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Comparison of Molecular Orientation in Ionomer-Related Polystyrene-Based Copolymers and Blends

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ABSTRACT: The molecular orientation, measured by infrared dichroism, is compared for several polystyrene-based systems stretched uniaxially above their glass transition temperatures. These systems contain controlled amounts of interactions of various types and strengths. For all those involving hydrogen bonding with carboxylic acid, such as poly(styrene-*co*-methacrylic acid) (PS–MAA) and blends of PS–MAA with poly(styrene-*co*-4-vinylpyridine) (PS–VP), there is no increase in the orientation measured compared to that of polystyrene. The orientation increases significantly, however, for the more strongly interacting poly(styrene-*co*-styrenesulfonic acid) (PS–SSA) copolymer. Greatest orientation is observed in blends of PS–SSA with PS–VP, known to be characterized by intermolecular ionic interactions. The results are discussed in terms of the strong interactions slowing down chain relaxation or acting as effective cross-links in the time scale of the experiment.

Introduction

The segmental orientation measured in polymer systems subjected to uniaxial strain is generally composed of two principal factors. One is the orientation induced by the act of stretching; this is governed by the number of effective cross-links between chains, as is well-known from the theory of rubber elasticity. The other is related to the chain relaxation that inevitably occurs during the stretching process and which reduces the induced orientation to some extent. Chain entanglements, for instance, act as effective cross-links; thus, polymers with a smaller average molecular weight between entanglements have greater orientation than those with a higher average molecular weight between entanglements, when stretched under the same experimental conditions relative to their glass transition temperature. On the other hand, an increase in the temperature of stretching decreases the orientation measured because the relaxation rate of the polymer chains increases with temperature. It is also well-known that the existence of specific interactions between chains increases the orientation measured in these systems by retarding the rate of chain relaxation.

In this paper, we will compare the orientation observed in polystyrene-based systems, in which controlled numbers of specific interactions of various types or strengths are present. These systems include three copolymers, poly(styrene-*co*-methacrylic acid) (PS–MAA), poly(styrene–*co*–styrenesulfonic acid) (PS–SSA), and poly(styrene-*co*-4-vinylpyridine) (PS–VP), and stoichiometric blends of PS–VP with PS–SSA. In the acid copolymer systems, PS–MAA and PS–SSA, there are hydrogen-bonding interactions generally thought to be of two very different strengths. The PS–VP copolymer is a non-self-associating system. In blends of PS–VP with PS–SSA, it is known that proton transfer from the acid to the pyridine occurs, leading to hydrogen-bonded ion–ion interactions.[1–4] These interactions may act as effective cross-links in the time scale of the stretching experiment.

Experimental Section

Sample Preparation. The various copolymers and blends were prepared by standard methods as indicated in Table 1 along with the appropriate literature references. The molecular weights were determined in THF by size exclusion chromatography using polystyrene standards. The polydispersity in all cases is 1.7–2.2. The PS–SSA copolymers, after precipitation and washing in methanol or water, depending on their acid content, were dried in a vacuum over for 1 day at room temperature and 1 week at 60 °C. The other copolymers were dried for at least 2 days at about 100 °C.

To obtain the complexed blends, the sulfonic acid and vinylpyridine copolymers of similar co-unit contents were stoichiometrically blended[1–3] as follows. The copolymers were first dissolved separately in a THF/methanol (90/10) solution, following which the PS–VP solution was added dropwise to the vigorously stirred PS–SSA solution. The gellike precipitate which resulted for all blends except that of the lowest co-unit content was further precipitated in methanol; for the lowest co-unit content, the entire solution was precipitated in methanol. The PS–MAA/PS–VP blend, which did not form a gel, was prepared similarly. The samples were dried in a vacuum over at room temperature for 1 day and at 120 °C for 3 days.

Thin films (50–100 μm) of uniform thickness for the uniaxial stretching experiments were prepared, in most cases, by compression-molding well above the T_g of the material (e.g., about T_g + 45 °C for PS–SSA and T_g + 75 °C for the blends), using a SPECAC–IR film-making mold, followed by cutting into appropriate strips. Films (ca. 40 μm) of the copolymers, PS–MAAandPS–SCA[poly(styrene-*co*-styrenecarboxylicacid)], were prepared by solution-casting from 4% chloroform solutions onto glass plates; the resulting films were cut into strips and then further dried in vacuum at room temperature for 1 day and at 140 °C for 2 days, followed by slow cooling. All strips were about 20 mm in length and 6 mm in width. It was verified, for the copolymers, that a solution-cast film gave the same result in orientation as a molded film; solution-casting was not possible for the PS–SSA/PS–VP blends.

T_g Measurements. The glass transition temperatures (T_g) were determined 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's were taken as the midpoint of the transition.

Stretching Conditions. To prevent slippage during stretching, Pyrotape (Aremco) was fixed to the extremities of each strip; it was then clamped vertically at its ends in a home-made stretching apparatus with a fixed lower clamp. The elongation process consisted of raising the upper clamp at an

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Table 1. Characteristics of the Polymers Studied

polymer[a]	source/synthesis	M_w (10^{-3})	T_g (°C)
PS	Aldrich	250	103
PS−0.036MAA	free-radical copolymerization[5]	150	108
PS−0.057MAA		150	111
PS−0.087MAA		150	120
PS−0.112MAA		160	124
PS−0.099SCA	carboxylation of free-radically polymerized PS[6]	120	118
PS−0.030SSA	sulfonation of Aldrich PS[7]		106
PS−0.050SSA			112
PS−0.072SSA			118
PS−0.099SSA			120
PS−0.010VP	free-radical copolymerization[8]	160	104
PS−0.045VP		160	106
PS−0.080VP		190	108
PS−(0.015SSA/0.010VP)	see text		105
PS−(0.050SSA/0.045VP)			121
PS−(0.080SSA/0.080VP)			130
PS−(0.047MAA/0.045VP)			108

[a] Numbers indicate mole fraction co-unit. Key: MAA, methacrylic acid; SCA, styrenecarboxylic acid; SSA, styrenesulfonic acid; VP, vinylpyridine.

exponential velocity, giving a constant strain rate, chosen as 0.026 s^{-1}. Various draw ratios were selected. The actual draw ratio and the uniformity of stretching were monitored by ink lines drawn across the width of each film before stretching. The stretch temperature, once attained, was allowed to equilibrate for at least 10 min before drawing. Immediately after completion of the stretching, the sample was quenched to room temperature by opening the front of the apparatus into which cool air was circulated by a fan; a maximum of 2 or 3 s passed between the end of stretching and the freezing-in of orientation at temperatures below the sample T_g.

Orientation Measurements. The polarized spectra were recorded at room temperature by a Mattson FTIR spectrometer (Sirius 100) equipped with an MCT detector. Usually, 100 interferograms (in a few series, 400 interferograms) were accumulated, with a resolution of 4 cm^{-1}. A fixed wire-grid polarizer was used, and the samples were rotated 90° via a home-made motorized device to obtain the spectra parallel and perpendicular to the polarization plane of the infrared beam.

The infrared dichroic ratio, R, is equal to $A_{\parallel}/A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are the measured absorbances (intensities) 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 following relation:

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

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 is 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 usually five or more, areas of the stretched sample; in some cases, these values were checked against those obtained for separately prepared samples and (in particular for PS−SSA) for samples prepared and measured by two different researchers. It was also verified that unstretched samples gave P_2 values very close to zero (about 0.005 at most).

The two polystyrene bands most frequently used for orientation measurements[9] are located at 906 and 1028 cm^{-1}. Both bands are conformationally insensitive. The band at 906 cm^{-1} corresponds to the out-of-plane ν_{17b} mode of the benzene ring. With the angle α determined as 35°,[9] eq 1 reduces to

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

The band at 1028 cm^{-1} is attributed to the in-plane ν_{18a} CH bending mode of the benzene ring; with the angle α being 90°,[9] eq 1 for this band reduces to

$$\langle P_2(\cos\theta)\rangle_{1028} = -2\frac{R-1}{R+2} \qquad (3)$$

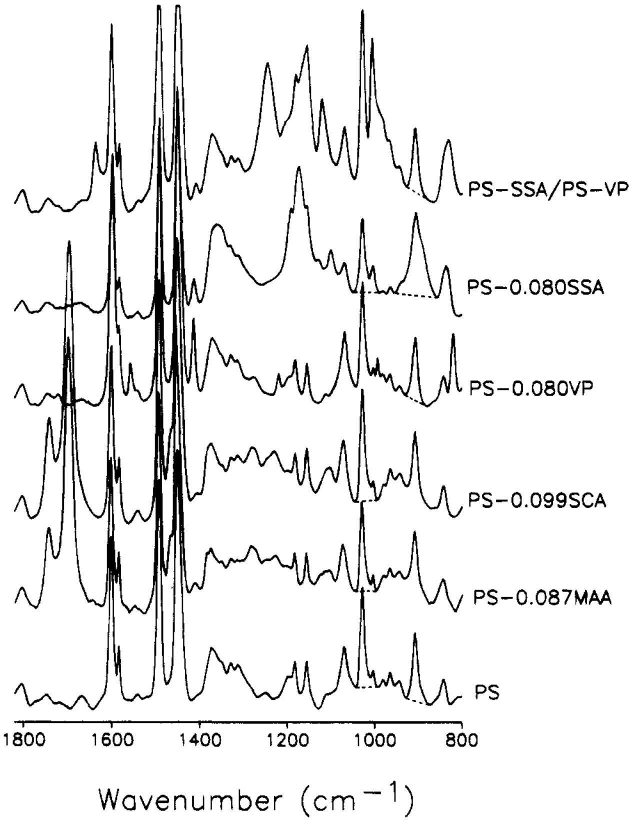

Figure 1. Infrared spectra of unoriented films of PS and various PS copolymers and a blend, with the baselines used for orientation measurements indicated by the dashed lines.

Examples of the spectra for various samples are given in Figure 1, with the baselines used for the analyses indicated. The bands attributed to the co-unit in the various samples are well-documented in the existing literature[1,3,4,10−12] and will not be re-explained here. In particular, the spectrum of the PS−SSA/PS−VP blend, indicating almost complete proton transfer between the SSA and VP groups creating ion pairs, is identical to those reported and analyzed in refs 1, 3, and 4. It will be noticed that, in most cases, both the 1028 and 906 cm^{-1} bands are apparently free from significant overlap with other bands which would compromise the orientation values measured.

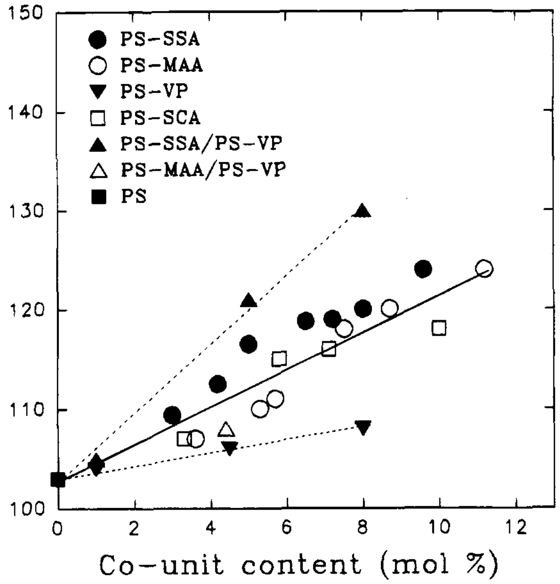

Figure 2. Glass transition temperatures, obtained by differential scanning calorimetry, as a function of co-unit content for the various copolymers and blends.

This was verified by checking, in nonoriented films, the ratios of the intensities of these bands to that of the isolated PS band at 1945 cm^{-1} and comparing them to the same ratios in PS. These ratios are 2.0 ± 0.2 for the band at 906 cm^{-1} and 3.2 ± 0.2 for that at 1028 cm^{-1}, except as noted below. The validity of the choice of the 1945 cm^{-1} band as an internal standard was, in turn, supported by the constancy of its ratio to a second isolated PS band at 1875 cm^{-1}, the intensity ratio of the 1875/1945 cm^{-1} bands in all the samples being 0.71 ± 0.02.[4] These verifications assure us that the choice of baselines and any slight overlap with neighboring bands do not introduce significant error in the P_2 measurements of the samples concerned. In any case, we believe that the precision of these measurements is determined primarily by the film preparation and stretching processes and that this is shown by the scatter of the points in the graphs of P_2 versus draw ratio. On the basis of that scatter and also that of the three or more determinations per point, we estimate the error of the P_2 values to be about ±0.01.

Notable exceptions to the above observations occur for the PS−SSA/PS−VP blends for which the intensity ratio of the 1028/1945 cm^{-1} bands differs significantly from that of PS; therefore, the 906 cm^{-1} band, whose relative intensity in the blends is the same as in PS, was used in determining the P_2 values. In addition, complications were found for PS−SSA, as will be specified subsequently. In the latter case, additional recourse was made to a third polystyrene band, at 2850 cm^{-1}, also conformationally insensitive.[9] This band is attributed to the CH_2 symmetrical stretching, for which the angle α was determined to be 70°.[9] Equation 1 then becomes

$$\langle P_2 (\cos\theta)\rangle_{2850} = -3.08\frac{R-1}{R+2} \qquad (4)$$

Results and Discussion

The characteristics of the copolymers and blends studied, and their T_g's, are listed in Table 1. The T_g's as a function of co-unit content are plotted in Figure 2. These data agree well with those already published.[1,4,8,11] Certain observations are to be noted. Compared to the non-interacting copolymer PS−VP, for which the T_g increases little with VP content,[8] the T_g's of the acid copolymers increase significantly with acid content. This is due, of course, to the presence of the self-associating acid groups in these systems.[10,11] It is noteworthy that the type of acid co-unit appears to have little effect: the T_g's of all of the acid copolymers analyzed increase at a rate of about 2 °C/mol % acid content in the composition range studied. The PS−VP/PS−SSA blends, on the other hand, have T_g's that increase more sharply with co-unit content. This has been shown to be due to the cross-linking effect of the ion−ion interactions.[1,4]

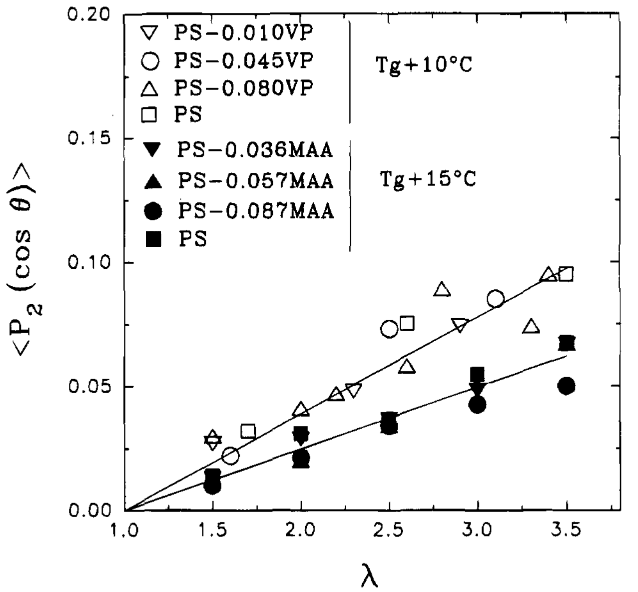

Figure 3. Orientation function versus draw ratio for PS, PS−VP, and PS−MAA at the stretch temperatures indicated, using the bands at 906 and 1028 cm^{-1} at T_g + 10 °C and T_g + 15 °C, respectively. The lines drawn in this and similar figures are a guide to the eye.

In a previous publication from this laboratory,[12] it was observed that the hydrogen-bonding interactions in PS−MAA (6 mol %) have no perceptible influence, within experimental error, on the segmental orientation measured, compared to PS. This was confirmed for the experimental conditions of this study, as shown in Figure 3, where the orientation function, P_2, is plotted versus draw ratio, λ, for several MAA contents and for PS, using T_g + 15 °C as the stretch temperature. As expected for the non-self-associating system, PS−VP, there is similarly no perceptible difference in the orientation measured for these copolymers and for PS, shown in Figure 3, with T_g + 10 °C as the stretch temperature. The P_2's measured for T_g + 15 °C are lower than those measured for T_g + 10 °C because, as explained in the Introduction, the greater the difference between T_g and the stretch temperature (when above the T_g), the lower the orientation measured.

In order to further confirm the ineffectiveness of the hydrogen-bonding interactions on the orientation of PS−MAA, measurements were also made on a copolymer with higher MAA content, 11 mol %. This was compared with a para-carboxylated polystyrene copolymer, PS−SCA, with similar acid content. The latter copolymer, with the acid moiety located on the benzene ring rather than directly attached to a main-chain carbon, provides a more direct comparison for the sulfonated copolymers. It should also be remarked that aromatic carboxylic acid is slightly more acidic than aliphatic carboxylic acid (the pK_a of the former is 4.2 compared to 4.9 for the latter[13]). The orientation behaviors of the PS−MAA copolymer and the PS−SCA copolymer, compared to PS, are shown in Figure 4. Again, it is observed that there is no noticeable difference in the orientation of the three materials. Thus, it can be concluded that the hydrogen-bonding interactions of the carboxylic acid type, which as specific interactions may be expected to retard chain relaxation during the

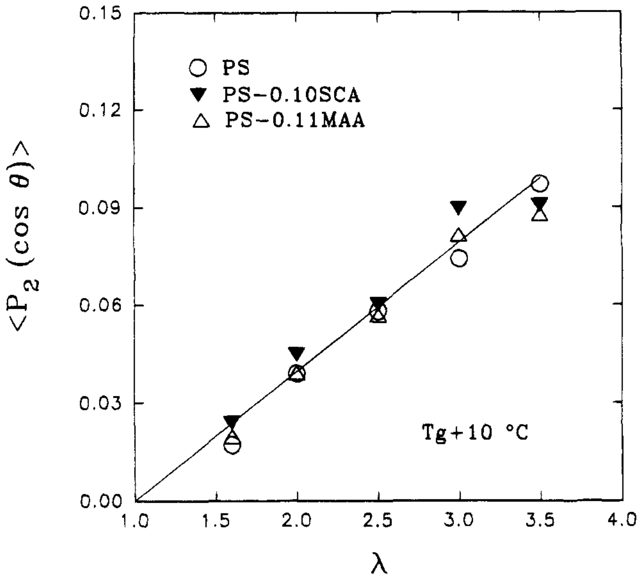

Figure 4. Orientation function versus draw ratio for the samples indicated, using the bands at 1028 cm^{-1}. The points for PS were obtained from a series of samples different from those in Figure 3.

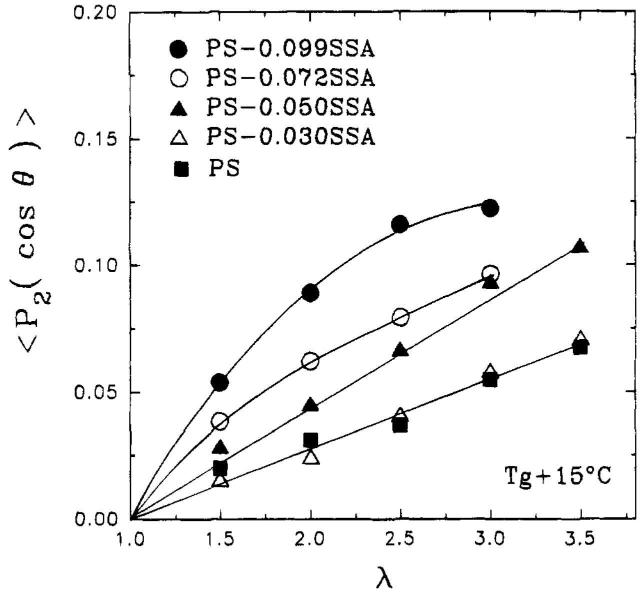

Figure 5. Orientation function versus draw ratio for PS and PS−SSA copolymers, using the band at 1028 cm^{-1}.

stretching process, do not in fact do so to any measurable extent at the acid contents studied and under the experimental conditions used.

In this connection, it is to be noted that, according to infrared studies, the carboxylic acid moieties exist predominantly as acid dimers at the stretching temperatures used. Lee et al.[14] calculated, for a poly(ethylene-*co*-methacrylic acid) copolymer with 20 mol % acid content, that the fraction of unassociated carboxyl groups is only 7.6% at 140 °C, and there is no reason to believe that the situation is very different for the PS−MAA or PS−SCA copolymers. On the other hand, these hydrogen-bonding interactions are undoubtedly quite labile at the stretch temperatures used, as is the case for many specific interactions.

In contrast to the carboxylic acid-containing copolymers, Figure 5 indicates that the orientation of the PS−SSA copolymers increases significantly with SSA content, beginning somewhere between 3 and 5 mol % SSA units for a stretch temperature of T_g + 15 °C. It is also to be noted that the increase in orientation with draw ratio is not linear for acid contents of about 7% and higher, at least at the higher draw ratios. Experimentally, the samples of higher SSA content were difficult to stretch to draw ratios greater than about 2.5; they also tended to be subject to some nonlinear deformation during stretching.

Clearly, the hydrogen-bonding interactions between sulfonic acid groups[10] are either acting as effective cross-links or they are drastically slowing down the chain relaxation during the deformation process. In fact, some controversy exists in the literature as to whether or not the sulfonic acid groups in PS−SSA aggregate to form multiplets or even clusters, based on dynamic mechanical and small-angle X-ray scattering data.[11,15] Our own dynamic mechanical tests give no evidence of aggregate formation up to 10 mol % acid content and 160 °C; a recent publication by Douglas et al.[16] also rules this out. On the other hand, according to the Eisenberg−Hird−Moore model of ionomer morphology,[17] dynamic mechanical analysis can rule out cluster formation but not multiplet formation, clusters here indicating regions of restricted mobility of a certain minimum volume fraction. Multiplets, that is aggregates of acid groups, perhaps exist in PS−SSA copolymers given the high strength of the sulfonate moieties and their tendency to form a network of associated acid groups, at least at high acid content.[10] Whether associated into pairs or into higher-order aggregates, the sulfonic acid interactions may in either case act as effective cross-links in the time scale of the stretching process or at the least retard the chain relaxation and thus account for the orientation behavior observed.

It is appropriate at this point to discuss two complications in determining accurate P_2 values for PS−SSA, although it will be argued that they do not, in fact, compromise the trends just described. First, PS−SSA is easily hydrated, as can be detected in the infrared spectra by the presence of bands at 1004 and 1128 cm^{-1}.[10,18] The spectra for the series of PS−SSA samples are shown in Figure 6, and it can be observed that only the samples of 5 mol % SSA and less appear completely dry. The presence of water molecules, which intervene in the acid associations,[10] may, of course, affect the orientation measured. However, it is difficult to verify samples of high acid content in which there are no remaining traces of water, since the samples are subject to degradation during prolonged drying at the necessary temperatures, and this would also affect the orientation measured. On the other hand, the fact that the orientation of the apparently completely dried 5 mol % SSA sample is higher than those of PS and of samples containing lower percentages of SSA is reassuring as to the validity of the trends observed in Figure 5. It is also noteworthy that the presence of a shoulder on the lower wavenumber side of the 906 cm^{-1} band, attributed to the single-bond S−O stretch of the acid group[3,4,10] and increasing in intensity with acid content, tells us that acid character is largely present in all of the PS−SSA copolymers.

Second, the band at 1028 cm^{-1}, used to determine the P_2 values of Figure 5, was preferred to the 906 cm^{-1} band due to the overlapping shoulder just mentioned. However, a closer analysis of the 1028 cm^{-1} band revealed that it also may be affected by the SSA content. Whereas the intensity ratio of the pure polystyrene bands, 1875/1945 cm^{-1}, is constant as noted above, the intensity of the 1028 cm^{-1} band relative to either one

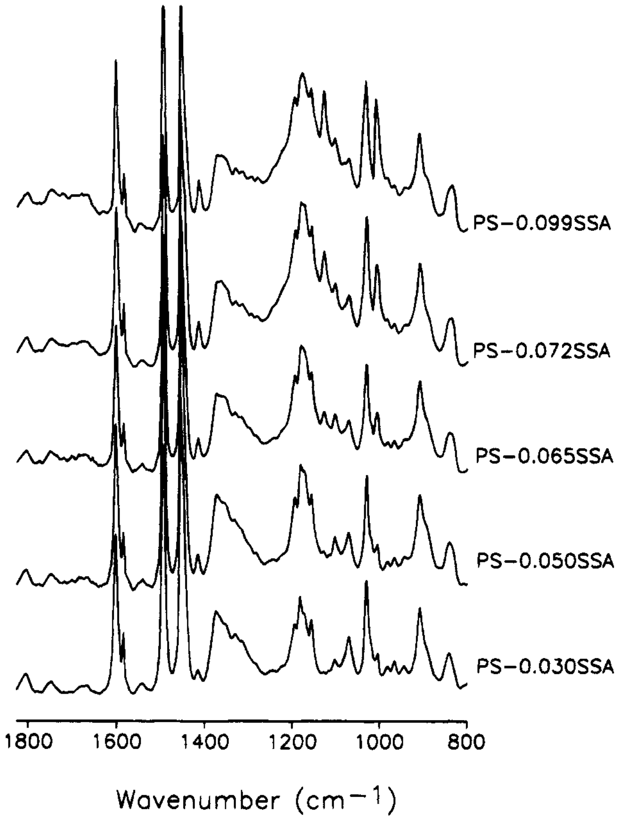

Figure 6. Infrared spectra of unoriented PS–SSA copolymers.

of the polystyrene bands increases with SSA content when above 5%. Possibly, the source lies with the hydrated SSA groups, which should give rise to a symmetric stretching vibration of the SO_3^- ion produced, reported to be at 1034 cm^{-1} in completely sulfonated PS,[10] but which may be coincident with the 1028 cm^{-1} band in partially sulfonated PS (this factor would also account for the high relative intensity of the 1028 cm^{-1} band observed in the PS–SSA/PS–VP blends, as noted above). Nevertheless, although this may affect the P_2 values determined for the higher acid contents, the completely dry 5% SSA sample is essentially free of the complication, and we can again conclude that its higher orientation compared to PS is real. As a further check, the P_2 values for the 5% sample were also determined using the band at 2850 cm^{-1} (although it, too, tended to increase in relative intensity with SSA content above 5%, perhaps related to OH stretching vibrations arising from SO_3H and/or H_2O[10]): the slope $dP_2/d\lambda$ was identical, within experimental error, to that determined using the 1028 cm^{-1} band. This is shown in Figure 7, with the P_2 values determined from the 906 cm^{-1} band also included for comparison. Table 2 gives the intensity ratios measured for the 906, 1028, and 2850 cm^{-1} bands.

The difference in orientation behavior between the carboxylic acid and the sulfonic acid copolymers contrasts sharply with the similarity in the T_g behavior of the two systems. A possible explanation may be related to the conditions under which the hydrogen-bonding interactions among the acid groups behave as effective cross-links. In the T_g range, they behave as cross-links in both PS–MAA and PS–SSA. Once longer-range chain mobility is possible, that is, above the T_g, the MAA interactions, being much weaker, become labile and can no longer act as temporary cross-links that affect the intrinsic orientation. The SSA associations, due to the strength of the interactions, presumably have a longer lifetime and thus continue to affect the measured orientation. We will return briefly to this point later.

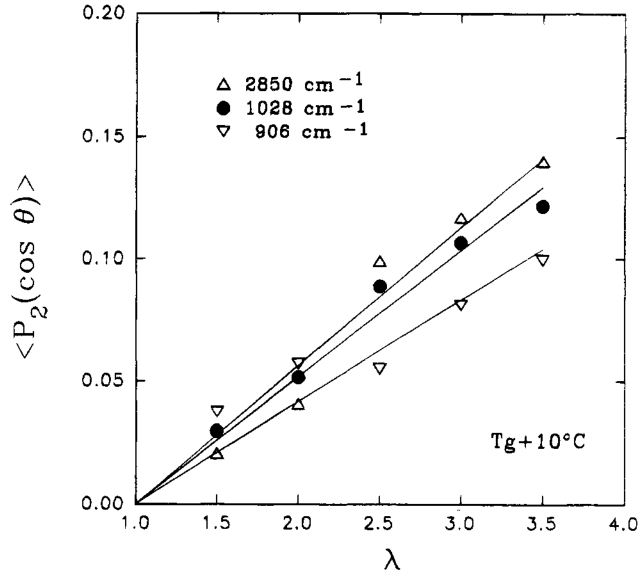

Figure 7. Orientation function versus draw ratio for PS–0.050SSA based on the infrared bands indicated.

Table 2. Intensity Ratios of the 906, 1028, and 2850 cm^{-1} Bands, Relative to the 1945 cm^{-1} Band, for PS and PS–SSA Copolymers

sample	$R_{906/1945}$	$R_{1028/1945}$	$R_{2850/1945}$
PS	1.9	3.4	3.5
PS–0.036SSA	2.7	3.2	3.6
PS–0.050SSA	3.1	3.4	3.6
PS–0.075SSA	4.2	3.8	3.9
PS–0.080SSA	4.4	3.9	3.9
PS–0.099SSA	5.1	4.3	4.0
PS–0.106SSA	5.9	4.1	4.2

When interchain ion–ion interactions are introduced into the polystyrene matrix, as is the case in the PS–SSA/PS–VP blends, the orientation measured again increases with co-unit content. This is shown for three co-unit contents for a stretching temperature of T_g + 10 °C in Figure 8. Even the blend with about 1 mol % interacting units is more oriented than PS. It is further noteworthy that, for a similar co-unit content, the orientation is higher for the blend than for the PS–SSA copolymer alone: at 5% co-unit content, which is the most reliable of the SSA contents and for which the orientation function is linear with draw ratio up to at least $\lambda = 3.5$, the slope of the orientation function versus draw ratio, $dP_2/d\lambda$, at T_g + 10 °C, is 0.095 for the blend compared to 0.055 for PS–SSA. Again, at high interacting group content, it is difficult to stretch the films to more than a draw ratio of about 2.5, due to sample breakage and nonuniform stretching. However, the curves of orientation versus draw ratio for the samples that could be stretched remain linear within experimental error (in contrast to the PS–SSA samples of higher acid contents). When PS–SSA is replaced by PS–MAA in the blend, where only hydrogen-bonding interactions between the acid and pyridine groups occur,[19] although of a stronger type than MAA–MAA interactions,[14] the orientation is reduced once more to that of polystyrene, as shown in Figure 8 for one such PS–MAA/PS–VP blend.

As for PS–SSA, the behavior in the blends can be attributed to the pyridinium–sulfonate interactions either acting as cross-links in the time scale of the

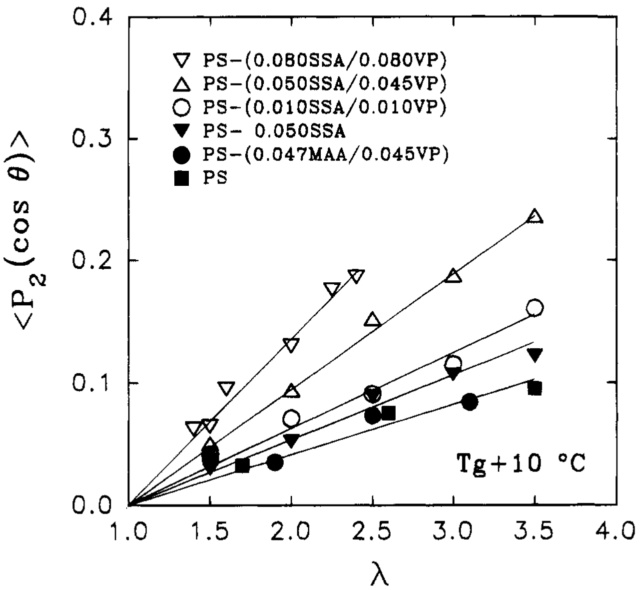

Figure 8. Orientation function versus draw ratio for PS and the blends indicated using the band at 906 cm^{-1} and for PS-0.050SSA using the band at 1028 cm^{-1}.

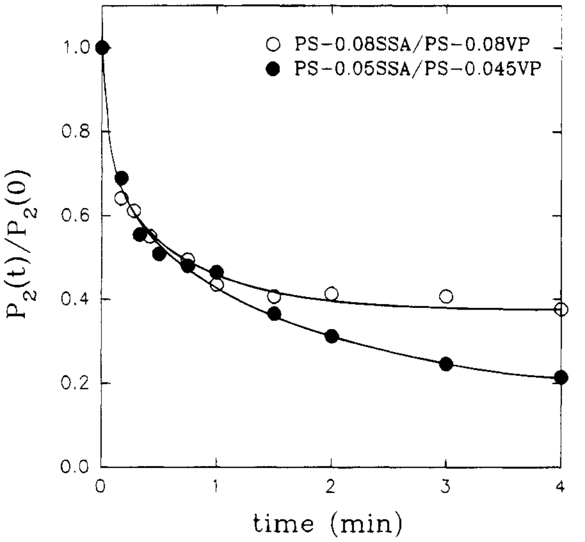

Figure 9. Normalized orientation function versus time for the blends indicated at a stretch temperature of T_g + 20 °C and a draw ratio of 3.

stretching process or drastically slowing down the chain relaxation that occurs during the deformation process. Figure 9 suggests that the interactions actually behave as effective cross-links. This figure presents normalized orientation relaxation curves for two of the PS−SSA/PS−VP blends stretched at T_g + 20 °C to a draw ratio of 3. It shows the orientation function $P_2(t)$, measured for samples that were maintained for the indicated aging times, t, at the stretch temperature following stretching and before quenching, and normalized to $P_2(0)$, measured for samples quenched immediately following stretching ($t = 0$). (All of the P_2's reported above are thus $P_2(0)$'s.) At aging times up to about 1 min, the relaxation rate of the two blends is identical; it differs only for aging times beyond 1 min, where it is slower for the blend with the higher ion content. Since the orientation of the blends at $t = 0$ increases with ion content (Figure 8), and since the variation cannot be attributed to measurable differences in relaxation rate at aging times up to 1 min (Figure 9), it must be due primarily to cross-linking effects.

In this connection, it is of interest to note that recent data[16,20] indicate the appearance of two overlapping maxima in lost tangent curves, leading to the conclusion that clusters exist in these blends. Earlier melt rheology data[1] of the same blends, in a temperature range beyond the reported cluster region, indicated that time−temperature superposition is valid (not observed in ref 16, but where the isotherms include the reported cluster region) and that there is no increase in the rubbery plateau with ion content above that due to entanglement coupling. Now, the stretch temperatures used for Figure 8 are about 15 °C below the reported cluster transition maxima (we estimate the tan δ maxima reported for the cluster transitions to correspond to roughly 145 and 155 °C if translated to DSC values for the 5 and 8% blends, respectively, according to our experience with the two techniques). From this point of view, our blends have been stretched in the presence of clusters; these, as demonstrated clearly in previous publications from our laboratory,[12,21] act as multifunctional cross-links. It is of interest to note that in ref 16 the functionality is estimated to be about 5−10, at about 15 °C below the tan δ maximum.

It should be added that, even if the ionic aggregates act primarily as effective cross-links under the experimental conditions of study, some ion-hopping which could affect the rate of chain relaxation is not ruled out; this would be the case, in particular, at higher stretch temperatures.[21] The occurrence of ion-hopping during stretching decreases, of course, the effective cross-link density. In this connection, the question may be posed as to what is the relationship between the relaxation times of strong interactions, such as the ion-pair interactions in the blends or the hydrogen-bonding interactions between SSA groups, and their behavior as effective cross-links (because their relaxation time is slower than the time scale of the experiment) or as interactions that simply retard chain relaxation (because their relaxation time is faster than the time scale of the experiment but slower than chain relaxation without these interactions). More detailed orientation relaxation investigations, in progress, are required to address this issue.

The higher orientation for the blends compared to that for the PS−SSA copolymers of similar interacting group content may also be related in part to the above issue. That is, depending on the relative strengths of the acid versus ion-pair association and hence their respective lifetimes, the interactions may behave primarily as effective cross-links or they may act primarily to slow down significantly the chain relaxation. Furthermore, the effectiveness of the interactions will be affected by differences in the functionality of the cross-link sites, by differences in the equilibrium distribution of the associated versus unassociated interacting groups (at the stretching temperatures used, the proton transfer is close to complete in the blends,[1,4] but the extent of association in the PS−SSA acids is not known), and by the fact that all of the interactions in the blends are necessarily intermolecular, whereas in PS−SSA intramolecular interactions may also occur.

In summary, the above study clearly shows that hydrogen-bonding interactions involving carboxylic acid have no measurable influence on the orientation of polymers at the acid contents studied and under the experimental conditions used. This reinforces a conclusion of an earlier publication[12] that specific interactions of this type, which might be expected to slow down chain relaxation during the deformation process and thus contribute indirectly to an increase in the measured orientation compared to a polymer without such interactions, in fact have no such effect. In contrast, the interactions among sulfonic acid groups and especially ion–ion interactions exert a clear influence on the orientation achieved. There is some evidence indicating that at least the ionic interactions in the blends behave primarily as effective cross-links during the orientation process under the experimental conditions of study. This may be related to the lifetime of the associations compared to the time scale of the stretching experiment.

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