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Molecular Orientation Behavior in Uniaxially Stretched Biphasic Polystyrene-Based Ionomers

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ABSTRACT: The molecular orientation behavior of poly[styrene-*co*-(sodium styrenesulfonate)] (PS–SSA-Na) and poly[styrene-*co*-(sodium methacrylate)] (PS–MAA-Na) is compared using infrared dichroism. The orientation functions of the ionomers are determined at several ion contents and stretch temperatures. It is observed that the orientation of the polystyrene segments of PS–SSA-Na ionomers is significantly greater than that of PS–MAA-Na ionomers. By comparing the orientation functions measured at stretch temperatures relative to the cluster transition temperature of each ionomer, much of the difference in orientation can be attributed to differing ionic strengths that cause the cluster transition of PS–SSA-Na to occur at a much higher temperature than that of PS–MAA-Na. The remaining difference in orientation can be attributed to differences in the detailed morphology, in particular in the volume fraction of the cluster phase where there is little orientation, as well as to differences in ion-hopping kinetics.

Introduction

In two recent publications,[1,2] we reported that uniaxial stretching of phase-separated ionomers at temperatures above their glass transition results in measured orientation values that are much higher than those of their acid precursors or parent homopolymers. Furthermore, the orientation increases with ion content. This behavior was attributed to the ionic aggregates present in the ionomeric materials which act as effective cross-links.

The purpose of the above publications was to compare the relative importance of cross-links and specific interactions in the orientation of polymers, for which purpose ionomers provided a convenient material. The present paper, on the contrary, focuses specifically on the orientation behavior in biphasic ionomers. Although it is valid to state that the ionic aggregates act as effective cross-links, this explanation is not very precise. It is well known that the morphology of ionomers is complex and depends on many factors—for example, the ion content as well as the nature and size of the ionic group and its counterion.[3] In fact, the term aggregate itself may refer either to aggregates of ion pairs, usually called multiplets, or to aggregates of multiplets, usually called clusters. According to the most recent understanding of ionomer morphology[4] (to be referred to here as the EHM model), the latter are considered to constitute a separate phase with its own glass transition at a temperature higher than that of the matrix. This glass transition is attributed to overlapping regions of reduced mobility which surround each multiplet.

Molecular orientation in a number of biphasic systems has been studied: in particular, in semicrystalline polymers,[5–9] block copolymers,[10,11] and immiscible polymer blends.[12–16] However, almost no attention has been paid to date to molecular orientation behavior in biphasic ionomers. Only one series of studies, involving birefringence,[17] X-ray diffraction,[18] and infrared dichroism[19] measurements, has been devoted to polyethylene-based ionomers. These are actually multiphase systems, with crystalline domains as well as amorphous matrix and cluster domains. The fact that the ionomers are not fully neutralized adds a complicating factor. It was observed for these materials that, as the temperature is raised, the orientation functions for both the amorphous hydrocarbon and ionic parts of the polymer pass through a maximum in the region of the cluster transition. This was attributed to a softening process in the ionic or cluster regions, which allows for greater orientation in the amorphous regions of the ionomer. This increased orientation is overtaken, upon further heating, by the competing process of viscous flow in the amorphous regions due to a decrease in the effective degree of ionic cross-linking.[19] In contrast, orientation in the crystalline domains decreases with heating, although at a faster rate in the cluster transition range. This is again related to the softening of the ionic domains (upon which less force is transmitted to crystal lamellae) as well as to increased mobility within the crystal.[18]

For the present paper, we investigated fully neutralized polystyrene-based ionomers which are free of any crystallinity. Their biphasic character arises from the formation of a cluster phase. The orientation behavior in sulfonated polystyrene ionomers and styrene–methacrylic acid copolymers, both neutralized with Na, are compared. This behavior is related to what is known from other studies about their respective morphologies and ionic interactions.

Experimental Section

Sample Preparation. Poly[styrene-*co*-(methacrylic acid)] (PS–MAA) copolymers of various acid contents were synthesized in this laboratory by free radical copolymerization as described in the literature.[20] The number-average molecular weight of the samples was approximately 120 000, with a polydispersity of about 2, according to size exclusion chromatography measurements in THF. To obtain poly[styrene-*co*-(styrenesulfonic acid)] (PS–SSA) copolymers, polystyrene purchased from Aldrich and reported to have an average molecular weight of 280 000 was sulfonated following literature procedures.[21] Acid contents were determined by titration using a standardized solution of NaOH in methanol with phenolphthalein as the indicator.

To prepare ionomer films, acid copolymer was neutralized in the same solution used for solvent casting. Specifically, the copolymer was dissolved to a concentration of 4.4% in THF/methanol (90/10 v/v), and a calculated amount of a standardized solution of NaOH in methanol (1 N) was added with a syringe (of better than 0.01-mL precision). The neutralized solution was then cast onto a glass plate and the solvent evaporated in air over a 24-h period. The film was cut into strips suitable for uniaxial stretching (ca. 50 μm in thickness, 6 mm in width, and 20 mm in length); these strips were put into a vacuum oven at room temperature for 1 day and at 120 °C for 3 days. The samples, with one end fixed, were stretched uniaxially in a homemade apparatus operating at a constant strain rate, chosen as 0.026 s^{-1},

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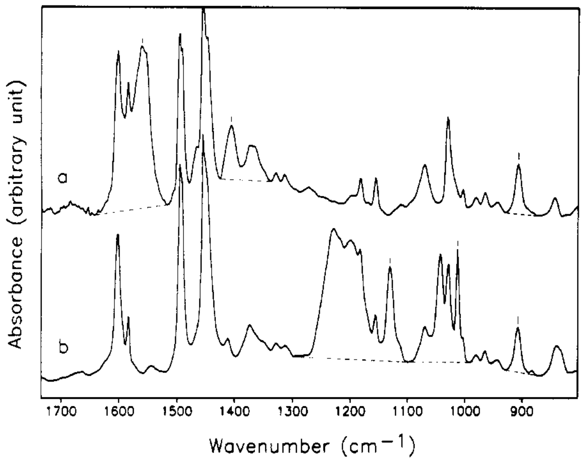

Figure 1. Infrared spectra of (a) poly[styrene-*co*-(sodium methacrylate)] and (b) poly[styrene-*co*-(sodium styrenesulfonate)] of 5.3 and 5.0 mol % ion content, respectively. The baselines used for measuring the dichroic ratios are indicated, and the bands that were analyzed are marked.

and a uniform temperature (±1 °C). Once stretched, the sample was quenched to room temperature by opening the front of the apparatus into which air was circulated by a fan.

Samples for dynamic mechanical experiments were prepared according to the classical procedure of neutralizing the copolymer in a benzene/methanol (90/10 v/v) solution, then freeze-drying, and further drying at 100 °C in a vacuum oven for 1 day. Samples were then compression-molded under a pressure of 5000 psi during which the temperature was raised to $T_g + 35$ °C (as determined by DSC) and maintained there for 15–20 min; samples were then allowed to cool under pressure over a period of 2 h. After unmolding, they were placed in a vacuum oven at 120 °C for 1 day.

Orientation Measurements. The polarized spectra were recorded by using a Mattson FTIR spectrometer at a resolution of 2 cm^{-1} from a total of 50 interferograms. To obtain the two polarization measurements, a wire-grid polarizer was used and the samples were rotated by 90°. 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 following relation:

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

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 and the stretching direction. The bands analyzed are always ensured to be in the linear region of absorbance.

The overall orientation function, P_2, of the samples was measured using the polystyrene absorption band at 906 cm^{-1}. As can be observed in Figure 1, this band is suitable in both copolymers, with no significant overlap with other bands and of an appropriate intensity. It is known to correspond to the out-of-plane ν_{17b} mode of the benzene ring with an angle α of 35°; it is also conformationally insensitive.[22] The orientation function for this band is reduced to

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

Each orientation value determined is an average of dichroic ratios measured from pairs of spectra taken of five or more areas of the stretched sample.

Several bands due to the ionic groups are also evident in the spectra of Figure 1. For PS–MAA-Na, the bands at 1557 and 1407 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of the carboxylate ion, respectively.[20] For PS–SSA-Na, several bands associated with the sulfonated benzene group[23,24] appear in the region between 1000 and 1250 cm^{-1}, notably bands at 1013 cm^{-1} (in-plane CH bending vibration of the para-disubstituted benzene ring), 1042 cm^{-1} (symmetric stretching vibration of the sulfonate ion), and 1131 cm^{-1} (in-plane skeleton stretching vibration of the substituted benzene ring with strong participation from the sulfonate ion) and a doublet at 1200 and 1229 cm^{-1} (antisymmetric stretching vibration of the sulfonate ion). Although neither the angle, α, for these bands nor their conformational sensitivity is known with certainty, those which are sufficiently free of overlap with other bands may give some indication of the segmental orientation in the vicinity of the ionic groups.

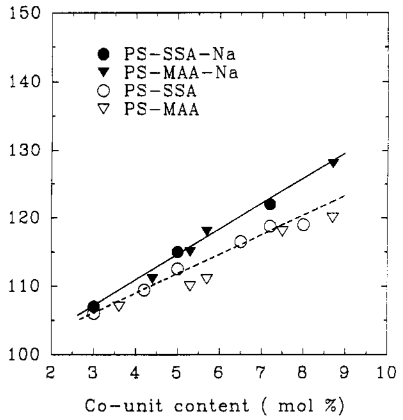

Figure 2. Glass transition temperatures as a function of co-unit content for PS–SSA-Na and PS–MAA-Na ionomers and their acid precursors, determined by differential scanning calorimetry.

Table I. Ion Contents and Glass Transition Temperatures (DSC) of the Ionomers Used

ionomer	ion content/mol %	T_g/°C
PS–MAA-Na	4.4	110
	5.3	115
	8.7	127
PS–SSA-Na	3.0	107
	5.0	115
	7.2	122

DSC Measurements. Glass transition temperatures (T_g) of the dried films were measured on a Perkin-Elmer DSC-4 differential scanning calorimeter 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.

DMTA Measurements. Dynamic mechanical measurements were conducted on a Polymer Laboratories Mk II dynamic mechanical thermal analyzer (DMTA) in the dual cantilever bending mode. All samples (2 × 10 × 35 mm, measured at a free length of 5 mm) were run under a nitrogen atmosphere at a heating rate of 0.5 °C/min, frequencies of 1 and 10 Hz, and a deflection of 64 μm.

Results and Discussion

Orientation as a Function of Ion Content Relative to the Glass Transition. When comparing molecular orientation measurements in systems of differing glass transition temperatures (T_g's), it is generally appropriate to choose stretch temperatures in relation to the T_g's. In the case of biphasic ionomers, this boils down to a reference temperature which represents the matrix or "softer" phase. Accordingly, a first series of orientation measurements were referenced to the T_g of the materials studied, as determined by DSC and reported in Table I.

In this context, it is of interest to highlight the T_g variations of the systems studied. For this purpose, the T_g's are plotted in Figure 2 as a function of ion content and compared with the unneutralized copolymers. In accordance with other studies,[25-27] it is observed that the T_g increases linearly with increasing co-unit content for both the copolymers and the ionomers. The rate of

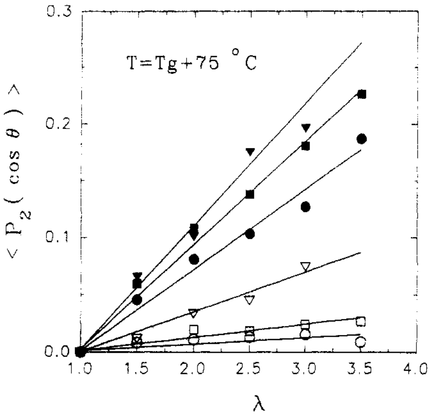

Figure 3. Orientation function versus draw ratio for PS–SSA-Na [mol % SSA-Na: (●) 3.0; (■) 5.0; (▼) 7.2] and PS–MAA-Na [mol % MAA-Na: (○) 4.4; (□) 5.3; (▽) 8.7] for stretch temperatures of T_g + 75 °C.

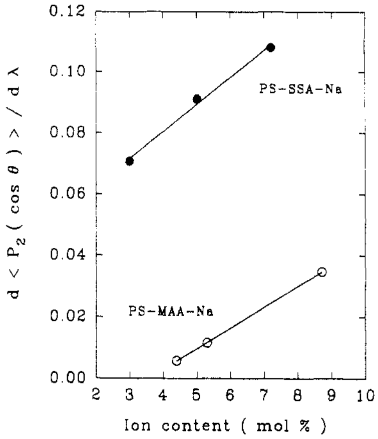

Figure 4. Slopes of the plots of Figure 3 versus ion content for PS–SSA-Na and PS–MAA-Na.

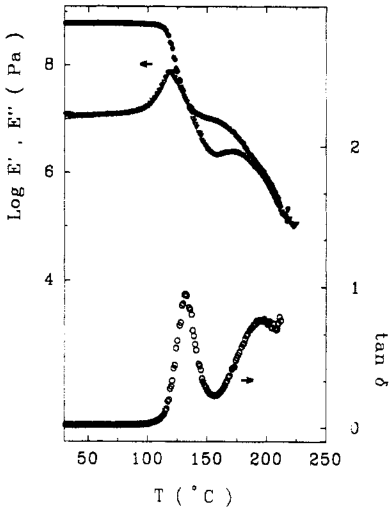

Figure 5. Young's storage and loss moduli and loss tangent at 1 Hz as a function of temperature for PS–0.053MAA-Na.

increase is somewhat greater for the ionomers than for the copolymers, 3.8 versus 2.8 °C/mol % co-unit, in good agreement with published results for sulfonated polystyrene ionomers and copolymers.[25] No significant difference is observed in Figure 2 either between PS–MAA and PS–SSA or between PS–MAA-Na and PS–SSA-Na.

In the previous publication involving molecular orientation measurements of polystyrene ionomers,[1] the stretch temperatures chosen were no more than 20 °C above the DSC-determined T_g. This limited the measurements to 6 mol % ion content for fully neutralized samples; partial neutralization was necessary to successfully stretch samples of higher ion contents. In part to avoid this limitation, T_g + 75 °C was chosen this time as the stretch temperature in a first series of measurements. The orientation functions versus draw ratio for three ion contents each of PS–MAA-Na and PS–SSA-Na, stretched at T_g + 75 °C, are shown in Figure 3.

As observed in the earlier study,[1] the orientation measured for PS–MAA-Na increases with ion content. As expected, the amount of orientation at T_g + 75 °C is considerably less than that[1] at T_g + 20 °C for the same ion content. This is due in part to the usual phenomenon of chain relaxation that occurs during stretching and which is favored at higher temperatures where thermal energy causes greater chain mobility. In the case of ionomers, another contribution to greater chain mobility at higher temperatures must be related to the particular biphasic morphology of ionomers. This point will be elaborated on subsequently.

Figure 3 further shows that the orientation of PS–SSA-Na also increases with ion content for the same stretching temperature relative to T_g. More importantly, the orientation of all of the PS–SSA-Na samples is much greater than that of all of the PS–MAA-Na samples shown. When the slopes of the curves in Figure 3 are plotted as a function of ion content, it is observed (Figure 4) that the rate of increase of orientation appears linear in both cases but that the rate is somewhat higher for PS–SSA-Na than for PS–MAA-Na.

Orientation as a Function of Temperature Relative to the Cluster Transition. To rationalize the differences between the two ionomers, the most obvious approach is to consider the transition temperature of the cluster or "hard" phase of each. In any biphasic material, both phases generally play a role in the orientation behavior of that material. In particular, if a transition temperature is associated with the second phase, as is the case with ionomers, the relation of the stretching temperature to this transition can be of as much importance as the relation to the glass transition of the first phase. To this end, dynamic mechanical thermal analysis (DMTA) was performed on the 5 mol % materials to access the cluster transition temperature (T_i). These materials were then stretched at various temperatures below and above that transition, and the orientation measured in the two materials was compared relative to T_i.

The storage and loss moduli and loss tangents obtained at 1 Hz for PS–0.053MAA-Na and for PS–0.050SSA-Na are shown in Figures 5 and 6, respectively. As will be seen subsequently, a fair amount of information is available from these curves. For now, we will restrict ourselves to the transition temperatures. That of the first transition, for which the loss tangent maximum is located at 132 and 130 °C for PS–0.053MAA-Na and PS–0.050SSA-Na, respectively, confirms the DSC results to the effect that the matrix T_g is practically identical for both types of ionomers at the same ion content. A maximum in the loss tangent corresponding to the cluster transition is visible for PS–0.053MAA-Na, but only a shoulder is apparent for PS–0.050SSA-Na. However, in both cases, a high-temperature, relatively broad maximum is visible in the loss moduli curves, located at 175 and 205 °C for the methacrylate and sulfonate ionomers, respectively. Thus, these temperatures will be used as the measure of T_i. The large difference in T_i between the two ionomers is consistent with literature results.[26,28–30]

The orientation functions against draw ratio at various temperatures are shown in Figures 7 and 8 for PS–

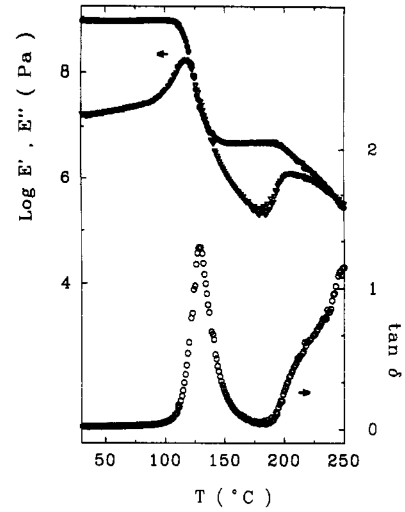

Figure 6. Young's storage and loss moduli and loss tangent at 1 Hz as a function of temperature for PS–0.050SSA-Na.

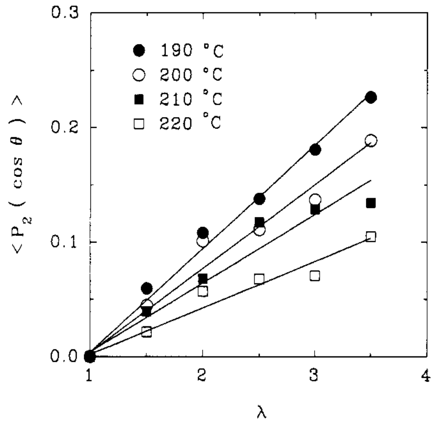

Figure 7. Orientation function versus draw ratio for PS–0.050SSA-Na at the stretch temperatures indicated.

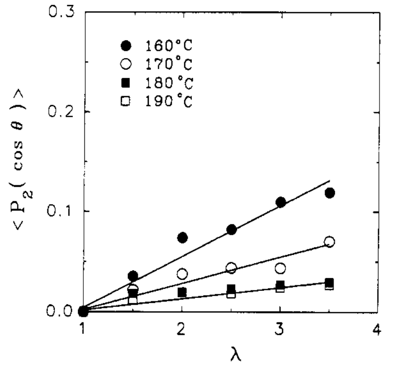

Figure 8. Orientation function versus draw ratio for PS–0.053MAA-Na at the stretch temperatures indicated.

0.053MAA-Na and PS–0.050SSA-Na, respectively. In both cases, as expected, the orientation decreases with increasing temperature. The slopes of the curves are plotted in Figure 9 as a function of the temperature difference from T_i. The points marked with an arrow represent the results obtained at $T_g + 75$ °C for the two ionomers. Since the T_i for PS–0.053MAA-Na is much lower than that of PS–0.050SSA-Na, the consequence of stretching at $T_g + 75$ °C is that the stretching temperature is above T_i for the former and below T_i for the latter. In choosing T_i as the reference temperature, the difference in orientation between the two ionomers is considerably reduced. Nevertheless, a significant difference remains.

Discussion. In taking into account the cluster transition, it is actually differences in ionomer morphology and ionic interaction strengths which are being partly taken into account. However, a more complete explanation for the differences in orientation behavior can be given qualitatively by a more detailed analysis of the ionic interactions and resulting morphology. As will be seen, a satisfactory rationale can be given using the EHM model for ionomer morphology.

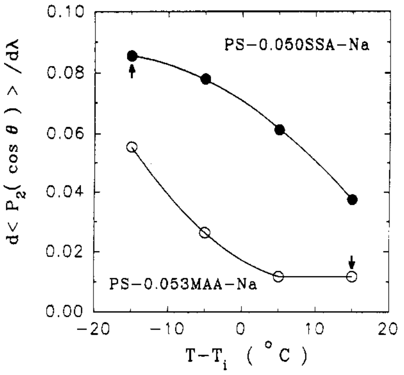

Figure 9. Slopes of the plots of Figures 5 and 6 versus the difference between the stretch temperature and the cluster transition temperature. Arrows refer to the stretch temperature of $T_g + 75$ °C.

Many studies reported in the literature[3,26–34] have already shown that electrostatic interactions between sodium sulfonate ion pairs are much stronger than those between sodium carboxylate ion pairs. This is manifested in Figures 5 and 6 by the much longer rubbery plateau for PS–SSA-Na than for PS–MAA-Na, and it is considered to be the principal reason for the T_i of the former occurring at a higher temperature than the T_i of the latter.

It has also been shown recently,[29] from an analysis of DMTA and small-angle X-ray scattering data interpreted in the light of the EHM model, that PS–MAA-Na ionomers contain numerous, small multiplets whereas PS–SSA-Na forms fewer, large multiplets. Since the corona of polystyrene segments of reduced mobility surrounding the multiplets has the same thickness regardless of the size of the multiplets, this results in a total volume fraction of reduced mobility regions that is much larger in PS–MAA-Na than in PS–SSA-Na of the same ion content.[29] This is manifested in Figures 5 and 6 by the somewhat higher modulus in the rubbery zone for PS–0.053MAA-Na than for PS–0.050SSA-Na, as well as by the lower intensity of the matrix T_g of PS–0.053MAA-Na compared to that of PS–0.050SSA-Na.

In fact, a detailed analysis of DMTA data for a series of PS–MAA-Na ionomers suggests,[34] on the basis of the relative intensities and areas of the T_g and T_i loss tangent maxima, that the reduced mobility phase and the matrix phase have approximately equal volume fractions for this ionomer at ca. 6 mol % ion content. Figure 5 indeed shows a T_g intensity at 5.3 mol % ion content that is only a little greater than that for T_i. For PS–SSA-Na ionomers, the ion content at which the two phases may be equal in volume has not yet been determined but must be significantly higher than 6 mol % (Figure 6 and ref 29).

The above picture can explain the contrasting orientation in PS–MAA-Na and PS–SSA-Na. In fact, it is likely that several factors contribute to the orientation measured. The importance of the relation of the stretching temperature (T_s) to T_i has already been demonstrated. Since the cluster phase is glassy below T_i according to the EHM model, there is presumably little or no orientation within the cluster phase when T_s is significantly below T_i.[19] The orientation actually measured, however, is an average over *all* polystyrene segments, including those in the clusters.

Consequently, for a given orientation in the matrix phase, the measured orientation at temperatures below T_i will be less for an ionomer with a larger volume fraction of cluster phase. As T_s approaches T_i and then passes through the transition, this factor must gradually decrease in importance. [This decrease is most likely gradual, since the T_i transition is a broad one, probably reflecting a progressive decrease in volume fraction of the cluster phase, due to variation in size, shape, and extent of reduced mobility in different regions.[4]]

Analysis of absorption bands associated with the ionic groups, although subject to precaution (due to the uncertainty in the transition moment angle and in sensitivity to conformation as well as in choice of baseline), seems to confirm that little orientation occurs in the ionic aggregates. In particular, the bands at 1407 and 1557 cm^{-1} for PS–MAA-Na and at 1013 and 1131 cm^{-1} for PS–SSA-Na were examined. The dichroic ratios in all cases were very low, between 1.0 and 0.85, for all of the stretching conditions investigated above. If the transition moment angle is assumed to be 90° (this is reasonable at least for the symmetric stretching vibration at 1405 cm^{-1} for the carboxylate ion if its molecular axis is oriented perpendicular to the chain axis; it is also reasonable for the band at 1013 cm^{-1} which is due to CH in-plane bending vibrations in the benzene ring as is the band at 1029 cm^{-1} for the nonsubstituted benzene ring for which α has been determined[22] as 90°), the highest P_2 determined from the bands is 0.1, which is much lower than the corresponding P_2 for the 906-cm^{-1} band (Figure 3). The small values of the dichroic ratios, coupled with the relatively high scatter in the points measured and the uncertainties mentioned above, precluded clear observation of trends as a function of ion content, temperature, or ionic group type, and thus these bands were not further analyzed.

As a brief digression, a corollary to the factor concerning volume fraction of cluster phase is that an ionomer whose cluster phase has become cocontinuous with, or dominates, the matrix phase should be difficult to stretch at temperatures significantly below T_i. Indeed, this probably explains why PS–MAA-Na samples above 6 mol % ion content, as noted above, could be stretched at T_g + 20 °C only when partially neutralized.[1]

As mentioned in the Introduction, it had been stated in ref 1 that, at low ion contents and at the stretch temperatures used (near the T_g), the ionic aggregates (clusters and multiplets) act as effective cross-links, thereby accounting for the increased orientation (compared to polystyrene) observed in the PS–MAA-Na ionomers where none was observed in their acid precursors. This factor remains undisputed and is probably influenced by the particular distribution, sizes, and shapes of the aggregates formed—both the clusters and the aggregates remaining in the matrix. Trapped entanglements may also play a role.[30,33] On the other hand, as the stretch temperature is increased and approaches T_i, the possibility of ion-hopping, and hence increased chain relaxation during stretching, may increasingly contribute to the orientation observed and hence must be taken into account as an additional factor influencing the orientation behavior observed. This factor must certainly be the primary factor influencing orientation values *above* T_i.

Since the Na sulfonate interactions are considerably stronger than the Na carboxylate interactions, the ionic aggregates in PS–SSA-Na persist as effective cross-links to higher temperatures than those in PS–MAA-Na (it has already been mentioned that this factor causes T_i to be higher in the former than in the latter). It is not known how the *rate* of ion-hopping may vary as a function of temperature for each type of ion pair, but this, too, may affect the orientation measured (relative to T_i). The essentially constant modulus value of the rubbery plateau for PS–0.050SSA-Na between T_g and T_i (Figure 6) suggests that there is no significant ion-hopping in this material until at least 190 °C. For PS–0.053MAA-Na, on the other hand, the rubbery zone between the two transitions is not constant in modulus, possibly indicating some ion-hopping.[29] If so, this ion-hopping may also contribute to the lower measured orientation in the PS–MAA-Na ionomer compared to the PS–SSA-Na ionomer at the same T_s relative to T_i (if it occurs in a time scale shorter than that of the stretching process).

In summary, the apparently large difference in orientation between PS–MAA-Na and PS–SSA-Na ionomers (relative to their T_g's) can, in no small part, be attributed indirectly to a large difference in aggregate strengths. The much stronger SSA-Na aggregates cause the cluster transition in PS–SSA-Na to occur at a higher temperature than that in PS–MAA-Na. Thus, it is more appropriate to refer the stretch temperature in biphasic ionomers to T_i than to T_g (except perhaps when close to T_g). This is all the more so, since T_i is more sensitive to ionic group type than is T_g. The remaining differences may be attributed to one or more additional factors. One is the difference in morphology, in particular the volume ratio of the two phases, between the two ionomers. Since the measure of P_2 includes the styrene units in the cluster phase, the greater volume fraction of cluster phase in PS–MAA-Na compared to PS–SSA-Na would result in a smaller P_2 for PS–MAA-Na than for PS–SSA-Na for the same orientation in the matrix phase and assuming little or no orientation in the hard phase. Possible differences in aggregate sizes and distributions in the matrix phase may also contribute. Finally, the possibility that there is more ion-hopping in PS–MAA-Na compared to PS–SSA-Na at the same temperature relative to T_i may be another factor contributing to higher measured orientation in the former. Once the cluster phase softens in either ionomer, the orientation observed can best be related to the rate of ion-hopping (and hence the strengths of the ionic interactions at the temperatures concerned).

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