Segmental Orientation in Ionically Cross-Linked Blends of Polystyrene and Poly(ethyl acrylate)

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ABSTRACT: Ionically complexed blends are potentially useful model compounds for studying selected aspects of segmental orientation behavior in blends. This paper presents a study of orientation behavior in stoichiometric blends of poly[styrene-*co*-(styrenesulfonic acid)] and poly[ethyl acrylate-*co*-(4-vinyl pyridine)] (heteroblends), where ionic cross-links are produced by proton transfer from the acid to the pyridine moieties, thus leading to an effective ionic network whose density is controlled by the counit content of the blend components. Orientation measurements were obtained by infrared dichroism. For blends composed of components with similar counit contents (symmetric blends), the segmental orientation of both the polystyrene and poly(ethyl acrylate) segments increases with ion content when compared at the same relative temperature, a direct result of the effective ionic cross-links. The polystyrene orientation is, however, significantly lower than that in previously-studied ionomer blends based solely on polystyrene (homoblends). This suggests that the orientation of the polystyrene segments in the heteroblends is reduced by a plasticization effect from the poly(ethyl acrylate) segments, attributed to relaxation coupling between the dissimilar chains during stretching. In an asymmetric blend of a sulfonated polystyrene copolymer of low acid content and a poly(ethyl acrylate) copolymer of high pyridine content, the orientation of the styrene segments is much higher than that in the symmetric blend of the same acid content. It is concluded that relaxation coupling is not present in the asymmetric blend, attributed to the high orientation of the ethyl acrylate segments and to the lower ethyl acrylate content.

Introduction

Studies of the segmental orientation of polymer blends are of value not only because of the industrial importance of polymer blends and the consequences of orientation (often present as a result of processing) on their properties but also because blends present a challenge to a more complete understanding of the various molecular factors affecting orientation behavior in polymeric materials. It is of particular interest to study orientation in blends using techniques, notably spectroscopic techniques, which can distinguish between dissimilar chains. The latter can potentially generate a profile of the segmental orientation and relaxation of each component in the blend and, at the same time, provide information about the specific interchain interactions leading to compatibility or miscibility of those components at the molecular level. Furthermore, by proper choice of blends, specific parameters can be highlighted in order to examine their role in the orientation process.

Cooper and co-workers[1] were among the first to investigate segmental orientation in polymer blends. More recently, Monnerie and co-workers,[2] Prud'homme and co-workers[3] and others[4] have published studies of orientation or orientation relaxation in a variety of blends. In some cases, the blends are miscible, in others simply compatible to varying extents, and in still others a crystalline component is also present. However, because the subject is complex, we are still far from an overall understanding of orientation behavior in polymer blends.

In this context, we believe that ionomer blends having complementary functional groups may serve as useful model compounds for the study of orientation behavior in blends in that they may allow the quasi-isolation of certain key factors affecting orientation. Such ionomer blends are characterized by a *controlled number* of interchain interactions between complementary groups, including acid/base, ion/ion, and ion/dipole interactions.[5] Depending on the *nature* of the complementary groups chosen, these interactions can act, at one end of the spectrum, as effective cross-links between polymer chains (thus simulating entanglements) or, at the other end of the spectrum, as points of contact (specific interactions) that contribute primarily to the effective friction coefficient among the chains that affect their relaxation times. Furthermore, initially incompatible blends made compatible or miscible through strong interactions can be studied. This also allows the possibility of relating the orientation behavior to the level of miscibility or size of microphase-separated domains.

To date, the orientation of only one ionomer blend with complementary functional groups has been investigated, namely the “homoblend”[6] poly[styrene-*co*-(styrene sulfonic acid)]/poly[styrene-*co*-(4-vinylpyridine)] (PS-SSA/PS-VP).[7] They were compared with other polystyrene-based systems, notably the copolymers poly[styrene-*co*-(methacrylic acid)] (PS-MAA) and PS-SSA. It was observed that the orientation both of the homoblends and of PS-SSA increases significantly with the number of interacting moieties, the homoblends more than PS-SSA, whereas the hydrogen-bonding interactions in PS-MAA have no measurable effect on the orientation. It was concluded that, at the functional group concentrations studied and under the experimental conditions used, strong interactions are necessary to influence the orientation of polymers. This is thought to be related primarily to the presence of effective cross-links introduced by the interactions, although a much

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decreased rate of relaxation due to those same interactions may also play a role.

For this paper, we have selected another ionomer blend, poly[styrene-*co*-(styrenesulfonic acid)]/poly[ethyl acrylate-*co*-(4-vinylpyridine)] (PS-SSA/PEA-VP), a "heteroblend",[6,8] where the orientation of the two types of segments can, in principle, be distinguished. It is well-known that the corresponding homopolymers are incompatible;[6,9] however, when small amounts of SSA in one polymer and 4VP in the other are incorporated, and the polymers mixed such that the functional groups are in stoichiometric proportions, essentially complete proton transfer takes place, thus leading to the formation of ion pairs involving the dissimilar chains.[6,9,10] This causes considerable phase mixing, the extent depending on the number of interactions.[6,11] At the segmental level, these blends are not miscible; that is, there is microphase separation of the dissimilar segments, the size range of the phases depending again on the number of interacting groups as well as their distribution along the polymer chains.[11] Chain diffusion is retarded drastically by the ionic interactions, resulting in a rubbery material over an extended time and temperature range.[8]

We are interested in studying segmental orientation behavior in this blend. Blends of various compositions, but always with stoichiometric proportions of interacting groups, are to be uniaxially stretched in the vicinity of their T_g. Blends whose components have similar counit contents will be referred to as "symmetric" blends; those for which the counit contents are widely different will be called "asymmetric" blends. The results will be analyzed and discussed in terms of the influence of the effective ionic cross-links and that of the PEA segments on the PS segments.

Experimental Section

Synthesis and Characterization of Copolymers. Poly[styrene-*co*-(styrene sulfonic acid)] (PS-SSA) of several acid contents was prepared by sulfonation of polystyrene following literature procedures.[12] The parent polystyrene (Aldrich) was reported to have an average molecular weight M_w of 280 000. Acid contents (3.6, 7.5, and 10.6 mol %) were determined by titration using a standardized solution of NaOH in methanol with phenolphthalein as the indicator. The glass transitions were verified by differential scanning calorimetry (Perkin-Elmer DSC-4, 20 °C/min, midpoint), and confirm those previously reported by us.[7,13]

Poly[ethyl acrylate-*co*-(4-vinylpyridine)] (PEA-VP) of several VP contents was synthesized through free-radical polymerization[6,11,14] in benzene. The conversions were restricted to about 10−15% to minimize molecular heterogeneity. The copolymers were recovered through precipitation in hexane and were dried for 3 days at 60 °C under reduced pressure. Pyridine contents (3.5, 7.0, and 11.0 mol %) were determined by titration using a solution of perchloric acid in glacial acetic acid with methylene violet as the indicator. The average molecular weight, M_w, measured in THF by size exclusion chromatography (Waters Model 590), using polystyrene standards, ranged from 200 000−500 000 with a polydispersity of about 2. The glass transition temperatures determined by differential scanning calorimetry (DSC) are compared with two sets of literature values (Figure 1). They compare favorably with those of ref 6, both giving a slope of 1.7 °C/mol % VP (the constant difference can be ascribed to the fact that the T_gs in ref 6 were determined by the loss tangent maximum as given by a free vibration torsion pendulum) and somewhat less favorably with those of ref 11a, also determined by DSC, that vary by 0.8 °C/mol % VP. Possibly, the latter difference is related to the fact that the degree of conversion and hence molecular heterogeneity is somewhat higher for the samples of ref 11a (20−30%) than for our samples and those of ref 6 (<15%).

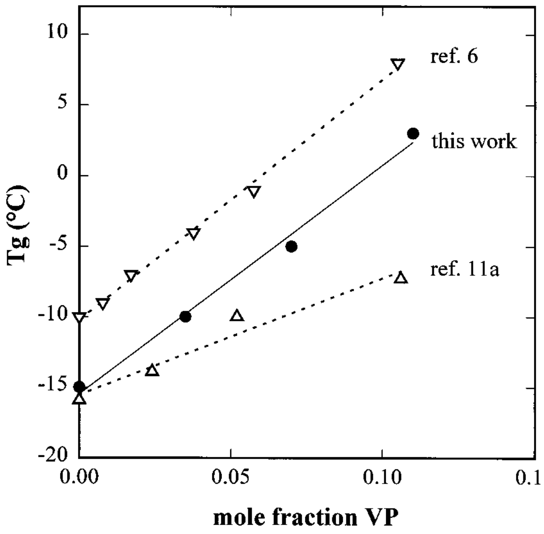

Figure 1. Glass transition temperature as a function of VP content for PEA-VP copolymers. Our data are compared with those of the two references indicated (△, ●, from DSC, 20 °C/min, midpoint ; ▽, from free vibration torsion pendulum, tan δ maximum).

Preparation of Blends. Stoichiometric blends of PS-SSA and PEA-VP were prepared by first dissolving calculated amounts of the polymers separately in THF to concentrations of 2% (w/v). Then, the PEA-VP solution was added dropwise to the vigorously stirred PS-SSA solution. A gel-like precipitate formed during the blending. After continuous stirring for about 1 h, the solvent was decanted and the gel was isolated in distilled water, which produced a fibrous material that could be dried easily. The final product was dried at room temperature for 24 h, and then at 60 °C under vacuum for 3 days (as was also done in ref 11 for the same blends). The resulting samples were kept in a desiccator containing fresh $CaCl_2$ until further use. Although the presence of residual (bound) water cannot be definitely excluded (as for the vast majority of studies involving ionomers), we expect this to influence, at most, the absolute values of the data obtained and not the trends observed.

DMTA Measurements. Dynamic mechanical thermal analyses were performed on a Polymer Laboratories DMTA, Mk II, in the dual cantilever bending mode. The samples (2 × 10 × 35 mm) were compression-molded at about 30 °C above their T_g under a pressure of 10 000 psi for about 20 min and then cooled to room temperature over a period of about 2 h while maintaining the pressure. All of the samples were run under nitrogen atmosphere at a heating rate of 1 °C/min, a frequency of 1 Hz, a nominal deflection of 64 mm, and a free length of 5 mm.

Orientation Measurements. To obtain thin films, the samples were molded, using a SPECAC-IR film-making mold, under a pressure of 5000 psi and at a temperature of about $T_g + 60$ °C for 3 min. The films, about 70 μm in thickness, were then cut into strips (about 6 × 20 mm) and fixed at their ends with pyrotape (Aremco). They were uniaxially stretched at a constant temperature (±1 °C), using a home-made stretching apparatus.[7,13] Before stretching, the samples were equilibrated at the stretching temperature for at least 5 min. The strain rate of stretching was constant, chosen as 0.026 s^{-1}. In order to freeze in the chain orientation, the films were quenched to lower temperatures immediately after stretching, by dispersing liquid nitrogen circulated through a fan into the chamber of the stretching machine. The actual draw ratio and the uniformity of stretching were monitored by ink lines drawn across the width of the film before stretching. The infrared spectra of the samples were taken almost immediately after the stretch−freeze process was completed.

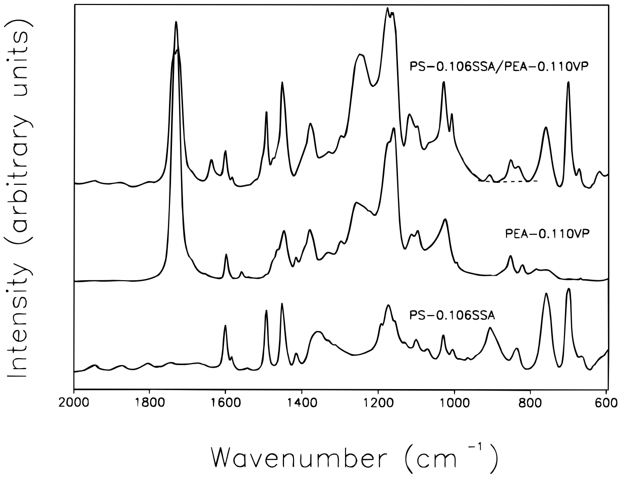

Figure 2. Infrared spectra of the 11% symmetric heteroblend and its individual components. The baselines used for the orientation measurements are indicated.

The polarized spectra were recorded at room temperature by a Mattson Sirius 100 FTIR spectrometer, from 100 interferograms at a resolution of 4 cm^{-1}. To obtain the two orthogonal polarization measurements, a fixed wire-grid polarizer was used, and the sample was rotated by 90° with a home-made motorized device. The infrared dichroic ratio, R, is equal to $A_{\|}/A_{\perp}$, where $A_{\|}$ and $A_{\perp}$ are the measured absorbances of the electric vector parallel and perpendicular, respectively, to the stretch 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 following relation

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

where $R_0 = 2\cot^2\alpha$, 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 bands analyzed are always ensured to be in the linear region of absorbance.

Each orientation value determined is an average of dichroic ratios measured from pairs of spectra taken of at least three, but frequently more than five, areas of the stretched sample. The choice of the bands, 906 and 852 cm^{-1}, used to determine the dichroic ratios are explained in the following section. The baselines used are indicated in Figure 2. The P_2 values of unstretched samples are close to 0, generally well within experimental error. The experimental error of P_2 is estimated to be ±0.01; it 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.[7] It is of interest to mention that of three samples chosen at random, the P_2 values measured about a year later (after ambient temperature storage) were unchanged for a 7% symmetric blend and an asymmetric blend and slightly decreased (by 0.02) for a 3% symmetric blend.

Results and Discussion

Choice of IR Bands for Orientation Measurements. The spectra of the (unoriented) blend with the highest interacting group content and the two blend components separately are shown in Figure 2. Previous infrared analyses of these and similar blends[6,10,15] have shown that proton transfer from SSA to VP is extensive and can be considered to be virtually complete. The data for our own blends corroborate that published. Evidence for ion-pair formation is shown, for example, by the appearance of the band at 1638 cm^{-1}, attributed to ring vibration of the pyridinium cation; this band increases linearly in intensity with VP content. Furthermore, as was also observed in ref 10, the ratio of the areas of the 906 to 759 cm^{-1} PS bands in all of our blends is constant (0.06 ± 0.01) and similar to that of PS. In contrast, it increases rapidly with acid content in PS-SSA copolymers.[7,10] The latter increase is due to the presence of a broad shoulder at 900 cm^{-1} arising from the acid group, assigned to the stretching vibration of the S−O bond with single-bond character.[16] The constancy of the A_{906}/A_{759} (A = area) ratio in the blends thus indicates that the acid groups are mostly or completely neutralized. (A weak absorbance by PEA-VP occurs in the region of the 759 cm^{-1} internal standard; however, the high intensity of the latter renders the effect of the former negligible.)

As a further check of the effective disappearance of the shoulder, we evaluated the area of the 906 cm^{-1} band relative to two other commonly used internal standards, notably the weak bands at 1875 and 1945 cm^{-1}.[7,15,17] Both of these are overlapped by very weak, unidentified bands originating from the PEA-VP component, so that the ratio of the intensities of the 1875 to 1945 cm^{-1} bands are 0.83 ± 0.02 in the symmetric blends rather than 0.71 in PS-based systems[15,17] and 0.73 in the asymmetric blend having a much greater PS content than the symmetric blends. Nevertheless, the ratio of the area of the 906 cm^{-1} band to the intensity of either one of the internal standards is constant as a function of interacting group content (at 32 ± 1 and 38 ± 2 for 1945 and 1875 cm^{-1}, respectively), again providing reassurance that proton transfer in the stoichiometric blends is virtually complete.

Now, as shown in previous publications from our laboratory,[7,17] the ionization of SSA renders useless one of the two polystyrene bands frequently used for orientation measurements, namely, the 1028 cm^{-1} band. On the other hand, the 906 cm^{-1} band, which is useless for orientation measurements of the acid form of PS-SSA due to the presence of the 900 cm^{-1} shoulder, is perfectly suitable when the acid group is neutralized. Moreover, this band is free from IR absorption by the PEA-VP copolymers. Thus, it is the obvious choice for the determination of P_2 values of the PS segments in the blends. This band, which is conformationally insensitive, corresponds to the out-of-plane ν_{17b} mode of the benzene ring with an angle α of 35°.[18] Therefore, the orientation function for the band becomes

$$P_2 = 1.97\,\frac{R-1}{R+2}$$

There are no reports, to our knowledge, of orientation measurements of PEA-based materials through infrared dichroism. Therefore, no PEA absorption bands have been analyzed (to determine the angle α) such that an orientation function, P_2, can be calculated from them. We can nevertheless hope to follow the relative variation in orientation simply from dichroic ratios. Inspection of Figure 2 shows that there is one sufficiently isolated PEA absorption band in the blends, at 852 cm^{-1}, that is suitable for analysis (the carbonyl band near 1730 cm^{-1} is far too intense to be useful). Figure 3 shows the expanded region of the 852 cm^{-1} absorbance band for all of the blends as well as for the PS and PEA homopolymers and representative copolymers. It is clear from this figure that the band indeed originates from PEA segments. It is possible that it is analogous

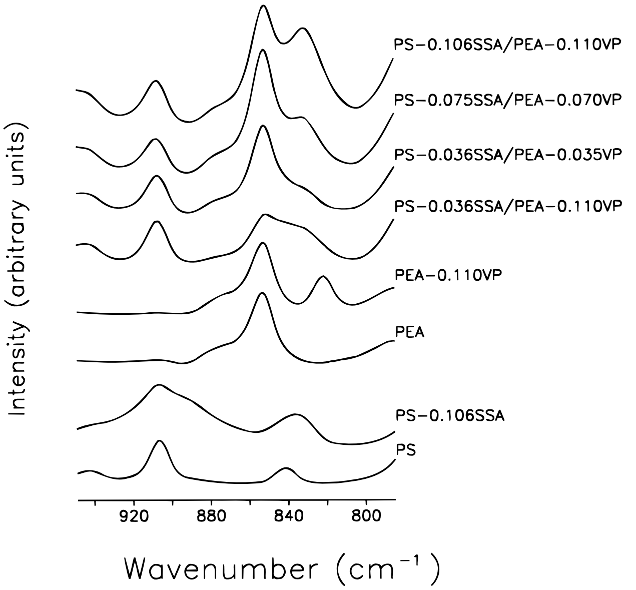

Figure 3. Infrared spectra in the 600−950 cm^{-1} region for the heteroblends studied, representative copolymers, and the corresponding homopolymers, as indicated.

to the 841 cm^{-1} band that appears in poly(methyl methacrylate) (PMMA), which is thought to be related to a deformation mode of the backbone CH$_2$, with an angle α of 90°.[19] If true (keeping in mind that the 841 cm^{-1} band in PMMA seems to have some conformational sensitivity, although it gives P_2 values that are only about 15% higher than those determined by a well-behaved and reliable PMMA band[19]), the 852 cm^{-1} band in PEA can be used, in principle, to obtain a first approximation for the P_2 values of the PEA segments in the blends.

Unfortunately, the 852 cm^{-1} band is subject to overlap from a band at 832 cm^{-1} whose intensity increases with increasing VP content (Figure 3). Indeed, the relative intensity of the 832 cm^{-1} band like that of the 1638 cm^{-1} band is linearly dependent on the pyridinium content, so that we can conclude that the former like the latter is related to the pyridinium cation. In principle, the 852 and 832 cm^{-1} bands can be band-fitted to obtain more accurate dichroic ratios. However, further investigation revealed that a composite band near 840 cm^{-1} arising from the out-of-plane bending vibrations of the CH groups in the benzene ring[16] (located at 841 cm^{-1} for unsubstituted PS and at around 836 cm^{-1} for PS substituted with sulfonated salts and sulfonic acid,[16] also evident in Figure 3) is present. Although not very intense (it is particularly evident for the PS-dominated asymmetric blends), it does contribute to rendering band-fitting arduous (not to mention the presence of the weak shoulder at around 875 cm^{-1} arising from PEA, as well as a possible weak band at 820 cm^{-1} in the case of residual nonquaternized vinylpyridine as shown in the spectrum of the PEA-VP copolymer in Figure 3). Attempts to band-fit worst-case examples (the 11% symmetric blend and the asymmetric blend) indicate that dichroic ratios determined without band-fitting tend to underestimate those determined with band-fitting. As will be seen subsequently, underestimation is favorable to us in the circumstances and despite the uncertainties will allow useful observations regarding orientation behavior to be made. This can be done simply on the basis of the dichroic ratios, permitting us to avoid the difficult task of band-fitting at this time.

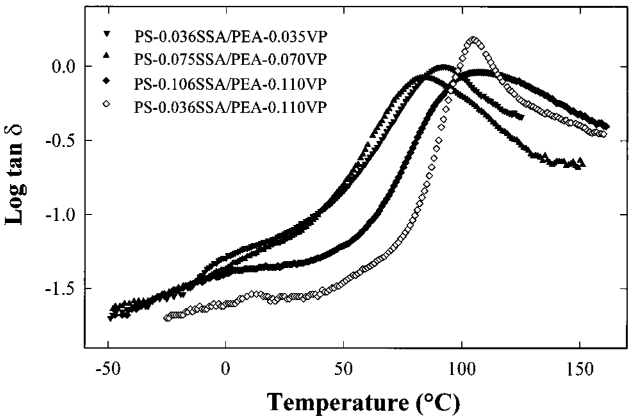

Figure 4. Dynamic mechanical loss tangent (1 Hz) as a function of temperature for the blends indicated.

Table 1. Principal Glass Transition Temperature of the Heteroblends Studied, As Determined by the DMTA Loss Tangent Maximum at 1 Hz

blend	T^g (°C)
PS-0.036SSA/PEA-0.035VP (3% symmetric blend)	92
PS-0.075SSA/PEA-0.070VP (7% symmetric blend)	84
PS-0.106SSA/PEA-0.110VP (11% symmetric blend)	107
PS-0.036SSA/PEA-0.110VP (asymmetric blend)	105

Dynamic Mechanical Analysis of the Symmetric Blends. Although glass transitions in the PS-PEA ionomer blends are detectable by differential scanning calorimetry, our own measurements and those published[11a] have shown that they are not consistently easy to pinpoint accurately. In order to have more definitive data with which to reference stretch temperatures in the different samples (in amorphous polymers, stretch temperatures are frequently referenced to T_gs), recourse was made to dynamic mechanical thermal analysis (DMTA). These data provide, in addition, information regarding the phase behavior in these blends, an aspect which is essential to keep in mind in interpreting the orientation behavior.

Figure 4 shows the loss tangents as a function of temperature for the three symmetric blends studied (the data for the asymmetric blend will be commented on later). The primary glass transition temperatures (T_g), taken as the maximum of the tan δ peaks, are given in Table 1. The storage modulus curves (not shown but similar to those of ref 11a) all have one main transition, rather abrupt, at those T_gs, with a small, gradual pre-T_g decrease in modulus that is perceptible beginning at about −10 °C and that is more pronounced the lower the ion content. For the 3% blend, the corresponding loss tangent curve denotes two transitions: one main transition that peaks at 92 °C and a small shoulder in the vicinity of 0 °C. This, together with the opacity of the sample, clearly shows that this blend is a phase-separated system with large domain sizes ($\gtrsim$4000 Å). At the same time, the fact that the main T_g of the blend is significantly lower than that even of polystyrene (~110 °C), let alone sulfonated PS, indicates that the phase in question is a mixed phase of PS and PEA segments.

For the blend containing 7% interacting groups, the main loss tangent transition peak has decreased to 84 °C and the shoulder is much less evident. Thus, the two transitions seem to have approached each other—a sign of enhanced miscibility. The molded sample is also transparent. Evidently, any phase-separated domains

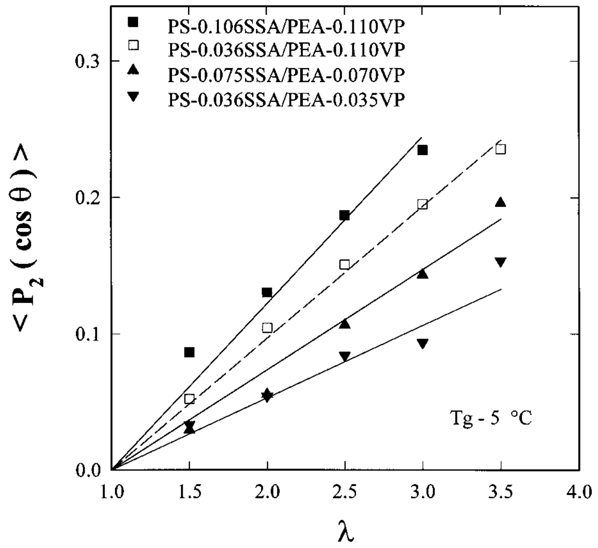

Figure 5. Orientation versus draw ratio, using the PS 906 cm^{-1} band, for the heteroblends indicated and drawn uniaxially at T_g(DMTA) − 5 °C.

must now be smaller than the wavelength of visible light. For the 11% blend, the main transition has moved upward in temperature, which can be attributed to the increasing number of effective ionic cross-links in the system which now overwhelms the effect of enhanced miscibility on the T_g.[6,11,15] A minor PEA-rich phase still seems to be present, but to a lesser extent. It is also noteworthy that the main loss tangent transition becomes increasingly broad with increase in ion content, no doubt reflecting increased compositional heterogeneity within the phase.

The above data correspond closely to what was observed by Douglas et al.[11] and by Smith and Eisenberg[6,9] for the same system (different ion contents). Douglas et al. concluded that the main transition reflects a mixed phase which is predominant in the system, whereas the minor low-temperature phase is a PEA-rich phase composed of EA sequences between VP units having lengths that result in domains sufficiently large to be detected by DMTA. The shorter sequence lengths of the PEA in the mixed phase give rise to domains that are smaller than the DMTA resolution. In short, the extent of phase separation depends on the topological constraints imposed by the ionic cross-linking interactions and their distribution within the polymer chains, and its detection depends on the resolution of the measuring techniques; with an increasing number of ionic cross-links, the phase-separated domains become increasingly small, too small to be detected clearly by DSC or DMTA .[11]

In this context, it is important to keep in mind that an orientation value that is determined using a particular IR band represents an average, for the segment concerned, of its orientation in all of the environments within which it is found.

Influence of Ion Content on Orientation Behavior in the Symmetric Blends. The orientation function, P_2, versus draw ratio at T_g − 5 °C for the PS segments in the equimolar, symmetric blends studied is shown in Figure 5. The stretch temperature in all cases is referenced to the T_g determined from the dominant DMTA loss tangent maximum. As mentioned above, this reference was preferred to the DSC T_g, since the latter are often more difficult to define accurately. Nevertheless, it is noteworthy that the DSC T_gs that we estimated are about 15 ± 5 °C below the DMTA T_g, which corresponds to the difference usually observed in our laboratory between the two methods under the conditions used. This also means that T_g^{DMTA} − 5 °C (the stretch temperature used for Figure 5) corresponds to about T_g^{DSC} + 10 °C, which will be useful for comparison with previously obtained data (see below). It should be noted that for the 11% blend it was impossible to attain draw ratios greater than about 3 at this stretch temperature, due to sample breakage.

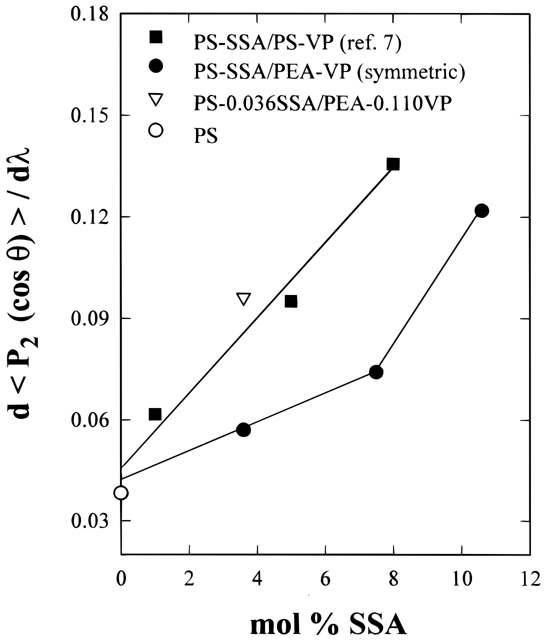

Figure 6. Slopes of the least-square fits of the P_2 versus draw ratio data (906 cm^{-1} band) as a function of SSA content for the blends and homopolymer indicated. The data for the PS-SSA/PS-VP blends and for PS were obtained from ref 7 (stretch temperature, T_g(DSC) + 10 °C). The heteroblends were stretched at T_g(DMTA) − 5 °C. See text for details.

As expected, the orientation increases with ion content, no doubt reflecting the increasing amount of effective (ionic) cross-links in the blends. It is, of course, well-known from the theory of rubber elasticity that the intrinsic orientation of polymer chains is governed by the number of cross-links (or effective cross-links) between chains. Interestingly, as shown in Figure 6, where the slopes of the curves, $dP_2/d\lambda$ (as determined by least-square fits forced through the point $P_2 = 0$ at $\lambda = 1$), are plotted as a function of ion content, the rate of increase of orientation in the three samples is apparently nonlinear with ion content, being greater at higher ion content. This behavior contrasts with our previous studies involving strongly interacting systems (PS-SSA-Na and PS-MAA-Na ionomers,[13] PS-SSA copolymers,[7] PS-SSA/PS-VP homoblends[7]), where the rates of increase of orientation with ion content do appear to exhibit linear relationships.

The data for the homoblends[7] at T_g^{DSC} + 10 °C are also shown in Figure 6. If, as argued above, the stretch temperatures are equivalent for the two systems, they can be compared. The rate of increase of P_2 with ion content for the homoblends not only appears linear but extrapolates fairly well to the orientation measured for PS, which can be considered as 0% ion content. It may or may not be significant that the rate of increase in P_2 for the heteroblends at lower ion contents can also be extrapolated approximately to the PS orientation, al-

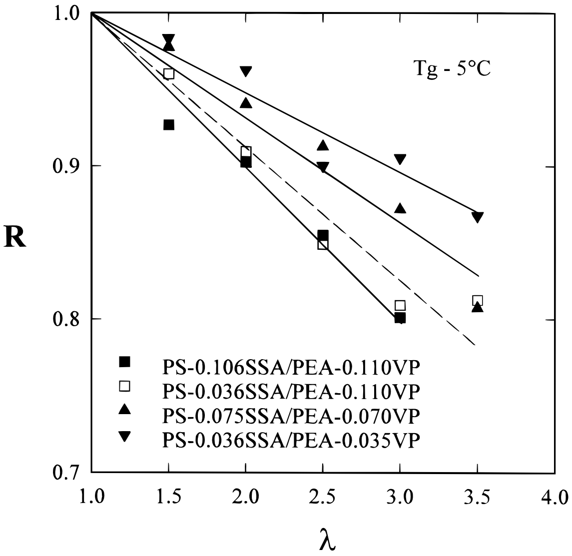

Figure 7. Dichroic ratio versus draw ratio, obtained from the 852 cm^{-1} PEA band, for the heteroblends indicated and drawn uniaxially at T_g(DMTA) − 5 °C.

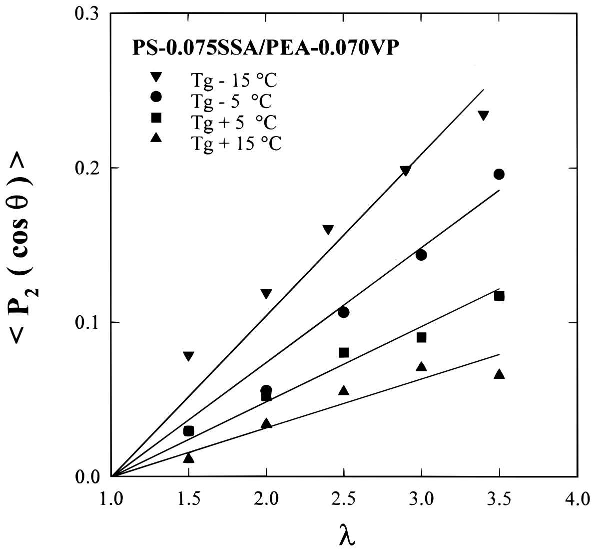

Figure 8. Orientation function versus draw ratio, using the 906 cm^{-1} band, of the 7% symmetric blend for the stretch temperatures indicated (T_g from the DMTA loss tangent maximum).

though with a much lower slope. Furthermore, the orientation of the homoblends at any given ion content is higher than that of the heteroblends.

This behavior suggests that whereas the orientation in the homoblends depends only on the number of effective (ionic) cross-links in the system, that of the heteroblends is also influenced by the PEA segments (above and beyond their effect on the T_g). The PEA segments or domains, with their much lower intrinsic T_g or greater flexibility compared to PS, may somehow be exerting a plasticizing effect on the PS segments. This can be understood better by realizing that during the stretch process and before the orientation is frozen in by quenching below the T_g, which can take up to 2 or 3 s, simultaneous chain relaxation occurs to some extent (see also the next section).[13,20] In this context, it is quite possible that the presence of the flexible PEA segments in the vicinity of the PS segments, as forced through the ionic interactions beween the sulfonate and pyridinium groups, may induce greater relaxation of the PS segments during the stretch process than would occur in the absence of the PEA component. This phenomenon, where the measured orientation of a polymer segment is less than otherwise due to faster relaxation times induced by surrounding segments is referred to as “relaxation coupling” or, more specifically, “tube relaxation”.[3e,21]

Determination of the dichroic ratio, *R*, of the PEA band at 852 cm^{-1} provides a comparison of the relative orientation of the PEA segments in the different blends. This is shown in Figure 7. The PEA chains are oriented, on average, in all the blends under the experimental conditions used, and this despite the fact that the intrinsic T_g of PEA, reflecting the flexibility of the PEA chains, is much lower than the stretch temperatures. Furthermore, like the PS segments, the PEA segments become increasingly oriented with increase in interacting group content, apparently also in nonlinear fashion. (It should be recalled here that the dichroic ratios of the blends with higher interacting group content are, if anything, underestimated, implying that the relative increase in orientation with interacting group content may actually be greater than what is indicated in Figure 7.) In other words, the PEA segments in the blends experience the same kind of constraints as do the PS segments, as imposed by the effective (ionic) cross-link density. These constraints prevent the chain segments between the cross-links from fully relaxing, similar to the situation in covalently cross-linked elastomers.

Influence of Stretch Temperature on Orientation Behavior in the Symmetric Blends. It was mentioned earlier that the 11% blend could not be stretched to high draw ratios at T_g^{DMTA} − 5 °C. The blends with lower ion contents could still be successfully stretched at lower temperatures, at least down to T_g^{DMTA} − 15 °C. The increased ease of stretching at temperatures below T_g for lower ion contents probably reflects the larger sizes of the phase-separated PEA domains with their much lower T_g. When the stretch temperatures were significantly above the T_g, notably at T_g + 25 °C for the 11% blend, the film underwent nonlinear deformation and was subject to simultaneous shrinkage during the deformation process. The studies of orientation as a function of stretch temperature were thus restricted to temperatures near the principal T_g.

The dependence of the PS orientation function versus draw ratio on temperature is shown in Figure 8 for the blend with about 7% interacting group content. The slopes obtained from such curves, $dP_2/d\lambda$, are plotted in Figure 9 as a function of the temperature difference from T_g^{DMTA} for all three blends. Evidently, the PS orientation decreases with increasing temperature in approximately linear fashion for each blend, in the range of temperatures studied. This is related to the usual reason that the higher the temperature, the greater the chain relaxation that occurs during the stretch process. In ionomer blends, there may also be some contribution from ion hopping, which may likewise be expected to increase with temperature, with the result that both the number of effective cross-links may diminish with increasing temperature, reducing the intrinsic orientation, and the rate of simultaneous chain relaxation may be further increased. It is noteworthy that the slopes in Figure 9 apparently steepen with increasing ion content such that the difference in orientation between the three blends tends to diminish as the temperature is raised. The same tendency had

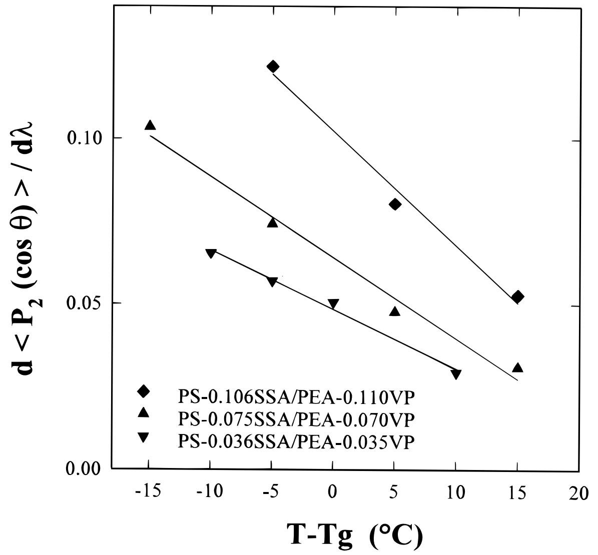

Figure 9. Slopes of the least-square fits of the P_2 versus draw ratio data (906 cm^{-1}) as a function of the difference between the stretch temperature and glass transition temperature (DMTA) for the blends indicated.

been noted for the homoblends.[22] This may again be related to possible ion hopping, which can be expected to be more pronounced at higher ion contents simply because the ion pairs or aggregates, being more numerous, are closer to one another so that ion hopping can occur through shorter distances and thereby be facilitated. Such an increase in ion hopping with both temperature and ion content will necessarily result in smaller differences in orientation between blends of different ion contents when the temperature increases.

Dynamic Mechanical Analysis and Orientation Behavior of an Asymmetric Blend. When the complementary functional groups in an asymmetric blend are equimolar, the dominant component is the one with the lowest functional group content. We prepared such an asymmetric blend from PS-0.036SSA and PEA-0.110VP. In this blend, there is about three times as much styrene as there is ethyl acrylate. On the other hand, the average length of the PS segments between effective cross-links in this blend is the same as for the 3% symmetric blend, PS-0.036SSA/PEA-0.035VP, whereas that of the PEA segments is the same as for the 11% symmetric blend, PS-0.106SSA/PEA-0.110VP. A comparison of these two pairs of blends may shed further light on the orientation behavior in the PS-PEA ionomer blend system.

First, to probe the phase structure, DMTA measurements were conducted. The loss tangent as a function of temperature of the asymmetric blend is included in Figure 4. Clearly, with less PEA present, the primary glass transition of the asymmetric blend undergoes less plasticization than the 3% symmetric blend; thus, it is found at higher temperatures. In fact, it has a T_g similar to that of the 11% symmetric blend but significantly narrower in width, reflecting greater compositional homogeneity. There is expected to be little detectable PEA microphase in the asymmetric blend, and, indeed, at most, there is only a hint of this as a weak shoulder at about 60 °C (the apparent small peak near 10 °C is an artifact thought to be due to imperfect temperature control during the DMTA run in the region concerned). If this shoulder does reflect a PEA phase, the increase in temperature compared to the 3% symmetric blend can be rationalized by the small, isolated PEA regions being surrounded by a rigid, predominantly PS phase, creating a "hard-wall" effect.

The PS orientation function versus draw ratio of the asymmetric blend, for a stretch temperature of $T_g^{DMTA} - 5$ °C, is shown in Figure 5. Since it is the average P_2s of the styrene segments only that are being measured and since the PS component in the PS-0.036SSA/PEA-0.035VP symmetric blend and the PS-0.036SSA/PEA-0.110VP asymmetric blend experiences the same number of effective ionic cross-links through the SSA groups, one might expect that, in the absence of other effects, both blends should have similar P_2s. However, Figure 5 shows that the orientation of the asymmetric blend is much higher than that of the 3% symmetric blend, and, in fact, is closer to that of the 11% symmetric blend.

The slope of the orientation curve, $dP_2/d\lambda$, for the asymmetric blend is marked on Figure 6. There, it is observed that the PS orientation in the asymmetric blend is, in fact, similar to that of a symmetric homoblend having the same SSA content. This suggests that the orientation in the asymmetric blend is governed principally by the effective ionic cross-links, like for the homoblend system.

If we examine the relative PEA orientation in the asymmetric blend, as given by the dichroic ratio of the 852 cm^{-1} band and included in Figure 7, we can observe that this ratio is close to that for the 11% symmetric blend (or perhaps even higher, since the underestimation of the dichroic ratios without band fitting, as referred to above, is likely to be the most pronounced for this blend). Evidently, the orientation of the PEA segments is governed strongly by the number of effective ionic cross-links they experience via their ion content, which is the same for PEA in the asymmetric blend and in the 11% symmetric blend.

These observations lend further credence to the idea that the orientation of the PS segments in the heteroblends is influenced by relaxation coupling with the PEA component. Without this factor, the PS orientation in the asymmetric blend and the 3% symmetric blend (as well as the 3% symmetric PS homoblend) should all be similar for the same relative stretch temperature. The fact that it is much lower for the 3% symmetric heteroblend compared to the other two blends indicates that relaxation coupling is operative in this blend. On the other hand, the similarity in PS orientation between the asymmetric blend and the corresponding homoblend indicates that relaxation coupling is not operative in the asymmetric blend.

The absence of relaxation coupling in the asymmetric blend can be attributed to two factors. The first is the high orientation of the PEA segments in this blend; since the PEA segments themselves are in a much less relaxed state in the asymmetric blend than in the 3% symmetric blend given their high orientation, they necessarily cannot induce the same relaxation of the PS segments in the former as they do in the latter. Secondly, there being less PEA present in the asymmetric blend compared to the 3% symmetric blend can also contribute to reducing the relaxation coupling, both directly as well as possibly indirectly through the effect on the blend morphology.

Concluding Remarks

We have said nothing so far about how either the microphase-separated PEA domains or the possible existence of higher-level ionic aggregates (multiplets and clusters) may influence the orientation behavior. Regarding the latter, it has already been concluded in previous publications[6,11b] that detectable clusters do not exist in these blends, probably due to plasticization by PEA. This does not rule out the existence of some ionic aggregates in the form of multiplets; however, at most, these would simply act as multifunctional cross-link sites that contribute to the effective ionic network density in the blends.

As for the PEA microphase-separated domains, they may well contribute to the relaxation coupling effect described above. For example, the larger the size of these domains, the less the segments in them must be oriented, since the number of effective cross-links in the larger domains is necessarily lower than those in the smaller domains. Thus the presence of larger PEA domains, where the segments are less oriented and more relaxed, may increase the possibility for relaxation coupling with the PS chains. On the other hand, the PEA segments in the larger PEA domains will have less contact with the PS chains (since this takes place through the ionic interactions), and this may contribute to reducing the relaxation coupling. In any case, the existing data, being average values for either PS or PEA segments, do not allow us to distinguish between the effect of the PEA segments in the larger (or microphase-separated) domains and those in the smaller domains (or mixed-phase regions). It should also be kept in mind that the size or extent of the microphase-separated domains probably vary in more-or-less continuous fashion as ion content is varied, and likely also within a sample of a particular ion content, and it is only the measuring method (DMTA) that gives rise to an apparent cut-off point due to its detection limit.

To conclude, the orientation behavior in the ionically-complexed PS-PEA heteroblends, compared to previously-studied PS homoblends, clearly demonstrates that the PEA chains can influence, in fact reduce, the orientation of the PS chains. This is attributed to relaxation coupling between the two types of chains. We believe that we have thereby been able, with the PS-PEA blend system, to highlight this particular factor. Hopefully, this will enable us to better understand its role in the orientation behavior of blends in general. To this end, further study of the PS-PEA blend system is warranted, focusing in particular on the *relaxation* from an oriented state of both types of segments.

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