Structure and Properties of Sulfonated Polysulfone Ionomers

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INTRODUCTION

It is now genrally accepted that the incorporation of ionic groups into a medium of low dielectric constant, such as a hydrocarbon polymer matrix, results in their aggregation. The degree of aggregation and the influence of such factors as ionic group type and concentration and the nature of the polymer backbone are still matters of controversy. In particular, although much indirect evidence is available pointing to the existence of microphase-separated ionic regions in most ionomers, the nature of this microphase remains a subject of active research at the present time.[1]

The polysulfone that is the subject of this investigation is the poly(arylether) sulfone first introduced by Union Carbide in 1967.[2] It is a high-performance engineering thermoplastic with good toughness and high impact strength. Sulfonation of the aromatic rings in this polysulfone leads to a material that has been suggested for use as a reverse osmosis desalination membrane.

The present paper addresses three major points: (1) the degree of ionic association in sulfonated polysulfone ionomers, (2) the effects of water and other polar diluents on properties, and (3) requirements for bringing about control of the properties of ionomers by understanding ionic interactions.

EXPERIMENTAL

Materials

Polysulfone (PSF)

The starting precursor polymer in this study is that commercially available from Union Carbide under the designation of Polysulfone P-1700. The weight-average molecular weight is approximately 75,000, and the number-average molecular weight is approximately 35,000[3]. The structure is
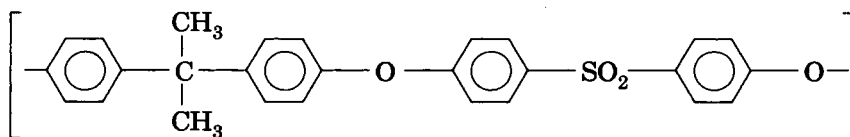
Sulfonated Polysulfone (SPSF)

The polysulfone mentioned above was sulfonated using a 2:1 ratio of sulfur trioxide (SO_3) to triethyl phosphate (TEP) complex in 1,2-dichloroethane at room temperature. The resultant sulfonic acid was neutralized with either sodium methoxide or cesium acetate depending on the salt form desired. Compositions ranging from approximately 0.25 ionic groups per polysulfone repeat unit ($-SO_3^-X^+$/PSF) to approximately 1.0 $-SO_3^-X^+$/PSF were prepared by varying the initial ratio of SO_3 to PSF. This synthetic procedure was performed by the Hybrid Cell Project Group of the Occidental Petroleum Company and the resulting samples kindly provided by them.

Sample Characterization

The materials used in this study were characterized by various techniques both at the facilities of the Occidental Petroleum Company and at the Materials Research Laboratories of the Polymer Science and Engineering Department, University of Massachusetts (Amherst, Massachusetts).

Elemental Analysis

Elemental analysis was used to determine the degree of sulfonation by comparison of the sulfur-carbon ratios of polysulfone and of the sulfonated materials. Using ratios of sodium or cesium to sulfur, the degree of neutralization was also determined.

Nuclear Magnetic Resonance (NMR)

NMR measurements were carried out on dimethylsulfoxide-d_6 solutions of the precursor, sulfonic acid, and salt forms using HMDS as an external standard. Proton NMR was used to determine if any cross-linking had occurred, as well as for the determination of the sulfonate group's location on the polymer chain. Carbon-13 NMR was used to determine the degree of sulfonation in conjunction with the elemental analysis.

Fourier Transform Infrared (FTIR)

Solvent cast films were prepared from dimenthylformamide solutions. FTIR spectra of these films were obtained with a Nicolet Series 7199 FTIR Spectra System between 4000 and 400 wavenumbers (cm^{-1}) at a resolution of 2 cm^{-1}. The determination of the sulfonation level by FTIR was based upon the ratio of the absorption at 1025 cm^{-1} (SO^{3-} symmentrical stretch) to that of either 1150 cm^{-1} (SO_2 symmentrical stretch) or 1015 cm^{-1} (aryl ether vibration). In addition, the infrared spectra were also used to give a qualitative estimate of the water content by examination of the 3200–3700 cm^{-1} region (stretching vibrations) and at the 1640 cm^{-1} (scissor vibration) region.

Differential Scanning Calorimentry (DSC)

The DSC experiments were performed using a Perkin-Elmer Model 2-B DSC with a computer-assisted baseline. The temperature range studied

varied depending on the particular experiment, but the range -35–365C was covered for a representative group of samples. The heating rate was 20°C/min. Indium, tin, and distilled deionized water were used as calibration standards. The glass transition was taken as the midpoint of the change in heat capacity. In addition to basic characterization, DSC was used to check for any phase separation that may have occurred between the polymer matrix and the ionic groups, as well as to study the effects of sulfonation, counterion, and water content on the ionomeric properties.

Experimental Technique

The polymers analyzed in this study were in the form of thin films. The films were prepared by solution casting from dimethylformamide, washed with water, annealed at 150°C from 15h in vacuum, and then stored in an appropriate slightly basic solution until further conditioning. The following designation will be used to describe the samples of this study:

1. The ionic content will be described in terms of the number of ionic groups per polysulfone repeat unit.

2. The counterion type will be designated by the accepted IUPAC abbreviation for that element.

3. Further conditioning of the samples will be noted by one of three terms:

Wet: Samples were washed with water, dried at 110° in vacuum for 24h, then immersed in water at 25°C until no further weight gain was recorded.

RH: Samples were washed with water, dried at 110°C in vacuum for 24h, then kept at ambient conditions to absorb moisture from the air. The samples were conditioned for 2 months this way without an equilibrium weight being achieved.

Dry: Samples were washed with water, dried at 110° in vacuum for 24h, then stored in a vacuum dessicator over Drierite R until use.

4. Any other characteristic information will be noted, especially if it differs from the above description.

Thus, 0.35 Cs-Wet refers to a cesium ionomer containing 35 ionic groups per 100 repeat units of the polysulfone backbone that has been saturated with water. A list of samples studied along with some characteristic information is in Table I.

1. X-ray scattering. Absorption and transmission coefficients were obtained by use of a Siemens D-500 wide-angle x-ray diffractometer. These coefficients were used to determine the optimum thickness for samples to be used in the small-angle x-ray scattering (SAXS) experiments. In addition, WAXS was also used to determine if any crystallinity was present in the samples. The SAXS measurements were performed with a Kratky small-angle x-ray camera and position-sensitive detector using nickel-filtered copper radiation.

2. Dynamic-mechanical analysis. The dynamic-mechanical analysis was done with a Vibron Dynamic Viscoelastometer (Rheovibron), Model DDV-II (Toyo Measuring Instruments Company). A temperature range of -160–320°C at a rate of about 2°C/min was examined. The samples were run under dry nitrogen at a frequency of 11 hz.

3. Water Absorption Measurements. The quantity and rate of water absorption was determined from timed experiments of water uptake. The

TABLE I
Sample Description[1a]

Sample	Film thickness (um)	T_g(Dry)[b] (°C)	T_g(Wet)[c] (°C)	Other[d]
Polysulfone	50	190	190	--
0.35 Na	50	240	235	--
0.50 Na	35 and 50	270	263	--
0.80 Na	35	290	270	--
1.00 Na	40	230–335[e]	320[e]	--
0.30 Cs	25 and 100	245	208	None
0.35 Cs	50	250	227	None
0.50 Cs	25, 50, and 100	273	256	0–3°C[d]

[a] The structure of the sulfonated polysulfone is 6-C2

[b] T_g taken as the average of three DSC scans between 150 and 325°C at 20°C/min.

[c] T_g taken as the average of three DSC scans between 150°C and $T_g + 25$°C at 20°C/min.

[d] Water-saturated sample blotted dry, cooled to -35°C, and run to 40°C followed by recooling to -35°C. This value is representative, but the size and shape of the peak changes with each DSC scan.

[e] Weak and/or broad transition.

3. Water Absorption Measurements. The quantity and rate of water absorption was determined from timed experiments of water uptake. The amount of water uptake was measured gravimetrically using a Mettler Microbalance with 0.01 mg accuracy. The samples were immersed in water, removed at the appropriate times, blotted dry with filter paper, and weighed before being returned to the water. The time out of water was kept to a minimum and averaged about 30 s. In addition to studies at 25°C, immersion at 50, 75, and 100°C, exposure to pure water vapor (100% humidity), and exposure to the relative room humidity under ambient conditions were also studied. Diffusion coefficients were obtained by the methods of Crank and Park.[4]

4. Solubility measurements. Films of sulfonated polysulfone and polysulfone resin were cut into 1-cm² pieces and placed into 10ml of a selection of "solvents." After a period of 2 days, the extent of dissolution was judged as either soluble, partly soluble, or not soluble. Using solubility parameter data for the solvents available in the literature[5], the one-dimensional solubility parameters for polysulfone and its sulfonated ionomers were determined. In addition, based on the three-dimensional solubility parameters of Hansen[6], a triangular diagram was constructed and a region of solubility determined for the polymers was well. Also, following the theory of Hansen, a two-dimensional plot of ∂_p versus ∂_h was constructed to qualitatively determine values of ∂_p and ∂_h for the polymers based on the assumption that the value of ∂_d does not change significantly ($<5\%$). In a similar fashion, the solubility of a given polymer was treated as a point in three-dimensional space so that the ∂_i values describe the components of the vector that determines the locus of that point in space and whose magnitude, $\sqrt{\partial_d^2 + \partial_p^2 + \partial_h^2}$, is the one-dimensional solubility parameter defined by Hildebrand.[16] Plots of $\sqrt{\partial_d^2 + \partial_p^2}$ versus ∂_h, $\sqrt{\partial_d^2 + \partial_h^2}$ versus ∂_p, and $\sqrt{\partial_p^2 + \partial_h^2}$ versus ∂_d were also made to obtain "calculated" values for of the polymers. Using these calculated values, cosolvent systems involving mixtures of two or three nonsolvents were predicted and their values plotted on the triangular diagram as well.

RESULTS

The Fourier transform infrared spectra show four major differences etween the polysulfone base resin and the sulfonated ionomers. Examples f spectra are shown in Figures 1 and 2. The major difference in the figures s the presence of an absorbance at 1025 cm^{-1} in the case of the ionomers, which is attributed to the symmetrical stretch of the sulfonate groups. The asymmetric stretch is believed to be near 1190 cm^{-1} but is not readily observable due to the presence of other overlapping absorbances in that area. The addition of the sulfonate groups also affects the absorbances related to the aromatic rings as well. Differences between the spectra are notable in the 835, 855, and 875 cm^{-1} regions and are attributed to changes in the C-H out-of-plane bending motions between parasubstituted and tri-subsituted aromatics. Lastly, the most notable difference is the presence of significant hydrogen bonding in the case of the ionomers. The usual absorbance in the 3700–3200 cm^{-1} region was used as a qualitative estimate of the water content in the ionomers.

The differential scanning calorimetry results, which are contained in Table I, show that the incorporation of sulfonate groups into polysulfone causes the glass transition temperature (Tg) to rise linearly as well as to become broader and less defined with increased ionic content. This trend is shown in Figure 3, where the glass transition is plotted against the degree of sulfonation. The slope of this line, dTg/dc, is about 1.5°C per mol% sulfonate. Another important feature of this plot is that the slope is constant throughout the entire sulfonation range studied.

The DSC scans exhibited no other transitions between range $-40°-325°C$, including those that were soaked in water. The study of the effects of water on the glass transition as measured by DSC was somewhat inconclusive in that the amount of water present at Tg is not known. In general, the wet samples exhibit slightly lower Tg than the dry samples, although this affect
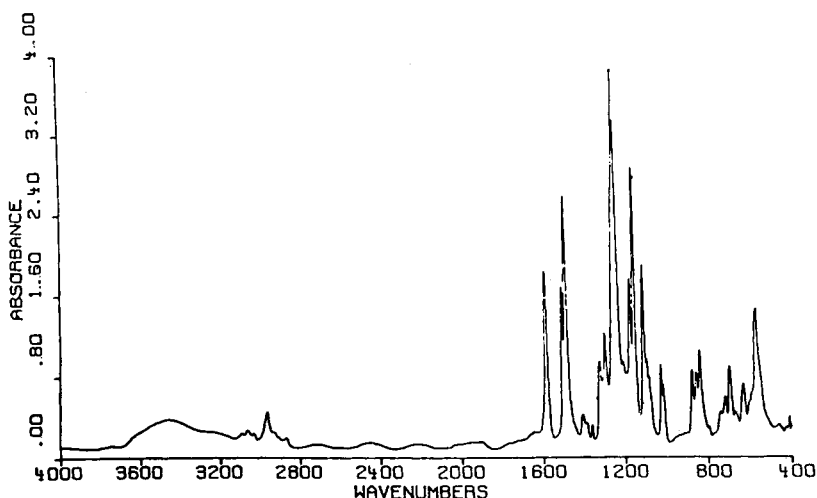

Fig. 1.   Fourier transform infrared spectrum of unmodified polysulfone.
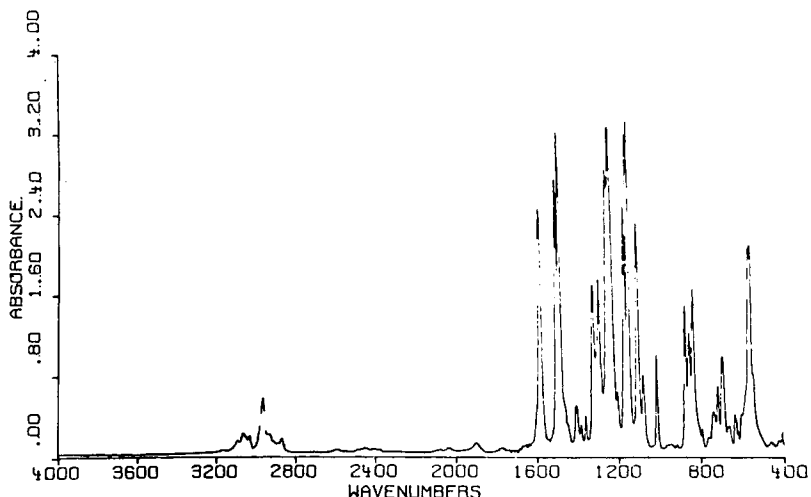
Fig. 2.   Fourier transform infrared spectrum of the 0.50 Na polysulfone ionomer.

is dependent on counterion type of sulfonation level. In addition, no evidence for a transition of the water itself was observed except in the case of the 0.50 Cs sample.

Wide-angle x-ray scattering was carried out to determine the optimum thickness of the samples for the small-angle x-ray scattering studies. The optimum thickness for polysulfone was calculated to be 0.190 cm; for 0.30 Cs-Dry, 0.045 cm; and 0.50 Cs-Dry, 0.020 cm. These differences arise mainly from the electron density differences between the mostly hydrocarbon polysulfone backbone and the metallic ionic side groups. Besides calculating the optimum thickness, the wide-angle scans also served to show that no crystallinity was present in any of the samples studied.
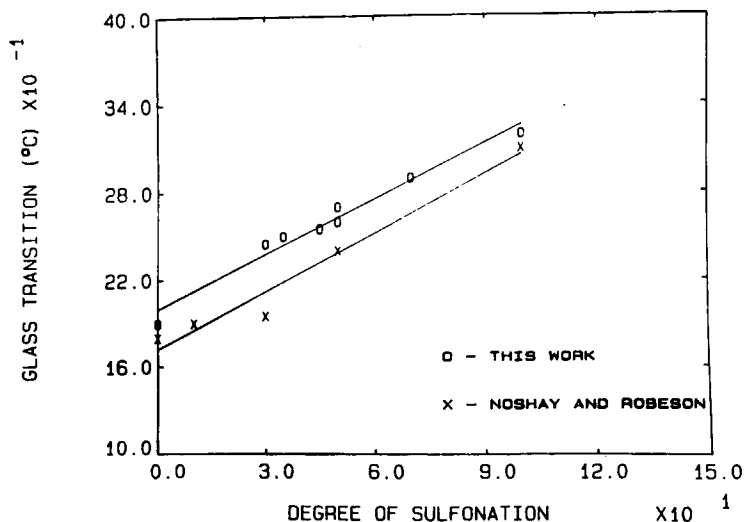
Fig. 3. Dependence of the Glass transition temperature on the degree of sulfonation in polysulfone ionomers.

Small-angle x-ray scattering was performed to investigate any ionic clustering present in these ionomers. Plots of scattered intensity versus scattering angle for an ionomer generally exhibit a peak or significant scattering intensity in the region of 2_θ 2 - 6°. The scattering profiles for 0.50 Cs-Dry and Wet are shown in Figure 4. Some scattering is suggested in the case of the dry sample, but it is several orders of magnitude smaller than that observed for other ionomers in which clustering is know to exist. Regardless of prior thermal history and ionic content, no significant scattering was found. Because of the low scattering intensity, these scans were not subjected to quantitative analysis. However, from these results, it is concluded that the percentage of any clusters that may exist must be small (< 10%). Thus, most of the ionic groups are present in the form of multiplets and are not phase separated from the hydrocarbon portion of the polymer.

Figure 5 shows the dynamic-mechanical relaxation behavior of polysulfone. There is an α transition near 190°C, a γ transition near −100°C, and a room temperature tensile storage modulus (E') of 1.65 GPa. Sulfonation of the polysulfone backbone results in mechanical relaxation behavior that exhibits three transitions depending on ionic content, counterion, water content, and thermal history. Comparing Figure 5 with Figures 6 through 8, one can see that the α relaxation of polysulfone is greatly increased by sulfonation and that the sodium salts are slightly higher than the cesium salts. The overall range of the α-peak temperature lies between values of 250°C for 0.35 Na-Wet to greater than 300° for 0.50 Na-Dry. The correlation between the α relaxation and Tg as measured by DSC is quite good. In general, water tends to slightly increase the α-relaxation remperature in the cesium ionomers and decrease it for the sodium ionomers.
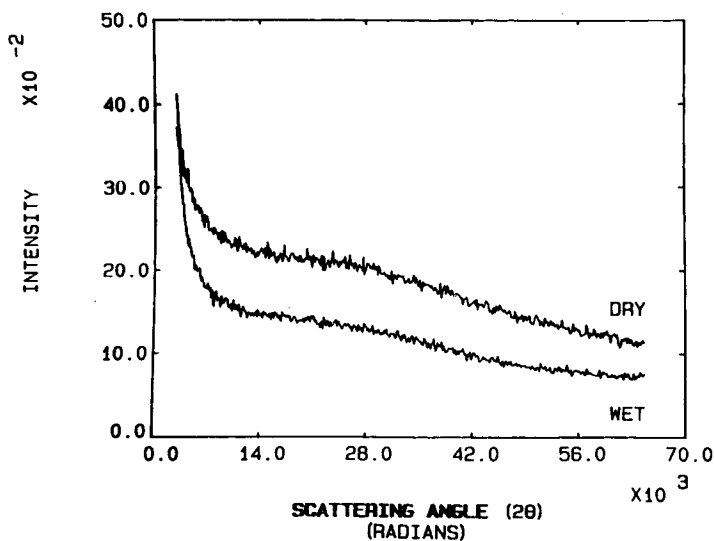

Fig. 4. Dependence of x-ray scattering intensity on scattering angle for the wet and dry 0.50 Cs polysulfone ionomers.
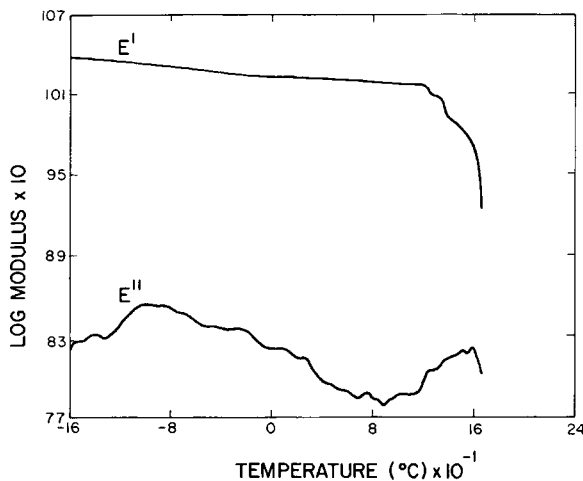
Fig. 5. Temperature dependences of the storage (E') and loss (E'') moduli at 11 hz for unmodified polysulfone.

Comparison of E' values at various temperatures for the samples in Figures 5 through 8 shows that sulfonation increases the modulus and is dependent upon the same factors as the α transition. Typical values range from 2.0 GPa for 0.35 Na or Cs-Dry to 3.3 GPa for a 0.50 Na-Dry. In general, water tends to increase the modulus of the sodium ionomers but has a variable affect on the cesium system, depending on the amount of water present. Overall, in the dry state the storage modulus of the ionomers decreases by only 1.5 GPa over the temperature range 175–225⁰C. Thus, the modulus is of the order of 1.0 GPa over a 400⁰C temperature range.

Incorporation of the ionic material into polysulfone causes the low-tempreature dynamic-mechanical behavior to become somewhat more complicated. A β transition appears in the ionomers and tends to move slightly to higher temperatures with sulfonation but does not appear to depend on
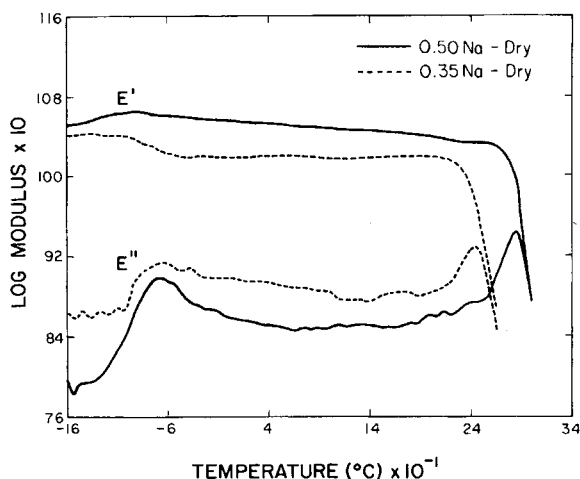

Fig. 6. Temperature dependence of the storage (E') and loss (E'') moduli at 11Hz for the 0.35 Na and 0.50 Na polysulfone ionomers.
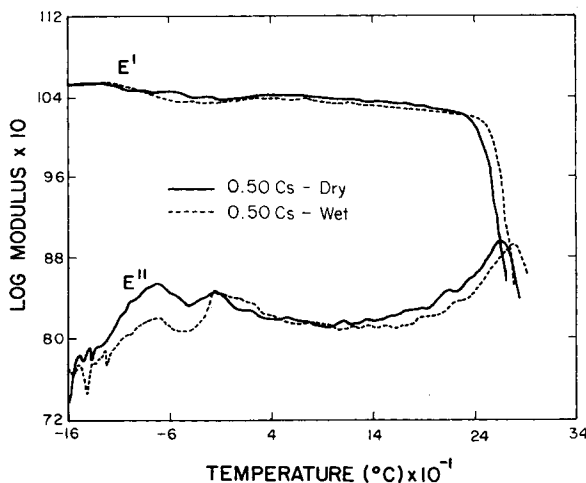
Fig. 7. Temperature Dependence of the storage (E') and loss (E'') moduli at 11 Hz for the wet and dry 0.50 Cs polysulfone ionomers.

cation type. Water tends to shift this peak slightly to lower temperatures with increased intensity. Typical values are between -13°C for 0.50 Na-Dry and -21°C for 0.35 Cs-Wet. Similarly, sulfonation causes the γ transition to occur 20–40°C higher and usually with increased intensity compared with polysulfone. In the sodium ionomers, water tends to shift the γ relaxation to lower temperatures with decreased intensity, an effect often referred to as antiplasticization. The cesium ionomers, however, show varying behavior, depending upon the amount of water present. In general, they exhibit only a slight decrease in the γ-relaxation temperature and relatively no change in intensity due to water. The results of the effects of water on polysulfone itself show the γ transition to be enhanced slightly as well as shifted to slightly higher temperatures.
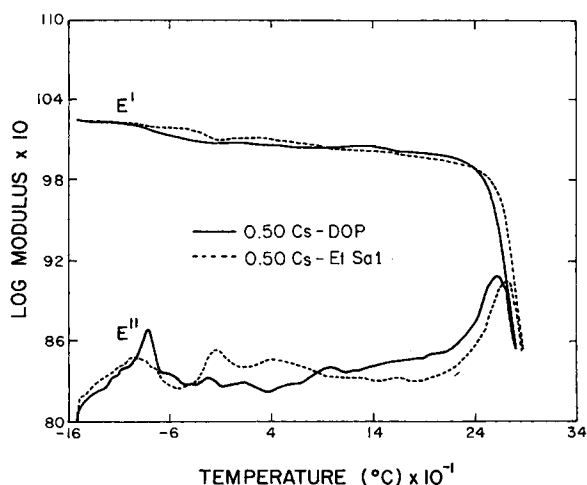

Fig. 8. Temperature dependences of the storage (E') and loss (E'') moduli at 11 Hz for 0.50 Cs polysulfone ionomers containing dioctylphthalate and ethyl salicylate.

Overall, the dynamic-mechanical behavior was found to be very depen-
dent on thermal history and water content. In particular, the way in which
the water is incorporated into the films was found to affect the β transition.
If the sample is immersed in water immediately as it comes from a 110°C
oven, the β relaxation will be more prominent and the E' value slightly
lower than if the sample is first cooled to room temperature gradually and
then immersed. In addition, the FTIR analysis shows that, even after sub-
jecting an ionomer sample to dynamic-mechanical testing throught the
range $-160-325$°C at a rate of about 2°C/min, some water ($\sim 10\%$) is still
present.

Besides water, the effects of other low-molecular-weight diluents on the
dynamic-mechanical spectra were examined. Most small polar molecules
tended to show behavior very similar to that of water. Generally, they
decreased the γ relaxation temperature, decrease the β-transition temper-
ature, and increase the β-transition magnitude. Their effect on the tem-
perature of a α relaxation is usually minimal, less than 20°C. Conventional
ester-type plasticizers tend to increase the γ relaxation temperature as well
as reduce or eliminate the β transition. Phenyl ether, an analog of part of
the polysulfone repeat unit, decreased the γ relaxation but increased the
β transition in both tempreature and magnitude. Overall, the majority of
diluents examined showed no major affect on the material properties. The
greatest plasticizing effect came from dodecanol, which decreased Tg by
25°C and the tensile storage modulus by 70%.

To better understand the role of water in determining the mechanical
properties, quantitative water absorption measurements were performed.
A typical absorption curve is shown in Figure 9. In most cases, an equilib-
rium was reached within 24 hs after immersion, but no equilibrium was
reached even after 2 months in the case of exposure to relative humidities
less than 90% at room temperature. No difference in the total amount of
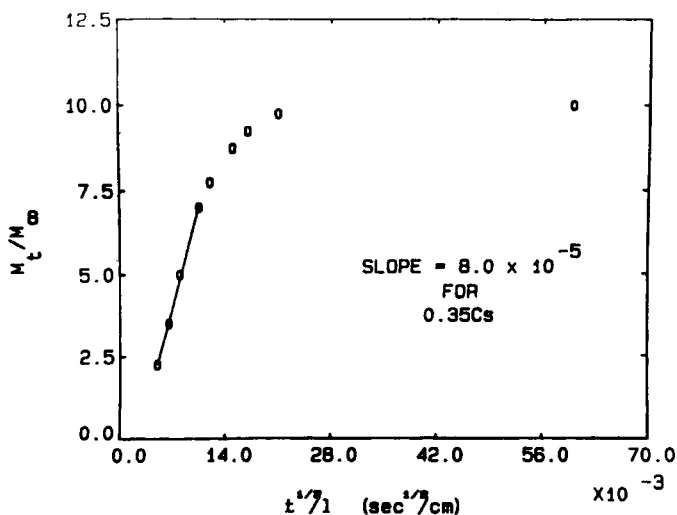

Fig. 9.   Dependence of (M_t/M_∞) on $t^{1/2}$ for the 0.35 Cs polysulfone ionomer.

water absorbed between submerging (liquid) and exposing to 100% relative humidity (vapor) was observed, although attainment of equilibium required longer times in the case of exposure to vapor.

The absorption of water in these materials was found to be proportional to the degree of sulfonation, with the ionomers absorbing 10–25 times more water than the unsulfonated polysulfone resin. Specifically, polysulfone absorbs about 0.5% by weight and the ionomers absorb upward of 15% at room temperature, depending on the sulfonation level and the counterion type. Comparison of the ionomers shows that the sodium forms absorb 1.7 times more water than the otherwise equivalent cesium forms. Specifically, the sodium ionomers absorb only 1.7–3.0. Absorption at relative humidity under ambient conditions produced no equilibrium value even after 2 months. At that time the sodium forms had absorbed 1.5–2.0 water molecules per ionic site and the cesium forms absorbed 0.7–0.8, values about half of those obtained by immersion.

Varying the temperature of the water had very little effect on the total amount of water absorbed and only a small effect on the rate of absorption. In general, the amount of water initially absorbed at $100^{\circ}C$ was almost twice that at $25^{\circ}C$, but this additional water was expelled when the sample was cooled back to $25^{\circ}C$, equilibrating at about the same value as that obtained directly at $25^{\circ}C$.

Using theory and equations developed by Crank and Park,[4] the diffusion coefficient of water through these materials was calculated from the initial slope, $4D^{1/2}/\pi^{1/2}$, of a plot of $Mt/M\infty$ versus $(t/l^2)^{1/2}$. The results are contained in Table II along with values for other polymers taken from the literature.[7] Many of these values were difficult to obtain because of the low water sorption of the polymers, and thus considerable error (as much as 100%) could exist in the values quoted in Table II.

TABLE II
Diffusion Coefficients

Sample	$\bar{D}_{25^{\circ}C}$(cm^2/s^{-1})	$\bar{D}_{100^{\circ}C}$(cm^2/s^{-1})	Equilibrium water uptake at 25°C (%)[a]
Polysulfone	3.3×10^{-11}	—	0.5
0.35 Na	5×10^{-11}	5×10^{-10}	5
0.50 Na	5×10^{-10}	2×10^{-9}	7
0.35 C$_s$	1×10^{-9}	1.5×10^{-9}	4
0.50 C$_s$	1.3×10^{-9}	1.5×10^{-9}	6.5
Self-diffusion of water	3×10^{-5}		
Acid nafion	2×10^{-6}		
Polystyrene	3.5×10^{-7}		
Polyvinyl alcohol	3×10^{-7}		
Polyethylene	2.3×10^{-7}		
Polyphenylene oxide	2×10^{-7}		
Polymethyl methacrylate	9×10^{-8}		
Polyoxymethylene	3×10^{-8}		
Polyvinyl chloride	2.5×10^{-8}		
Nylon 6	9.7×10^{-10}		
Polystyrene Ionomer	9×10^{-10}		

[a] Samples immersed in water until the attainment of constant weight.

It should be noted that Robeson et al.[15] report a diffusion coefficient of water in polysulfone of 3.8×10^{-8} cm$^{2-1}$ at 23°C. It is clear that an almost three orders of magnitude discrepancy is difficult to explain on the basis of experimental error. We can only state that the results reported in Table II are consisted from the unmodified polysulfone to the salts, and resolution of the discrepancy must await further investigation.

A major problem in dealing with ionomers is their limited solubility, especially at high ion concentrations. To maximize the understanding of the ionic interactions in sulfonated polysulfone, solubility experiments were performed. Form an average of the one-dimensional solubility parameters of solvents determined experimentally, the solubility parameter for poly-solfone was estimated to be 9.5 ± 1.0 and that of 0.50 Na-Dry as 12.8 ± 1.8. Using three-dimensional solubility parameters, a triangular diagram plotting

$$f_i = \frac{\partial_i}{\partial_d + \partial_p + \partial_h}$$

was constructed and a region of solubility determined for polysulfone and the 0.50 Na ionomer. From such a plot, additional solvents and solvent systems were found by determining if their values fell within this solubility region. In addition, this method was also used to find potential plasticizers by choosing solvents that are relatively large molecules, high boiling, and located near the edge of the solubility region.

Plots of ∂_p versus ∂_h were constructed to show the changes in ∂_p and ∂_h of polysulfone as it is sulfonated. The incorporation of one ionic group for every two repeat units in polysulfone raises these values by a factor of about 2. To precisely determine the three-dimensional solubility parameters for the ionomer and the base resin, plots of one component versus the square root of the sum of the squares of the other two were constructed. The values of the solvents contained in the solubility regions of all three of these plots plus the triangular diagram were then averaged and the following values obtained: For Polysulfone,

$$\partial_d = 8.5 \pm 0.5 \qquad \partial_p = 3.1 \pm 0.8 \qquad \partial_h = 3.0 \pm 0.8$$

so that

$$\partial_0 = 9.5 \pm 1.0$$

For 0.50 Na-Dry,

$$\partial_d = 8.5 \pm 0.6 \qquad \partial_p = 7.2 \pm 0.8 \qquad \partial_h = 5.8 \pm 1.2$$

so that

$$\partial_0 = 12.5 \pm 0.8$$

Additional mixtures of solvents and non-solvents were prepared and tested based on these ∂_i values. Of ten such mixtures, seven were found to be

solvents and the other three caused swelling. The major result from this experiment is that any mixture that falls in the solubility region is a potential solvent regardless of whether the mixture contains solvents. Good examples are THF/H_2O, acetone/H_2, and methyl acetate/methanol/formamide for the 0.50 Na ionomer.

DISCUSSION

Besides acid groups arising from incomplete neutralization, polysulfone ionomers may also contain acid groups arising from an oxidation reaction of sulfone radicals produced by chain scission, especially through thermal aging. Fourier transform infrared analysis showed no major difference between thermally aged and fresh samples. Thermal aging did, however, produce some changes in the physical properties. Besides some slight discoloration, thermal aging also caused a reduction in the glass transition temperature. This reduction was usually of the order of 10–20°C. For these reasons, the thermal history of the experimental samples was kept constant to prevent any anomalies.

DSC

The differential scanning calorimetry results show the importance of the incorporation of ionic groups in increasing the glass transition temperature through chain stiffening and/or ionic cross-linking effects. The importance of the specific ionic interaction between the cation and anion is also evident from the differences in the glass transition between the acid, sodium and cesium forms of equal ion content. This result can be explained by considering the effective ionic radii of the counterions. The closest-approach ionic radii for sodium and cesium are 0.95 and 1.69Å, respectively. Eisenberg has shown that this difference in counterion type does not affect the critical ion concentration necessary for clustering but only the stability of the clusters once formed since the cesium ions yield "cross-links" of lower stability than sodium[8]. Analysis of ionomeric properties by cation type (e.g., monovalent versus divalent) may thus lead to inconsistent results since the type of counterion will only affect those properties based on the stability of the cation-anion interaction. Thus, analysis by the nature of the cation, especially in the case of multivalent cations, should prove much more fruitful.

Another major result of the DSC studies is that there is no evidence of phase separation in these ionomers. It appears that incorporation of ionic groups does not lead to a new separate phase but instead increases the glass transition through chain stiffening and/or ionic cross-linking. Taking the glass transition of 1.0 Na-Dry (330°C) to be the glass transition of pure ionic material and applying a compolymerization equation gives Tg values for lower sulfonated materials similar to those actually measured by DSC. By plotting the increase in Tg with ion content, it was found that the increase is linear at a rate of 1.5°C/mol% sulfonate throughout the concentration range studied. Considering the repeat unit length of polysulfone to be about five times that of polyethylene, this value of 1.5 is in accordance with that of ethylene-sodium methacrylate and ethylene-magnesium methacrylate.[9] In addition, this value is also close to the values of the initial slopes for

ionomer systems below the critical ion concentration, such as polypentenamers[10] and styrene-sodim methacrylate.[11] In these two systems, though, the curves depart from linearity at the critical ion concentration for clustering. Thus, the results of these DSC studies, although not conclusive, indicate that clustering is not present in these sulfonated polysulfone ionomers.

SAXS

As is pointed out in the results section, little evidence was found for the existence of clustering by SAXS. It is not necessary, however, to have a sharp ionic peak to have such a phase-separated region. In fact, a peak may complicate the interpretation of the scattering profile. Instead, the presence of significant scattering intensity in the angular region of $20 = 1-6^0$ is good evidence that ion-rich regions of 25–50 Å size exist. This scattering intensity can be enhanced by use of heavy metals, such as cesium, since this will create a large electron density difference between the ionic groups and the hydrocarbon matrix, although this is not necessary to obtain evidence for clustering.

Regardless of prior thermal history, conditioning, and subjection to low—molecular-weight diluents, no scattering was observed. In addition, the lack of significant scattering intensity from the cesium ionomers has important implications. Since no evidence of phase separation is detected by either SAXS or DSC, then the ionic groups should only impart a chain-stiffening effect, as is borne out by the linear increase in Tg with ionic content. In addition, the dynamic—mechanical results tend to confirm and extend this conclusion.

Dynamic-Mechanical Analysis

To present a clearer view of the dynamic-mechanical behavior of these ionomers, their behavior is discussed by treating each relaxation region individually and then summarizing the overall results.

α Relaxation

The α relaxation in these ionomers is taken to be associated with the glass transition of the matrix since it correlates well with the only transition measurable by DSC. The actual temperature of this transition was found to depend on sulfonation level, counterion, thermal history, and the presence of any low-molecular-weight diluent. These effects are similar to those observed in the DSC experiments as well as by Noshay and Robeson.[12] Therefore, it is again concluded that the ionic radius of the cation is an important factor in determining the cation-anion interaction and thus the material properties.

In the case of sulfonated polysulfone ionomers, water tends to have a slightly different effect on the α relaxation of the cesium sales than on the sodium salts. In both the DSC and dynamic-mechanical experiments, water lowered the temperature of the α relaxation of the sodium ionomers. In the case of the cesium ionomers, a difference in behavior between the DSC and the dynamic-mechanical experiments was observed. Although water

decreased the glass transition temperature of the cesium ionomers, it some-
times increased the α-relaxation temperature in the dynamic-mechanical
experiments. A possible explanation for this may be related to the difference
in the amount of water present at Tg in the two salts as well as from
cesium's ability to form contact ion pairs. This idea was tested by performing
dynamic-mechanical analysis on specimens exposed to water for different
lengths of time. This showed that the α relaxation first increases then
decreases as a function of water content in the cesium ionomers. Thus as
small amounts of water come in contact with the ion pairs, it tends to
disrupt them, creating more free ions and thus increasing the α-relaxation
temperature. As additional water reaches the ionic regions and all or most
of the ion pairs are disrupted, hydration of the free ions can then occur,
again decreasing Tg.

The effects of low-molecular-weight diluents other than water on the
cesium ionomers was also examined in the hope of bringing about conditions
more conducive to ionic clustering, as well as to gain information on the
control of ionomeric properties. In the case of alcohols, such as methanol
or ethanol, the α-relaxation temperature was again increased but not to
the same extent as with water. Higher alcohols, which are more lipophilic,
tended to slightly reduce the α relaxation temperature. Thus, intermediate-
molecular-weight alcohols may be the most useful in disrupting ionic in-
teractions since they probably interact with both the ionic regions and the
hydrocarbon backbone.

Overall, the behavior of the low-molecular, weight diluents cannot be
readily explained using free-volume theory. In conventional polymers,
diluents increase the free volume, decrease the polymer segment concen-
tration, and thus decrease Tg. In the case of ionomers, however, there is
the additional feature of intermolecular interactions among the ionic
groups.

β Relaxation

The β relaxation is not present in polysulfone itself and thus must arise
from motion of the sulfonate groups. Determination of the nature of this
relaxation is somewhat complicated by the fact that it is dependent on the
type of counterion, thermal history, and water content. Overall, the cesium
salt β relaxation is slightly more intense than the sodium salt. A possible
reason for the difference in behavior may again be due to the differences
in hydration and association between cesium and sodium. The sodium salts,
which have the higher affinity for water, may contain small amounts of
water regardless of the drying technique. Increasing sulfonation would also
increase this water content and may thus account for the slight shift to
lower temperatures of the β relaxation with either increased sulfonation
or water content. That cesium ions may bind directly to the anions could
account for the greater magnitude of the cesium salt β relaxatin compared
with that of the sodium salt. Cesium's ion pairing tendencies may also
explain the effects of water on the cesium ionomer's β relaxation.

A possible explanation for the β relaxation was initially as follows. If one
were to view the ionic regions as concentrated salt solutions, then the
melting point of any water located there should be depressed. Theoretical

calculations show that this depression should be of the order of 15–20°C for a hydrated sodium ionomer (4H$_2$O per ionic site). Water under these conditions may not freeze as it would in a pure state. This idea was somewhat supported by the appearance of a small transition near −120°C for saturated samples, which could be the glass transition of such water. This view was questioned, however, when incorporation of other low-molecular-weight hydroxyl-containing diluents into dry ionomers resulted in a β relaxation at approximately the same temperature but not always with the same magnitude. Other diluents, such as dioctyl phthalate, which should be good plasticizers of the hydrocarbon backbone, did not produce a β relaxation.

It is therefore believed that the β relaxation in these ionomers is due to hindered motions of the pendant sulfonate groups and not due to ionic interactions, although the latter most likely contribute to the hindrance effect. If this relaxation were due only to ionic interactions then water would tend to destroy or greatly alter it, and this was found not to be the case. Thus, if the β relaxation is due to the portions of the polymer containing the pendant sulfonate groups, water should tend to facilitate the relaxation, especially in the case of cesium, in which ion pairing may exist, and this is actually the case.

Robeson, and colleagues[13] postulated that relaxations of the sulfonate-containing φ-0-φ links of the backbone, in the presence of water, are the same as those of the unsulfonated φ-0-φ links, which are dry. They also propose that the γ relaxation is due to a coupled motion of the φ-0-φ and φ-SO$_2$-φ portions in the presence of water as well. If this is true, then the rotational energies of the φ-0-φ and φ-SO$_2$-φ links would have to be about the same so that one portion rotates as easily as the other. Sulfonation of some of the φ-0-φ portions should hinder their rotation so that rotation of the φ-SO$_2$-φ portions should predominate in the presence of water. Thus, the β relaxation may be due to the rotation of the sulfonated φ-0-φ portions of the backbone, and in the presence of water the remaining unsulfonated portions remain coupled with the φ-SO$_2$-φ links, creating the γ relaxation. Good backbone plasticizers may be able to plasticize all φ-0-φ links whether or not they contain a sulfonate group. This idea is supported by the fact that the γ relaxation of these ionomers is enhanced by the presence of such plasticizers.

γ Relaxation

As just discussed, the origin of the γ relaxation is not readily apparent. If one accepts the results of Robeson's group, then this relaxation is due to motions of both the φ-0-φ and φ-SO$_2$-φ portions of the backbone and is dependent on water content. They report that water shifts the γ peak to lower temperatures and *increases* its magnitude. The higher temperature for the dry sulfonated polysulfone γ relaxation compared with that of the unmodified polymer is that intermolecular interactions between ionic groups increase the barrier to rotation. Water, which destroys these interactions, shifts the peak to temperatures similar to unmodified polysulfone. This explanation may seem plausible for highly sulfonated materials but questionable for lightly sulfonated ionomers. If, for example, the polymer

contained 50% sulfonated φ-0-φ links and 50% unsulfonated φ-0-φ links, then it would seem that two relaxations should be present in the dry state, but this is not the case in the studies of Robeson or in this investigation.

The results of this study dealing with the γ relaxation differ slightly from those of these other investigators in one important respect. By incorporating water into the ionomers immediately after thermal treatment, it was found that the water did shift the γ peak to lower temperatures but *decreased* its magnitude. This behavior is very typical of antiplasticization. From this result and that of Robeson and colleagues,[13] it is believed that the γ relaxation is due to both φ-0-φ and φ-SO$_2$-φ rotations regardless of the presence or absence of water. This conclusion is supported by the work of Kurz, who showed that the existence of a relaxation near −100°C is not dependent on water or the concentration of φ-0-φ links. Therefore, it is postulated that water increases the relaxation of the φ-SO$_2$-φ portions but decreases the φ-0-φ contributions so that the net intensity of the coupled motion in the wet state is less than in the dry state. Thus, the more φ-0-φ links that are present (lower degrees of sulfonation), the greater is the effect of water on the γ relaxation, which is the case. This explanation is also supported by the fact that alcohols and esters have practically no effect on the γ-relaxation magnitude although they shift it to lower temperatures.

Overall, the dynamic-mechanical results show that the salt groups stiffen the chains significantly. The modulus values for the sample studied support the phenomenologic explanations just presented for the relaxations of sulfonated polysulfone ionomers. In the case of the sodium ionomers, water increases the modulus over almost the entire temperature range studied. This and the decline in temperature and magnitude of the γ relaxation support the proposed idea of antiplasticization (Fig. 10) Cesium ionomers, which may exhibit ion pairing in the dry state and which have a lower affinity for water than the sodium ionomers, show only a small increase in modulus upon absorption of water.
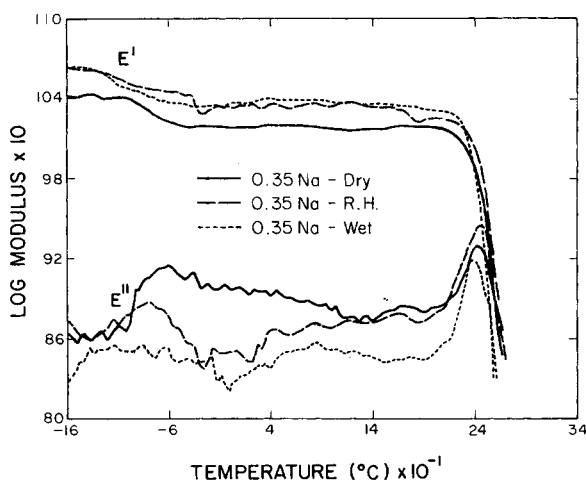

Fig. 10. Effect of water on the temperature dependence of E' and E'' for 0.35 Na ionomers at 11 hz.

Thus it may be concluded that sulfonation of the polysulfone backbone creates a new transition (β) due to the rotation of the sulfonate-containing portions of the backbone. The γ relaxation, present in both the sulfonated and unsulfonated forms, arises from the coupled motion of the ϕ-0-ϕ and ϕ-S0$_2$-ϕ portions regardless of the presence of water. Finally, it is concluded that sulfonated polysulfone ionomers are not clustered to any significant extent. Their structure may best be described as consisting largely of ionic multiplets composed mainly of ion pairs and quartets. These ionic interactions are thus responsible for imparting the stiffening effect of the backbone, which leads to the increased moduli and glass transition temperatures of these ionomers.

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