Sulfonated Polystyrene Ionomers Neutralized by Bi- and Multifunctional Organic Cations. 2. Orientation and Dynamic Mechanical Study

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ABSTRACT: A study of the orientation and dynamic mechanical behavior of lightly sulfonated polystyrene ionomers (PS-0.050SSA) neutralized by ten small organic cations, containing bi-, tri-, and quadrifunctional amine and pyridine groups, is presented. From infrared dichroism measurements, it was found that the orientation function, P_2, of these ionomers increases linearly with the degree of proton transfer calculated in the previous paper.[1] This result shows that the magnitude of segmental orientation is proportional to the effective cross-link density in these ionomers, the cross-links arising from the ion pairs that result from the proton transfer process. Dynamic mechanical thermal analysis indicates that the ion pairs aggregate to an extent which depends largely on the degree of ionization. In the ionomers for which high proton transfer was measured, a second, higher temperature transition is apparent, indicating the existence of clusters in these systems. The effect of the cluster phase on the orientation behavior is discussed.

Introduction

In the previous paper of this series,[1] our attention was focused on the formation of ionic cross-linking interactions in sulfonated polystyrene (PS-SSA) blended with small organic molecules containing two or more basic nitrogens. Through infrared spectroscopic analysis, it was established that proton transfer from the acid to the basic sites occurs, leading to ionization, the extent depending on the basicity of the nitrogens involved. Quantitative calculations of the degree of proton transfer, based on the normalized infrared absorption band and shoulder at 906–900 cm^{-1}, provided a means of ordering the small molecules in terms of the potential ionic network density they provide. The maximum density is obtained for those with primary amine groups (whether aliphatic or aromatic), for which over 90% proton transfer was determined. These systems thus give rise to direct ionic cross–links via the multifunctional cations. The ionic cross-link network is much less developed for those with heterocyclic aromatic nitrogens, for which as little as 40% proton transfer was calculated, although the distribution of proton transfer among the molecules (whether singly-charged or multiply-charged) could not be determined.

Now, it is well-known that ionic groups in metal-neutralized ionomers tend to aggregate, since they are in a nonpolar matrix, thus forming what are termed multiplets whose rigidity depends on the strength of the ionic interactions involved.[2] This allows singly-charged counterions to also provide effective cross-linking sites. The multiplets, in turn, give rise to a cluster phase when they are sufficiently dense so that the regions of reduced mobility surrounding each multiplet overlap and thereby form larger regions of reduced mobility, often called clusters, that are detectable as a second phase with a higher glass transition temperature than that of the matrix phase.[2]

With this perspective, it is of much interest to investigate both the molecular orientation behavior of the organically neutralized ionomers of the previous paper and their dynamic mechanical properties. The former reflects the effective ionic cross-link network present,[3–5] and the latter allows detection of any cluster phase that may be present.[2,6]

In previous studies,[3–5] we have shown that the molecular orientation that can be achieved in stretched samples is increased significantly by the presence of strongly interacting groups. In PS-SSA copolymers, for example, the orientation measured increases with SSA content.[5] It is still greater in the presence of intermolecular ionic interactions of the type formed in blends of PS-SSA with PS-VP [poly(styrene-*co*-4-vinylpyridine)],[5] where there is almost complete proton transfer[7,8] forming direct, intermolecular ionic cross-links.

On the other hand, it was observed for metal-neutralized ionomers that the orientation achieved is very much affected by the characteristics of the cluster phase.[3,4] When it is not predominant, but exists more or less as isolated patches in the matrix phase, it can be considered to form part of the effective ionic cross-link network present, and the orientation achieved can be quite high if the cluster glass transition temperature (cluster T_g) is significantly higher than that of the stretch temperature. Nearer the cluster T_g, ion-hopping may contribute to reducing the orientation values. For stretch temperatures below the cluster T_g, the measured orientation may also be reduced, compared to the real orientation in the matrix phase, when the cluster phase is significant in volume fraction, since this phase, being vitrified, experiences little orientation although it contributes to the overall orientation actually being determined. When the cluster phase is the continuous phase, stretching of the sample is practically impossible below the cluster T_g.

In the present study, we wish then to determine how the orientation in stretched samples depends on the extent of proton transfer, and hence the ionic cross-link density in these systems. Since the creation of ionic groups potentially gives rise to ionic aggregation and hence a cluster phase, which may also influence the orientation behavior, as just explained, it is essential to investigate this aspect as well.

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Experimental Section

1. Measurement Procedures. Sample Preparation. As in the previous paper,[1] poly[styrene-*co*-(styrenesulfonic acid)] was obtained by chemical modification of polystyrene (Aldrich), following literature procedures.[9] Although only the copolymer of 5.0 mol % acid content was used systematically in the studies reported, a copolymer of 9.3 mol % SSA was also utilized for complementary data. The ten organic small molecules (Aldrich) used are identical to those of the previous paper.

Films for orientation measurements were prepared in exactly the same way as described for the infrared analysis in the previous paper,[1] notably by adding dropwise solutions of accurately weighed small molecules to copolymer solutions (to slightly in excess of stoichiometric ratios between functional groups), and then solution casting. The films obtained, 70–80 μm in thickness, were cut into strips (6–7 mm in width and 20–25 mm in length), taped down to their extremities to avoid deformation, and dried under reduced pressure at room temperature for 1 day and at 120 °C for 3 days.

In order to orient the samples, the films, fixed on both ends with pyrotape (Aremco), were stretched uniaxially in a homemade apparatus operating at a constant strain rate, chosen as 0.026 s^{-1}, and a uniform temperature (±1 °C) that was equilibrated for 5 min before stretching. Unless otherwise specified, the stretch temperature was chosen as $T_g + 15$ °C. Once stretched, the films were quenched to room temperature by opening the front of the apparatus into which cool air was circulated by a fan; a maximum of 2–3 s passed between the end of stretching and the freezing-in of orientation at temperatures below the sample T_g. As usual, the actual draw ratios and the uniformity of stretching were monitored with ink lines drawn across the width of each sample before stretching. Only the orientations of samples made from PS-0.050SSA were studied. Preliminary tests of some made from PS-0.093SSA could not be successfully solution-cast to make films, because of sample precipitation problems during neutralizing; recourse was made to molded films, but these were subject to breakage when stretched at $T_g + 15$ °C, and in some cases up to about $T_g + 50$ °C.

To prepare samples for dynamic mechanical experiments, the freeze-drying technique was chosen in order to facilitate adequate drying of the larger batches involved. The blending procedure itself was similar to the above and to that described in the previous paper,[1] except that the PS-SSA was dissolved in benzene/methanol (90/10 v/v) and the final solution concentration was about 1%. After stirring for an hour, the samples were freeze-dried and the resulting fluff was further dried at 100 °C under reduced pressure for 2 days. Samples were then compression-molded under a load of 10 000 psi, during which the temperature was raised to $T_g + 40$ °C (except for PS-0.050SSA-PPD, where the temperature was raised to only $T_g + 20$ °C in order to avoid its greater tendency to be squeezed out of the mold at higher temperatures), and maintained there for 5–10 min; they were then allowed to cool under pressure over a period of 2 h. All of the molded blends were transparent, although tinted with the original colors of the small organic molecules. Elemental analysis of these samples gave results comparable to those for the films, as described in the previous paper,[1] with the PUR sample also apparently near stoichiometric proportions this time.

DSC Measurements. Glass transition temperatures (T_g) of the dried films were measured with a Perkin-Elmer differential scanning calorimeter, DSC-4, calibrated with indium, at a heating rate of 20 °C/min and a sample weight of about 10 mg. The T_g was identified with the midpoint of the transition. The T_g values obtained for the ten blends are listed in Table 1.

Table 1. Glass Transition Temperatures for PS-SSA Neutralized with the Small Organic Cations Indicated

polymer	$T_g^{DSC\,a}$ (°C ± 2)	$T_g^{DMTA\,b}$ (°C ± 2)
PS-0.050SSA	110	120
PS-0.050SSA-DAB	114	127
PS-0.050SSA-HDA	112	126
PS-0.050SSA-PDA	112	128
PS-0.050SSA-HMT	113	124
PS-0.050SSA-TAZ	111	121
PS-0.050SSA-APS	112	126
PS-0.050SSA-TPY	113	127
PS-0.050SSA-PPD	112	124
PS-0.050SSA-PYR	112	123
PS-0.050SSA-PUR	110	125

[a] Midpoint, 20 °C/min. [b] tan δ maximum, 1 Hz, 1 °C/min.

Orientation Measurements. The polarized spectra were recorded by using a Mattson Sirius 100 FTIR spectrometer from a total of 100 interferograms at a resolution of 4 cm^{-1}. In order to obtain the two orthogonal polarization measurements, a fixed wire-grid polarizer was used and the samples were rotated by 90° via a homemade motorized device. The infrared dichroic ratio, R, is equal to $A_\parallel/A_\perp$, where $A_\parallel$ and $A_\perp$ are the measured absorbances of the electric vector parallel and perpendicular, respectively, to the stretching direction. Dichroic ratio measurements allow calculation of the second moment of the orientation distribution function $\langle P_2(\cos\theta)\rangle$, or P_2, in accordance with the relation:

$$\langle P_2(\cos\theta)\rangle = \frac{1}{2}(3\langle\cos^2\theta\rangle - 1) = \left(\frac{R-1}{R+2}\right)\left(\frac{R_0+2}{R_0-1}\right)$$

in which $R_0 = 2\cot^2\alpha$, α being the angle between the dipole moment vector of the vibration under consideration and the chain axis, and θ the angle between the chain axis and the stretching direction.

The orientation function, P_2, of the samples was determined using the polystyrene absorption band at 906 cm^{-1}, in isolated cases checked against that given by the band at 2850 cm^{-1}. It is known that the 906 cm^{-1} band corresponds to the out-of-plane ν_{17b} mode of the benzene ring with an angle α of 35°, and the 2850 cm^{-1} band corresponds to the CH_2 symmetrical stretch with an angle of 70°.[10] These bands are conformationally insensitive.[10] With α known, the orientation functions for the bands are reduced to:

$$\langle P_2(\cos\theta)\rangle_{906} = 1.97\frac{R-1}{R+2}$$

$$\langle P_2(\cos\theta)\rangle_{2850} = -3.08\frac{R-1}{R+2}$$

Each orientation value determined is an average of dichroic ratios measured from pairs of spectra taken from at least three, but usually more, areas of the stretched sample. The bands analyzed are always ensured to be in the linear region of absorbance. The base lines used are indicated in the spectra shown in the previous paper of this series.[1] The precision of the P_2 measurements, estimated to be ±0.01, is determined primarily by the film preparation and stretching processes and is reflected in the scatter of the points in the graphs of P_2 versus draw ratio.[5] Unstretched samples always had P_2 values close to zero (0.01 at the most).

DMTA Measurements. Dynamic mechanical measurements were conducted using a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA), Mk II, in dual cantilever bending mode. All samples (2 × 10 × 35 mm, measured at a free length of 5 mm) were run under nitrogen atmosphere at a heating rate of 1 °C/min, a frequency of 1 Hz, and a nominal deflection of 64 μm.

2. Testing for Possible Chemical Reactions between the Functional Groups. Since the sulfonic acid and primary amine functional groups used in this work may be chemically reactive with one another,[11] it was deemed necessary to test whether or not any such reactions take place under our conditions of study. If chemical reactions do occur in these blends during the above experiments, then the interpretation of the orientation data in particular will be invalid, as these are very sensitive to any cross-linking. Thus, a series of tests on PS-0.050SSA-HDA were carried out, HDA having the functional group which is the most likely to react with the acid. First, no detectable differences were observed in either the

NMR (Bruker, 200 MHz) or IR spectra before and after a DMTA scan to more than 200 °C. Second, a sample scanned by DMTA twice in a row gave the same result. An isothermal test of a sample at 185 °C for 1 h using the Rheometrics Mechanical Spectrometer, RMS-System 4, with parallel plates (for which purpose, the sample was first held at 250 °C for 10 min) gave dynamic moduli and viscosity data that were constant in time ($G' \simeq 3.2 \times 10^5$ Pa, or about 1/3 of the E' value at 185 °C given by the DMTA). The same sample, remolded for another DMTA scan, gave essentially identical results to the earlier DMTA scans. Finally, this same, by now rather harshly treated, sample was completely soluble in appropriate solvents, such as pyridine, THF/methanol, and $CHCl_3$/methanol. Solubility tests of several additional samples after exposure to high temperature gave the same result. We conclude that any chemical cross-linking reactions or significant degradation under our experimental conditions can be ruled out.

Results and Discussion

Since the stretching temperatures in orientation studies of amorphous polymers are generally referred to the T_g's of the films being studied, these were first determined using DSC. These values are reported in Table 1. There is clearly little variation in T_g among the ionomers, and furthermore, their T_g's are similar to that of the PS-0.050SSA copolymer, at most 4 °C higher. With the experimental error usually estimated at ±2 °C for DSC-measured T_g's, all the samples can be said to have identical T_g's at 112 °C. The width of the T_g is also essentially constant. There is, therefore, no discernible effect, on the T_g, of the ionization induced by the functional organic cations. This may appear contrary to what is generally observed in ionomers, notably, that the T_g increases with ion content.[2,4,6] On the other hand, the metal-neutralized ionomer, PS-0.05SSA-Na, has a T_g of 115 °C,[4] which is in the same range as the T_g's in Table 1. In other words, at 5 mol % SSA content, the difference between 0% and 100% neutralization is not sufficient to allow distinct trends to be observed as a function of proton transfer.

The organically-neutralized PS-0.050SSA films prepared for orientation were all stretched at 15 °C above their DSC-measured T_g's. The orientation function, P_2, obtained as a function of draw ratio, λ, is shown in Figures 1 and 2. For clarity, Figure 1 assembles the curves for the bifunctional small molecules, and Figure 2 those for the molecules with more than two basic sites. The data shown are those calculated using the 906 cm^{-1} band, but the results are the same for those calculated using the 2850 cm^{-1} band. This is shown in Figure 3, where the P_2 data determined from both bands are compared for PS-0.50SSA-PYR and for PS-0.050SSA-PDA.

It should be mentioned that the orientation function, P_2, for polystyrene can be determined from any one of three well-characterized absorption bands for which α is known, namely, the bands at 2850, 1028, and 906 cm^{-1},[10] with preference generally given to the latter two, since the 2850 cm^{-1} band is actually overlapped by an intense neighboring band. In PS-SSA, all three of these bands are affected to some extent by the presence of the sulfonic acid groups; however, it was shown in an earlier paper[5] that the error introduced, at least up to 5 mol % SSA content, is less than the experimental error from other sources for all three bands. This has since been confirmed independently by birefringence measurements.[12]

As shown in the previous paper of this series,[1] there is a progressive decrease in the shoulder to the 906 cm^{-1} band (the only source of interference for this band) with increase in proton transfer in the organically-neutralized ionomers of this study; thus, the minor error introduced by the shoulder into the P_2 determination of the PS-SSA copolymer using this band is reduced even further in the ionomers. On the other hand, the interference in the 1028 cm^{-1} band, which is minor for the PS-0.50SSA copolymer, becomes serious following proton transfer due to the superposition of the SO_3^- symmetric vibration (as explained in the previous paper);[1] this excludes the use of this band for P_2 determinations for neutralized PS-SSA. Therefore, it is the 906 cm^{-1} band which is systematically used to determine P_2 in the present study, checked in isolated cases against that given by the 2850 cm^{-1} band.

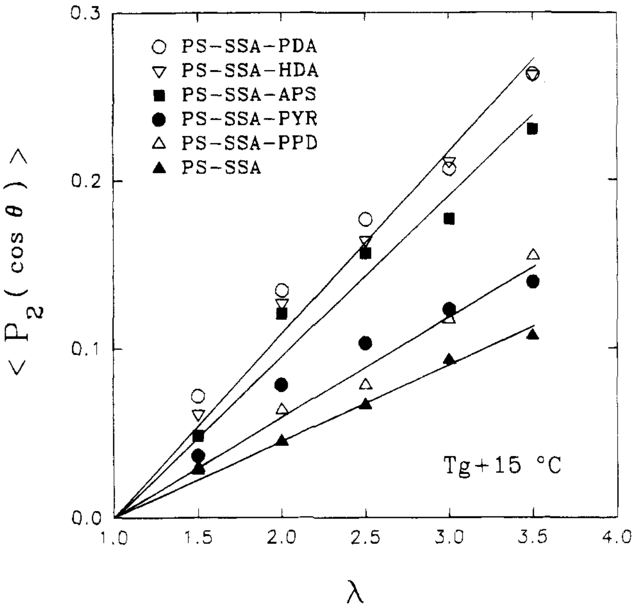

Figure 1. Orientation function versus draw ratio for PS-0.050SSA and its blends with the (bifunctional) small molecules indicated, stretched at T_g + 15 °C. For clarity, a single least-squares fit combines the data for the PDA and HDA ionomers and another the data for the PYR and PPD ionomers.

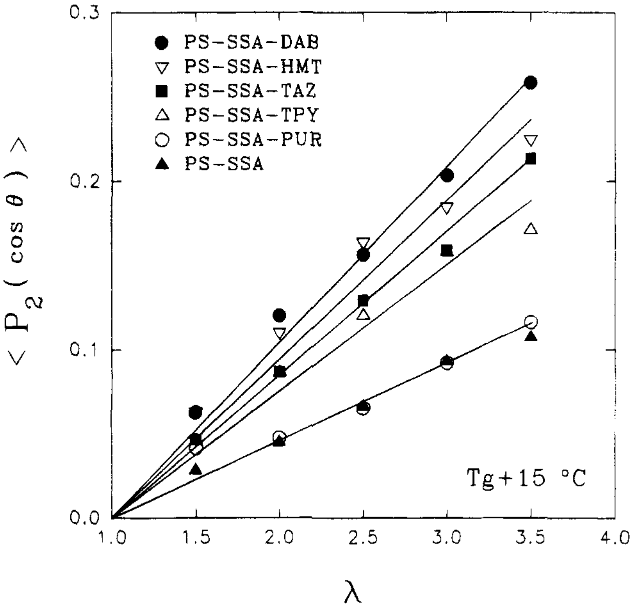

Figure 2. Orientation function versus draw ratio for PS-0.050SSA and its blends with the small molecules indicated, stretched at T_g + 15 °C. For clarity, a single least-squares fit combines the data for PS-0.050SSA and the PUR ionomer.

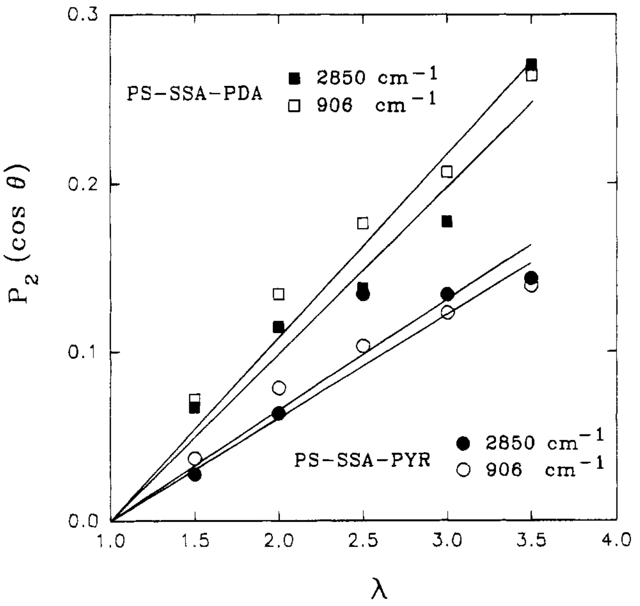

Figure 3. Orientation function versus draw ratio for the PDA and PYR ionomers, calculated using the infrared bands indicated.

It can be observed in Figures 1 and 2 that the magnitude of the orientation function, P_2, is related to the degree of proton transfer or ionization, as determined in the previous paper.[1] The lowest orientation is found for PS-0.50SSA-PUR, characterized by about 40% proton transfer.[1] It is similar to that observed for the unneutralized copolymer, PS-SSA, which is characterized by strong hydrogen-bonding interactions among the acid groups that increase the orientation achieved compared to polystyrene.[5] Those for which the proton transfer was determined to be essentially complete, the DAB, PDA, and HDA ionomers, give the highest orientation.

The relationship between the orientation function and ionization is shown graphically in Figure 4, where the slopes, $dP_2/d\lambda$, are plotted as a function of percentage proton transfer. [The slopes, $dP_2/d\lambda$, were determined by a least-squares fit forced to go through the point of no orientation for an unstretched sample ($P_2 = 0$ at $\lambda = 1$).] Figure 4 shows that the orientation function increases linearly, within experimental error, with percentage proton transfer in the organically neutralized ionomers, regardless of the functionality or other molecular details. Interestingly, extrapolation to 0% proton transfer according to a least-squares fit of the points gives a $dP_2/d\lambda$ of 0.018, which is comparable within experimental error to that for polystyrene, where there are no H-bonding or ionic interactions (*ca.* 0.025).[5]

This result indicates that the orientation achieved is determined primarily by the degree of proton transfer leading to ionization, in other words by the effective cross-link network provided by the ionic interactions: the greater the number of ionic cross-links present, the greater the segmental orientation achieved. This is supported by the data obtained[5] for the PS-SSA/PS-VP blend (mentioned in the Introduction), where extensive proton transfer (estimated at 90 ± 10% from refs 7 and 8) leading to ionic cross-links occurs. As shown in Figure 4, the value of $dP_2/d\lambda$ for this blend, at about 5 mol % interacting unit content, is similar to that of the organically-neutralized PS-SSA ionomers that have essentially complete proton transfer.

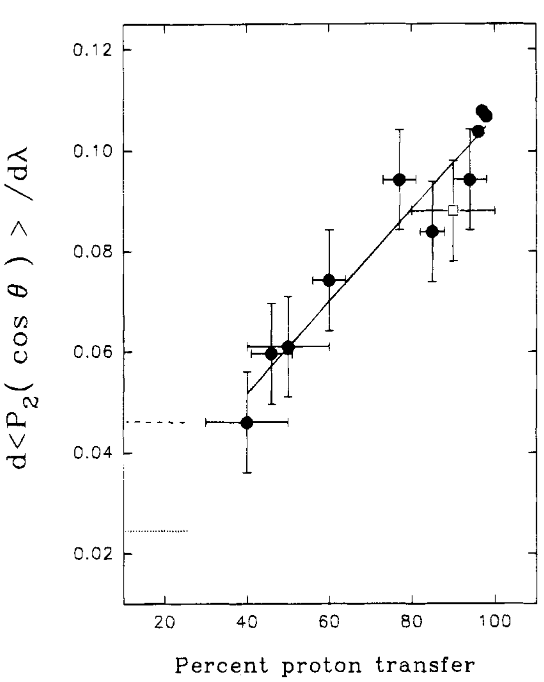

Figure 4. Slopes of the least-squares fits of Figures 2 and 3 versus percent proton transfer (filled circles). For clarity, the error bars for the right-most three points are not included. The open box represents the point for a 5% PS-SSA/PS-VP blend, as estimated from refs 5, 7, 8, and 21. The dotted and dashed lines represent the $dP_2/d\lambda$ values of PS (ref 5) and PS-0.050SSA, respectively.

The increase in orientation with increase in ionization reflects the increasing presence of what can be considered as primary interaction structures, i.e., the effective cross-links. However, as mentioned in the Introduction, the presence of ionic groups in ionomers tends to lead to ionic aggregation, which often results in biphasic morphologies, observed also in the PS-SSA/PS-VP blends.[13] These secondary structures must also be considered in discussing the orientation behavior of these materials, as was done for metal-neutralized ionomers[4] and the PS-SSA/PS-VP blends.[5] To probe this aspect, dynamic mechanical thermal analysis (DMTA) was performed. The Young's storage moduli (E') and loss tangents ($\tan \delta$) obtained for the ten ionomers of 5 mol % SSA content are plotted as a function of temperature in Figures 5 and 6. For clarity, the bifunctional cations are separated from the other cations, as for Figures 1 and 2.

The first observation is that the glass transition temperature, as specified by the maximum of the loss tangent and listed in Table 1, is approximately the same at 125 ± 3 °C for all ionomers. As for the DSC data, no clear dependence of the T_g on the degree of proton transfer can be detected. (It should also be noted that the 10–15 °C difference between the DSC and DMTA T_g's, as we measure them, corresponds with what we generally observe.)

On the other hand, the intensity of the T_g transition does appear to be related to the degree of proton transfer. It is the lowest for the ionomers with the greatest amount of proton transfer, namely, for the DAB ionomer followed by the PDA and APS and then by the HDA ionomers [it should be mentioned that the three DMTA scans for the HDA ionomer mentioned in the Experimental Section gave the same intensity for the $\tan \delta$ maximum (1.0 ± 0.2)]. The intensity is the highest for the PUR, PPD, and PYR ionomers, for which the lowest degrees of proton transfer were determined.

In ionomers, a significant decrease in the matrix loss tangent maximum is associated with the loss of a certain

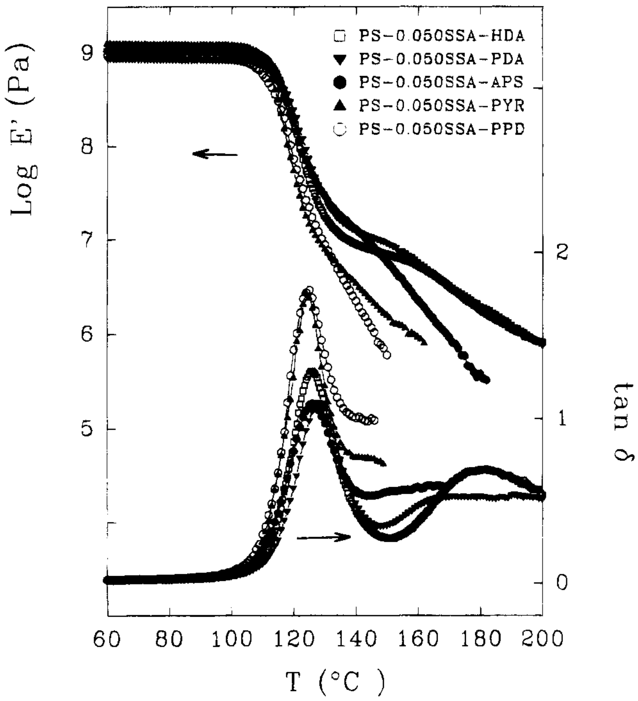

Figure 5. Young's storage modulus and loss tangent at 1 Hz as a function of temperature for the five ionomers indicated (the small molecules involved are all bifunctional).

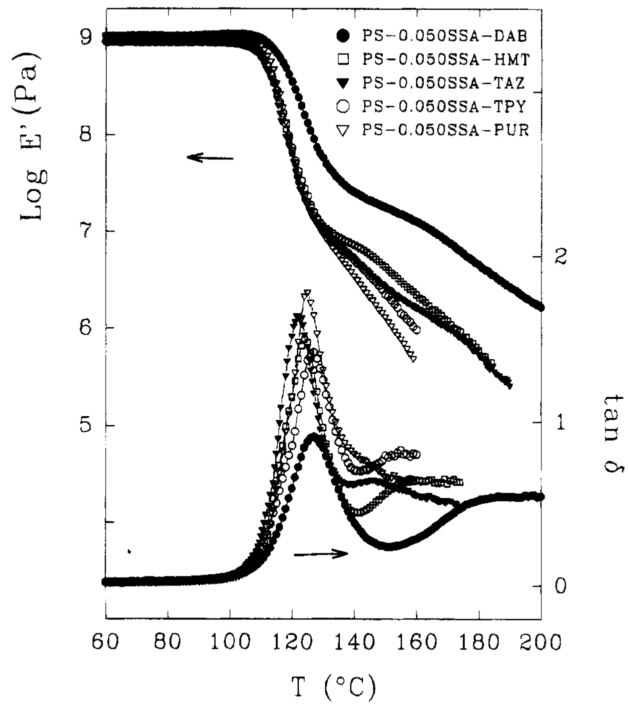

Figure 6. Young's storage modulus and loss tangent at 1 Hz as a function of temperature for the five ionomers indicated.

fraction of segments to the second phase, namely, the cluster phase, which generally gives rise to another loss peak at a higher temperature.[2,4,6,14] Indeed, a second peak can be seen clearly in several of the organically-neutralized ionomers, in particular, PS-0.050SSA-HDA, for which the second maximum is both relatively intense and at high temperatures (about 180 °C). A broad loss maximum, in the form of a plateau, in the same temperature region, is observed for the DAB and PDA ionomers. The same features can be observed, although to a lesser extent, for the ionomers with intermediate degrees of proton transfer, namely, for the APS and HMT ionomers, for which a plateau-like loss is apparent, and for the TAZ ionomer, which shows a weak loss peak near 145 °C. It is noteworthy that plateau-like loss regions have also been observed for other ionomers, notably, poly(butyl acrylate)-based zwitterionomers.[15]

The dynamic storage modulus curves for the ten ionomers (Figures 5 and 6) also show features reminiscent of biphasic ionomers, particularly in the rubbery plateau zone. Those with the least amount of proton transfer, namely, the PUR, PPD, PYR, and TPY ionomers, have the most rapidly decreasing moduli after the T_g and give no evidence of any well-developed rubbery plateau. In contrast, the rubbery zone is extended considerably for the ionomers with the highest amounts of proton transfer, in particular, the PDA, HDA, and DAB ionomers. For these, the inflection point marking the transition from the rubber-like plateau to rubbery flow[16] is found at 153 °C (PDA), 162 °C (HDA), and 168 °C (DAB), respectively. The HMT ionomer has a clearly discernible, but relatively short rubbery plateau (the inflection point marking its upper limit is at 148 °C); this is despite a high proton transfer measured for this ionomer, above 90%. Its inflection point is only a little higher than that for APS (142 °C) and TAZ (135 °C), for which lower proton transfer, less than 85%, was determined. This suggests that the strength of the ionic interactions provided by HMT is less than that provided by PDA, HDA, and DAB, possibly for steric reasons.

The height of the rubbery plateau in ionomers generally reflects the extent of phase separation or development of cluster phase.[2,4,6,13-16] This is clearly highest for the systems with most proton transfer. It is also surprisingly high for APS, although, at temperatures higher than the inflection point at 142 °C, its modulus decreases much more rapidly than that for the ionomers with more than 90% proton transfer, indicating a lower ionic strength probably due to a lower ion content. An attempt was made to correlate the height of the rubbery modulus and the extent of proton transfer by plotting log E' at T_g + 15 °C (the T_g in this case corresponding to the loss tangent maximum) versus the percentage proton transfer. Figure 7 shows that, despite a significant amount of scatter in the points (the variation in the E' values in the glassy region is probably an indication of the experimental error of the E' values in the rubbery region), there appears to be a roughly linear relationship between the two variables. Since the orientation measured for the samples also depends on the degree of proton tranfer, there is necessarily a similar relationship between the height of the rubbery modulus and $dP_2/d\lambda$. These data are consistent with a progressive development of the cluster phase as proton transfer (or ion content) increases; it also indicates that the clusters simply contribute, along with the multiplets, to the effective cross-link density that determines the orientation achieved.

In order to further verify the biphasic nature of the organically-neutralized ionomers, an HDA ionomer of 9.3 mol % SSA content was analyzed by DMTA. The result is shown in Figure 8. Clearly, both transitions are increased in temperature, whereas the intensity of the first transition is decreased and that of the second increased. Once more, this is behavior typical of biphasic ionomers.[2,4,6,13-16] The increase in the two T_g's reflects the increase in ion content in both phases, and the changes in intensity reflect the decrease in volume fraction of the matrix phase and concomitant increase

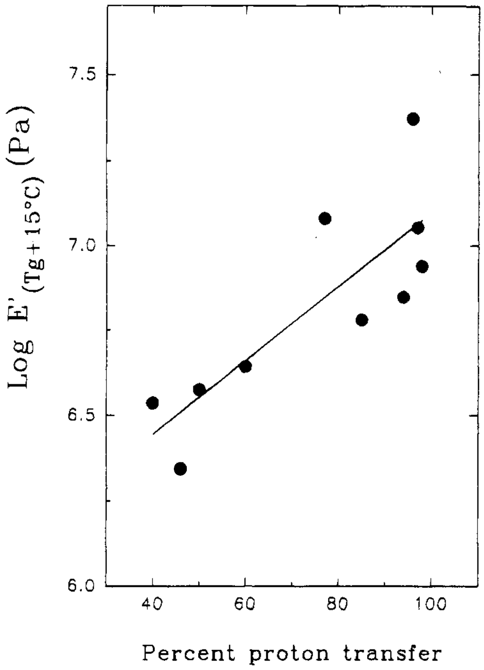

Figure 7. Young's storage modulus, determined at $T_g + 15$ °C, versus percent proton transfer (calculated in ref 1) for the ionomers of Figures 5 and 6 (PUR excluded). The T_g's used were obtained from the loss tangent maxima.

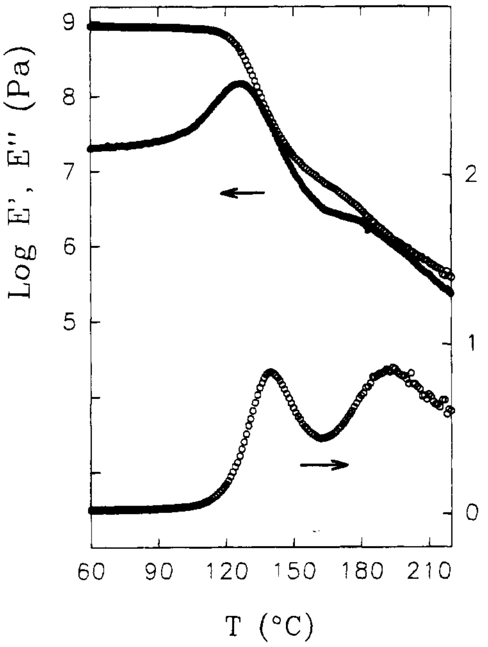

Figure 8. Young's storage modulus and loss tangent at 1 Hz as a function of temperature for the PS-0.093SSA-HDA ionomer.

in the cluster phase. In fact, the similarity of the intensities of the two transitions in PS-0.093SSA-HDA suggests, according to Hird and Eisenberg,[14] that the volume fraction of the two phases is similar and that, therefore, they are co-continuous at this ion content. For all the organically-neutralized ionomers based on PS-0.050SSA, the matrix phase is dominant, implying that the cluster phase where it exists is present in isolated patches.

It can be concluded that ionomers neutralized by (multifunctional) organic molecules are characterized by a biphasic morphology just as is the case with metal-neutralized ionomers. The extent of aggregation leading to clusters, however, depends strongly on the basicity of the small molecules, which determines the degree of proton transfer leading to ionization; in other words, the development of the biphasic morphology is dependent on the ion content, like in metal-neutralized ionomers. Indeed, the DMTA results that are observed for the organically neutralized ionomers with variable degrees of proton transfer can be compared, in particular, to those published recently[17] for a polystyrene ionomer containing 5 mol % methacrylic acid, which is neutralized to various extents by Na^+: in the latter, no cluster peak was observed in the loss tangent curves for neutralization well under 50%, whereas for intermediate neutralization levels the cluster peak is weak and occurs at lower temperatures than that of the fully neutralized ionomer.

It should be added that a weak cluster peak was also observed in blends of PS-SSA (8.1 mol %) with monofunctional amine molecules (both flexible and rigid), to which essentially complete proton transfer occurs.[18] In comparing the DMTA data for the HDA ionomer with that for the ionomers neutralized by equivalent monofunctional flexible amines, it appears that clustering is significantly enhanced in the former. This is reasonable in view of the fact that multicharged amines introduce little or no plasticization effects as do flexible alkyl tails[18] and that they are expected to have a higher energy barrier to ion-hopping.[19] On the other hand, metal-neutralized ionomers are generally characterized by much more extensive clustering still, principally because of the comparatively small size of the metal cations, which allows for both denser packing of ionic groups into multiplets and stronger electrostatic interactions.

It is also worth mentioning that there are indications that the aggregation in organically-neutralized ionomers may be modulated by specific molecular features such as flexibility or steric factors. For example, it is possible that the HDA ionomer may have a higher fraction of matrix phase (higher intensity) and a better-defined cluster phase (distinct loss peak) than the DAB and PDA ionomers, all of which have the same ionization level, because of the greater flexibility endowed by the alkyl segment in HDA. Furthermore, it is likely that the bulky nature of HMT, with its tertiary amines, is the source of somewhat weaker ionic interactions (lower cluster T_g or lower temperature of flow) of the HMT ionomer compared to the ionomers neutralized by PDA, HDA, and DAB, which all have primary amines. There may also be a correlation between the fact that, of the organically-neutralized ionomers studied, it is the PPD ionomer that apparently reaches its flow zone at the lowest temperatures, according to Figures 5 and 6 (and this is consistent with the observation made in the Experimental Section regarding the temperature of molding), and the possibility evoked in the previous paper[1] that PPD molecules may be primarily singly-charged because of the significant difference in basicity between its two types of amines. However, in all, more detailed data are necessary in order to draw definitive correlations between cluster formation and specific molecular features of the counterion.

In the light of the dynamic mechanical studies, it is of interest to note the effect of temperature on the orientation achieved in the clearly biphasic ionomers, namely, PS-0.050SSA-HDA, PS-0.050SSA-PDA, and PS-0.050SSA-DAB. The slopes, $dP_2/d\lambda$, of the plots of orientation versus draw ratio at three temperatures are shown in Figure 9 as a function of the temperature

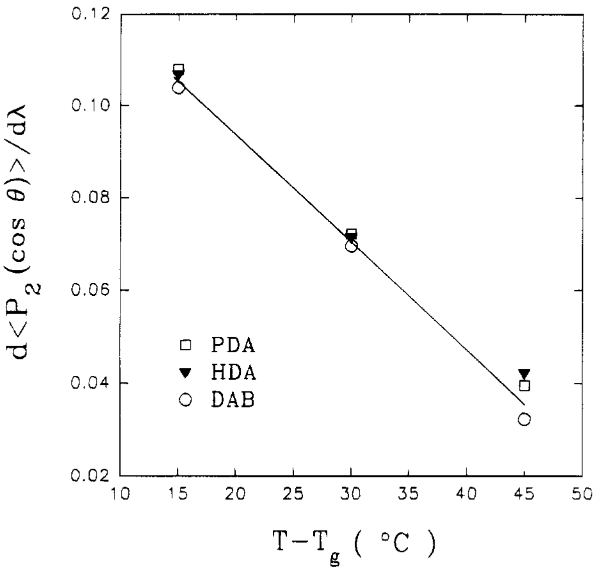

Figure 9. Slopes of the least-squares fits of the P_2 vs λ data obtained for the PS-0.050SSA ionomers blended with the small molecules indicated as a function of the difference between the stretch temperature, T, and the DSC-determined T_g.

difference from T_g (DSC). As is generally true, the orientation decreases with increasing temperature due to the increase in relaxation of the chains with temperature during the stretching process.[20] This decrease appears linear in the temperature range studied and, within experimental error, is identical for all three ionomers. It is noteworthy that all three stretch temperatures are significantly below the cluster transition temperature, noted to be at about 180 °C for the HDA and DAB ionomers, and at about 170 °C for the PDA ionomer (according to the loss tangent maximum), whereas the highest stretch temperature is 160 °C. That these materials can be oriented at these temperatures is consistent with the fact that the matrix phase is the predominant (and no doubt continuous) phase in these materials, as indicated by the loss tangent data. In this connection, the inability to stretch the 9.3 mol % ionomers at T_g + 15 °C, as mentioned in the Experimental Section, undoubtedly reflects the importance of the cluster phase, which for the HDA ionomer, as noted above, is apparently comparable in volume fraction to that of the matrix phase, making the two phases co-continuous. It has been noted before that rapid stretching well below the cluster T_g of an ionomer whose cluster phase is continuous is not possible.[3,4]

Finally, a word should be said about the possible contribution of ion-hopping to the orientation measured. The rate of decrease in rubbery modulus with temperature is, in part, a reflection of this process.[16] Ion-hopping is likely to decrease, at a given temperature relative to the T_g, with increase in proton transfer, not only because there are fewer acid groups to facilitate such a process,[17] but also because the development of a cluster phase with an increasing T_g progressively vitrifies the chain segments that surround the ionic groups (for temperatures below the cluster T_g). From this point of view, the decrease in ion-hopping with percentage proton transfer is progressive and may thus contribute to the progressive increase in the effective cross-link network. Ion-hopping would, of course, increase with temperature,[4] and this may well be part of the increasing rate of chain relaxation processes that decrease the orientation measured when the temperature is raised, as observed in Figure 9. On the other hand, it is not at all certain that, at least at the lower stretch temperatures, ion-hopping contributes significantly to lowering the orientation achieved, if the rate of ion-hopping is slower than the time scale of the stretching process.[5]

Conclusions

In the previous paper,[1] it was shown that proton transfer from the sulfonic acid groups in PS-SSA to small, organic molecules with multiple basic sites occurs, the extent of this transfer depending on the basicity of the sites involved. This leads to ion pair formation and, hence, direct ionic cross-links via the multiply-charged small molecules when there is sufficient proton transfer. The orientation results of the present investigation show that an ionic cross-link network is indeed present in these organically-neutralized ionomers. Furthermore, the effective density of this network, as it manifests itself in the molecular orientation process, depends directly on the extent of of proton transfer or ionization that occurred (studied up to maximum of 5 mol % ion content); that is, the orientation achieved at a given stretch temperature relative to the T_g is linearly dependent, within experimental error, on the percentage proton transfer measured. No additional dependence of orientation on the molecular details of the small molecules could be detected (perhaps masked by the experimental error).

From dynamic mechanical analysis of the systems, it was shown that the ionomers (5 mol % SSA) for which high proton transfer occurs are, in fact, biphasic. In particular, a second, higher temperature loss tangent maximum and a well-developed rubbery plateau, indicative of a cluster phase, are present for the small molecules with strong basicity. These features are absent for those of lowest basicity. The existence of the cluster phase was confirmed for the HDA ionomer, where essentially complete proton transfer occurs, at 9.3 mol % SSA content. For this ionomer, the intensities of the two loss tangents are similar, suggesting that the matrix and cluster phases are similar in volume fraction and, therefore, co-continuous. The extent of development of the cluster phase for a given PS-SSA copolymer depends primarily on the degree of proton transfer, or ion content; however, there are some indications, not explored in-depth, that there is a secondary dependence of specific characteristics of the cluster phase on the molecular details of the small molecules involved.

Finally, the ability to orient the organically-neutralized PS-0.50SSA ionomers indicates that the clusters present simply contribute to the overall effective cross-link network, understandable from the point of view that the cluster phase is relatively minor in volume fraction and therefore exists as isolated patches in the oriented polystyrene matrix. (This does not, of course, rule out a probably small but progressive decrease in measured orientation, compared to the real orientation of the matrix phase, due to the fact that the clusters probably experience little or no orientation since they are vitrified, and yet contribute to the overall orientation measured since they also contain polystyrene segments.[4]) Any ion-hopping would contribute negatively to the effective cross-link network, although this process, if it takes place, probably decreases progressively with increasing proton transfer at a fixed stretch temperature relative to the T_g. When the cluster phase is co-continuous, as may be the case for PS-0.093SSA-HDA, rapid stretching is difficult or impossible at temperatures well below the cluster T_g.

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