and thus it must have preferentially swelled the hydrocarbon phase. The decrease of the intensity of the SAXS peak is due to the decrease in the volume fraction of clusters and an increase in the electron density of the continuous phase, which decreased the X-ray contrast between the clusters and the matrix.

The addition of glycerol to the 2.65Mn–SPS increased the intensity and breadth of the ionic peak and shifted it to smaller angles. Although the exact nature of the morphological changes cannot be determined from these limited SAXS data, it was apparent that unlike DOP, glycerol perturbed the ionic cluster microstructure. The shift and increase in intensity of the peak can be explained by an increase in the volume fraction of the clusters, which is consistent with the larger characteristic size corresponding to the smaller scattering angle. A more quantitative description of how the microstructure changed is model dependent, and there is currently no universally agreed-upon picture of the internal structure of the ionic clusters. The large increase in intensity for the sample containing 10% glycerol was probably due to phase separation of glycerol, and this will be discussed in more detail later in this paper.

The differences in the ability of a polar solvent such as glycerol and a nonpolar solvent such as DOP to solvate ionic interactions is demonstrated by the ESR spectra of solutions of 1.65Mn–SPS in toluene/alcohol solutions, Figure 4. The aliphatic content of the alcohol was varied from methanol to heptanol in order to adjust the polar nature of the alcohol. With no alcohol, the ionomer exhibited only a single, broad-line ESR spectrum, characteristic of associated Mn(II) ions.[9] Adding methanol resulted in resolution of the hyperfine structure in the ESR spectrum, which was due to the presence of isolated Mn(II) ions.[9] As the alkyl chain length of the alcohol increased, the resolution of the hyperfine structure became poorer, indicating poorer solvation of the ionic associations.

The effects of different DOP and glycerol concentrations on the dynamic mechanical behavior of 2.59Na-SPS are shown in Figures 5 and 6. The addition of DOP depressed T_g and broadened the glass transition, which is similar to its effect in plasticized poly(vinyl chloride).[10] The depression of T_g for the DOP-plasticized ionomer, Figure 7, followed the Fox equation[11]

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \tag{1}$$

where w_1 and w_2 are weight fractions of the polymer and

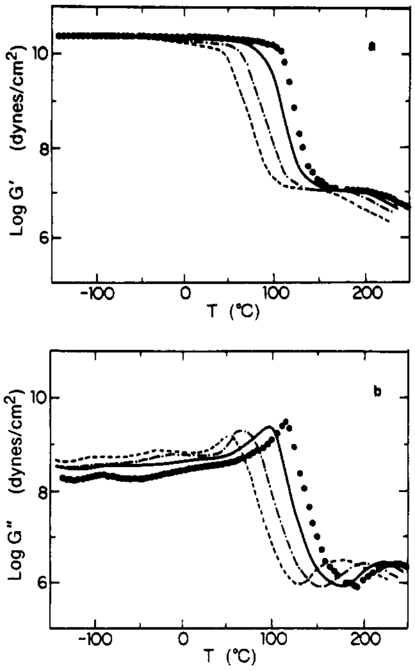

Figure 5. Dynamic mechanical behavior of 2.59Na–SPS with (●) 0%, (—) 5%, (···) 10%, and (- - -) 18% DOP (f = 1 Hz).

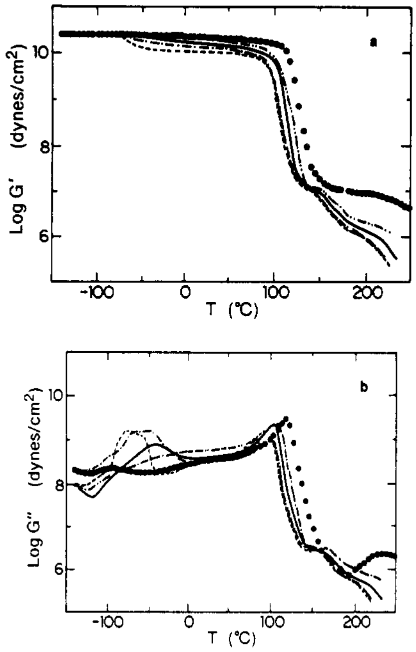

Figure 6. Dynamic mechanical behavior of 2.59Na–SPS with (●) 0%, (-···-) 3%, (—) 8%, (···) 12%, and (- - -) 23% glycerol (f = 1 Hz).

plasticizer, respectively. The temperature of the G'' peak at a frequency of 1 Hz in the transition region from Figure 5 was taken as T_g of the ionomer; the T_g of DOP is −85 °C.[12] The solid line in Figure 7 is the prediction of the Fox equation, which worked well for the DOP-plasticized samples.

Although the rubbery plateau of the ionomer moved to lower temperatures with increasing DOP content, the plateau modulus remained constant. The intensity of the loss modulus peak at T_g decreased as the peak broadened with increasing DOP, but the intensity and shape of the peak corresponding to T_c were unperturbed. When the dynamic mechanical data above the glass transition region for 2.59Na-SPS with the different amounts of DOP were plotted against ($T - T_g$) to eliminate the effects of T_g, Figure 8, all the curves superposed within experimental error. Thus, although the addition of DOP changed T_g of the nonionic phase, it had no effect on the viscoelastic processes that were dominated by the motions within the ionic clusters. This is in contrast to the effect of diethylbenzene (ϵ = 2.4) on the dynamic mechanical behavior of Na-SPS ionomers reported by Bazuin and Eisenberg.[13] In that study, the addition of diethylbenzene lengthened the rubbery plateau and lowered the plateau modulus.

The addition of glycerol to 2.59Na–SPS had only a minor effect on T_g, which decreased slightly with increasing glycerol up to about 12% glycerol and then remained constant, Figure 6. The decrease of T_g was probably due to limited solubility of glycerol in the hydrocarbon-rich phase as a consequence of the presence of multiplets. The

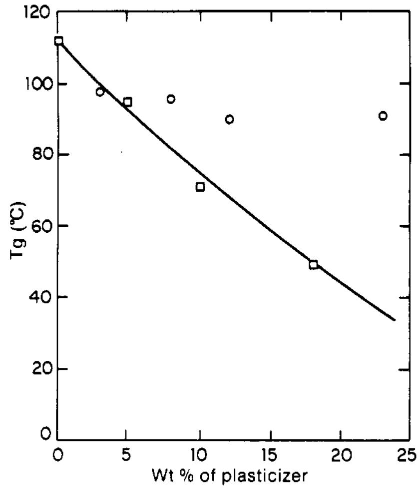

Figure 7. T_g vs plasticizer concentration for 2.59Na–SPS. (□) DOP, (○) glycerol. The solid line is the Fox equation prediction (eq 1) for both plasticizers.

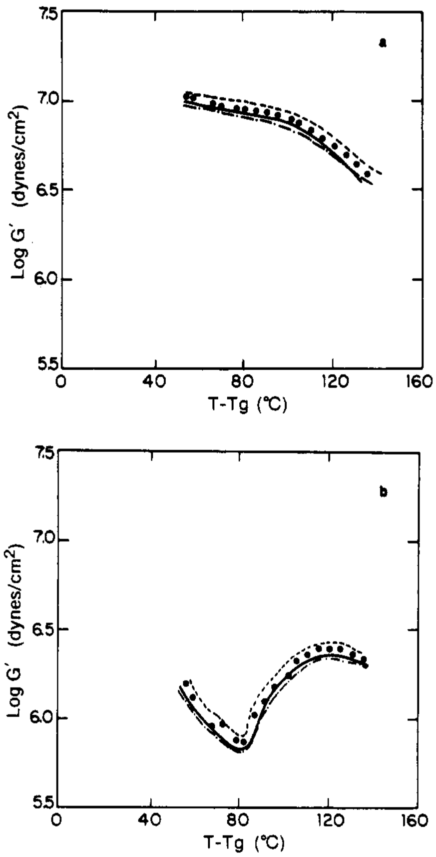

Figure 8. G' and G'' vs ($T - T_g$) for DOP-plasticized 2.59Na–SPS. (●) 0%, (—) 5%, (···) 10%, and (- - -) 18% DOP.

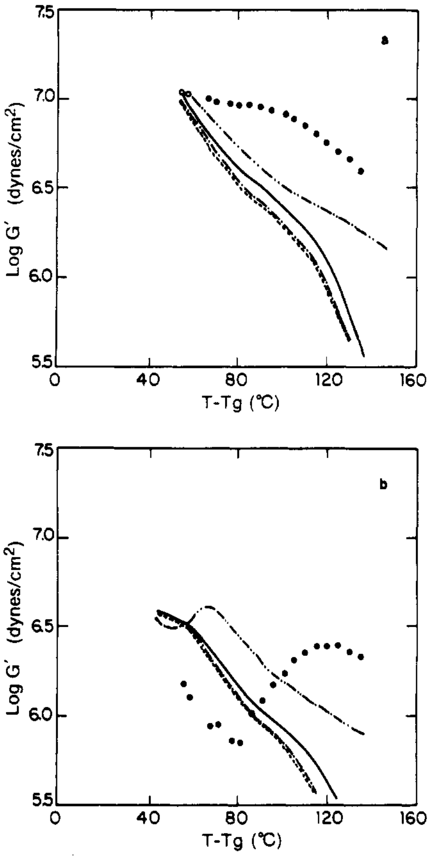

Figure 9. G' and G'' vs $(T - T_g)$ for glycerol-plasticized 2.59Na–SPS. (●) 0%, (- · · · -) 3%, (—) 8%, (- · · -) 12%, and (- - -) 23% glycerol.

major changes in the dynamic mechanical behavior were a diminution in the extent of the rubbery plateau in G' above T_g and a shifting of the high-temperature ionic relaxation in G'' to lower temperatures. Figure 9 shows the T_g-normalized G' and G'' data above T_g for the glycerol-plasticized ionomer, and in this case, it is clear that glycerol disrupted the ionic interactions and weakened the effects of the ionic phase on the viscoelastic behavior.

The post-T_g peak did not disappear, but at high glycerol concentrations, this relaxation overlapped with the matrix glass transition. The concentration dependence of T_c was consistent with its assignment as a *glass transition* for the clusters and with the conclusion that glycerol was an *ionic-phase plasticizer*. The dynamic mechanical evidence for the persistence of a dispersed ionic-rich phase in the glycerol-plasticized ionomers agreed with the SAXS data in Figure 3b that show the clusters exist at these plasticizer concentrations. Higher temperature SAXS studies[8] of a 2.65Mn–SPS containing 10 wt % glycerol showed that considerable phase mixing between the glycerol-swollen clusters and the ion-poor matrix occurred between 70 and 140 °C, which agreed well with the data in Figure 6 that show a T_c of ca. 140 °C for that system. (It should be recognized that in the discussion above, comparisons were made between viscoelastic data for Na salts and SAXS data for Mn salts. Elevated temperature SAXS measurements of the plasticized Na salts were not made. The general conclusions given above are, however, believed to be justified on the basis of studies of the structure and viscoelastic behavior of several different salt derivatives of SPS that indicated similar behavior.)

Sub-T_g Dynamic Mechanical Relaxations. For the DOP-plasticized ionomers, two low-temperature relaxations were observed in G'' below T_g, Figure 5. The lower peak, at about −95 °C in the neat ionomer, corresponds to the γ-relaxation process of PS, which results from rotation of the phenyl groups. This occurs at about −132 °C in PS, and the increase in temperature of this relaxation in the ionomers is due to more restricted rotation of the phenyl rings due to association and steric hindrance of the ionic groups. A similar effect was reported for poly(*p*-bromostyrene) for which the γ-relaxation occurred at −115 °C.[14]

The γ-relaxation of the ionomer decreased slightly with the addition of DOP. This might be expected since DOP swells the PS-rich phase, which should increase the mobility of the chain and the rotational freedom of the phenyl groups. Illers and Jenckel, however, found that the addition of DOP to PS actually *increased* the γ-relaxation.[15]

A broad shoulder corresponding to the β-relaxation of PS was observed ca. 30 °C in G'' of the neat ionomer. The origin of this relaxation in PS is not well understood, and it has been attributed to such different mechanisms as motion of chain segments in which the phenyl groups are not as sterically hindered as in the bulk of the chain, motion of chain ends, and local mode twisting of the chain.[12] For the plasticized ionomers, the β-relaxation decreased to about −30 °C, which was consistent with previous studies of the effect of phthalate plasticizers on the relaxation processes of PS.

Figure 6 shows the low-temperature dynamic mechanical properties of the glycerol-plasticized ionomers. The sample containing 8% glycerol exhibited a transition in G' at ca. −50 °C, which moved to lower temperature with increasing glycerol concentration. This was believed to be caused by phase separation of glycerol. Two low-temperature relaxations were observed in G'', one of which was believed to be the β-relaxation process of polystyrene and the other the glass transition of glycerol. The T_g of pure glycerol is −85 °C.[16] These results indicate that the glycerol was phase-separated at concentrations of 8% and above. In addition, the gradual falloff of G' starting at ca. −30 °C and what may be a broad peak in G'' for the ionomer containing 3% glycerol suggested that phase separation may have also occurred in this sample.

The samples containing 3% and 8% glycerol were optically clear, while the ionomers containing higher concentrations of glycerol were opaque. This observation is contrasted with mixtures of PS and glycerol that became opaque at glycerol concentrations of 1% or less. Thus, at concentrations up to 8%, any separate glycerol phase was sufficiently small as not to scatter light, i.e., <ca. 1 μm. The small phase size was presumably due to interactions between the sulfonate groups and the phase-separated glycerol. This is analogous to what happens in zinc stearate plasticized sulfonated EPDM in which microcrystalline regions of the zinc stearate are stabilized by interactions with the metal sulfonate groups of the ionomer.[17]

Above 8% glycerol, the phase-separated glycerol formed sufficiently large domains to scatter light. The growth in the size of the glycerol phase as the plasticizer concentration increased may explain the shift of the low-temperature G'' peak from about −50 °C for 8% glycerol to near −85 °C at 23% glycerol. The high value for the glycerol T_g in the 8% sample, i.e., −50 °C, was probably due to restriction of the molecular mobility of the glycerol because of interactions with the metal sulfonate groups. As the glycerol domains grew larger, the sulfonate groups had less of an effect on the glycerol transitions and its T_g accordingly. The assignment of the G'' peaks is somewhat

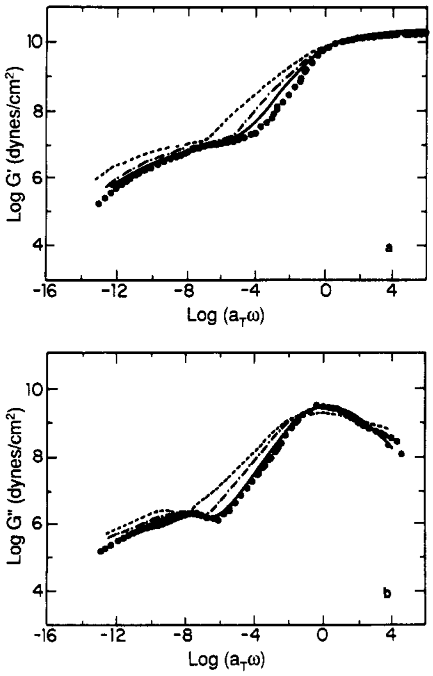

Figure 10. Dynamic mechanical mastercurves for DOP-plasticized 2.56Na–SPS. The line symbols are the same as in Figure 8.

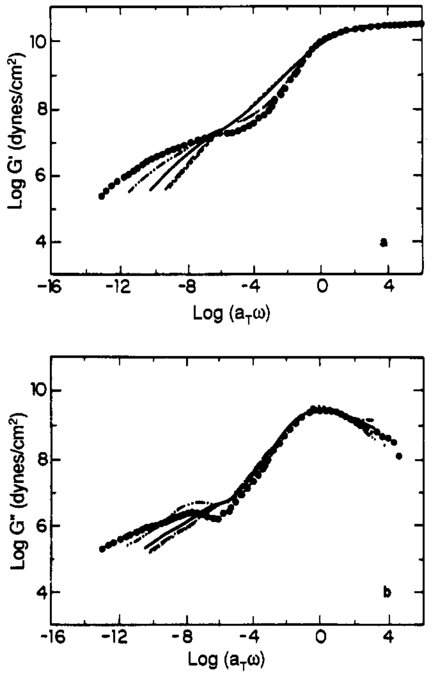

Figure 11. G' and G'' master curves for glycerol-plasticized 2.59Na–SPS. The line symbols are the same as in Figure 9.

tentative due to the complication of the presence of two distinct low-temperature relaxations and the apparent disappearance or shift of the γ-relaxation of PS observed at about −95 °C in the neat ionomer.

Frequency–Temperature Superposition. Moduli–frequency mastercurves referenced to T_g are given in Figures 10 and 11 for the DOP- and glycerol-plasticized 2.59Na–SPS. Frequency–temperature superposition applied in all cases. As the DOP concentration increased, the transition region broadened and the rubbery plateau moved to lower frequencies, Figure 10. The lower frequency G'' loss peak persisted, but it also moved to lower frequency with increasing DOP concentration. The relaxation time spectra for these compounds, each referenced to T_g, are given in Figure 12. These showed a broadening of the relaxation times associated with the glass transition of the nonionic phase, and the relaxation processes due to the clusters moved to longer times relative to the matrix glass transition. That and the fact that the shape of the distribution at long times did not change when DOP was added are consistent with the conclusion that DOP only plasticized the nonionic phase and did not disrupt the ionic network.

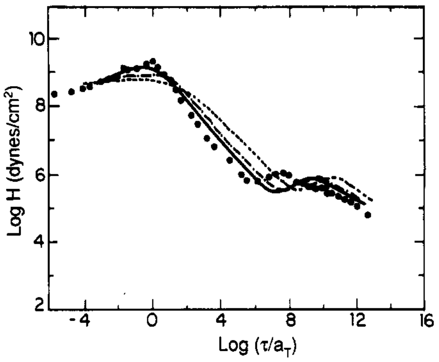

Figure 12. Relaxation time spectra for DOP-plasticized 2.59Na–SPS. The line symbols are the same as in Figure 8.

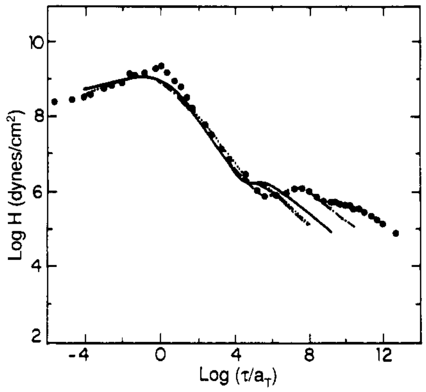

Figure 13. Relaxation time spectra for glycerol-plasticized 2.59Na–SPS. The line symbols are the same as in Figure 9.

Glycerol, however, did perturb the ionic cross-links as seen from the viscoelastic data in Figure 11. The primary transition region broadened with increasing glycerol concentration, though not as much as with DOP, and the rubbery plateau diminished and eventually disappeared at higher glycerol content. G'' in the primary transition region was relatively unaffected by the addition of glycerol, but the low-frequency loss process moved to higher frequencies. There also was an increase in the intensity of the of the low-frequency loss peak, which could be due to an increase in the cluster volume due to swelling by the glycerol or to changes in the breadth of the relaxation.

Although neither the neat ionomer nor the DOP-plasticized ionomers exhibited terminal viscoelastic behavior, even at reduced frequencies of the order of 10^{-14} s^{-1}, the data in Figure 11 for the more highly glycerol-plasticized materials approached the terminal linear viscoelastic region at frequencies of the order of 10^{-10} s^{-1}. In contrast, the unmodified PS showed terminal behavior at frequencies ca. 10^{-8} s^{-1} at $T = T_g$.

The effect of glycerol on the relaxation time spectrum of 2.59Na–SPS is shown in Figure 13. The intermediate relaxation times associated with the primary glass transition were unchanged. The higher relaxation times due to the ionic clusters were, however, systematically eliminated by the addition of glycerol. Accordingly, the viscosity of the ionomer, which is dominated by the longer relaxation times, was significantly reduced by the addition of glycerol.[5]

Conclusions

The two-phase morphology of ionomers offered two separate approaches for modifying the viscoelastic behavior: (1) plasticization of the ionic domains or (2) plasticization of the hydrocarbon-rich continuous phase. Dynamic mechanical analysis and SAXS showed that DOP was a matrix plasticizer and glycerol was an ionic-phase plasticizer.

DOP lowered T_g of the ionomer and broadened the glass transition. It also lowered the temperature of the ionic domain transition, which was attributed to the synergistic effect of the mobility of the continuous phase on the relaxation behavior of the clusters. DOP did not alter the existence or the general characteristics of the clusters, which continued to dominate the viscoelastic properties.

Glycerol preferentially affected the ionic domains. Some glycerol may have dissolved in the continuous phase as a result of the presence of multiplets, but its effects on the viscoelastic response and the structure of the clusters were much more important. Glycerol lowered the temperature of the relaxation of the ionic phase, and at high glycerol concentrations, this loss process became coincidental with the primary glass transition. Although glycerol preferentially interacted and weakened the ionic interactions responsible for the physical cross-links and ionic clusters, it did not eliminate the clusters. It did, however, reduce the temperature at which the microstructure began to disorder.

DOP had only a minor effect on the high-temperature relaxation times that control viscosity, while glycerol eliminated the long-time processes. Accordingly, glycerol was a more effective plasticizer for SPS ionomers, though it also reduced many of the desirable features of the ionomer, such as high-temperature rigidity and dimensional stability. DOP, though a good plasticizer for PS, was less effective at reducing the viscosity of the ionomer. It did, however, provide some viscosity reduction without significantly degrading the properties attributable to the ionic clusters.

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