the first two statistical moments involves essentially (i) a data acquisition method that limits the incidence of noise on elution profiles and (ii) a chromatographic assembly where most extra-column contributions to dead volume have been eliminated. The mass ratio of the solute distributed at equilibrium between the mobile and stationary phases is obtained, from which relative retention volumes and absolute partial molar enthalpies, both independent of flow rate, can be calculated. Measurements of retention of chloroform on polystyrene confirm the inadequacy of the peak maximum as a measure of retention and the feasibility of moment analysis.

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Registry No. PS, 9003-53-6; chloroform, 67-66-3.

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Infrared Dichroic Study of Orientation Using Ionomers

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ABSTRACT: A comparison was made of chain orientation in polystyrene (PS), poly[styrene-*co*-(methacrylic acid)s] (S-MAA) of different acid contents, and their sodium- and cesium-neutralized ionomers. Infrared dichroism measurements show that for a stretching temperature normalized to the glass transition temperature (T_g) chain orientation is much higher in ionomers than in either the copolymers or PS; moreover, the greater the ion content, the greater the observed orientation. This result can be attributed to the ionic aggregates in the ionomers, which act as effective cross-links, thereby modifying the density of the temporary network structure. On the other hand, it is found that the presence of randomly distributed hydrogen bonding interactions in the S-MAA copolymer does not lead to any increase of chain orientation compared to that of PS. These results indicate that the role of the rubberlike network is more important than that of specific intermolecular interactions to the chain orientation achieved in amorphous polymers stretched uniaxially above their T_g; an increase in network density results in a higher average chain orientation.

Introduction

The chain (or molecular) orientation attained in an amorphous polymer stretched uniaxially above its glass transition temperature is governed by two opposing processes. The first is the chain alignment, or orientation as such, in the stretching direction that is induced by the extensional forces. The second is the chain relaxation that inevitably occurs during stretching and that gives rise to a loss of orientation.

In the case of an amorphous rubber network, it has been shown both theoretically and experimentally[1-3] that molecular orientation is inversely proportional to the number

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Table I
Characteristics of the Polymers Used

polymer	sample	MAA, mol %	ioniztn deg, %	neutralizing cation	M_w, kg/mol	M_w/M_n	T_g, °C
poly[styrene-co-(methacrylic acid)]	S–0.02MMA	2			155	2.35	109
	S–0.06MAA	5.9			144	1.43	114
	S–0.10MMA	10.1			150	1.52	122
	S–0.12MMA	12.3					129
ionomers	S–0.06MAA–Na	5.9	50	Na^+			118
	S–0.06MAA–Na	5.9	100	Na^+			121
	S–0.06MAA–Cs	5.9	50	Cs^+			118
	S–0.06MAA–Cs	5.9	100	Cs^+			120
	S–0.12MAA–Na	12.3	25	Na^+			136
	S–0.12MAA–Na	12.3	50	Na^+			142
polystyrene	PS				250		98

of segments between cross-link points; that is, stretching results in greater orientation in a network of higher cross-link density. This relationship can be extended to amorphous, un-cross-linked, entangled polymers, which may be considered as temporary networks; from this point of view, the average spacing between entanglements is an important molecular parameter influencing orientation in these polymers.

Chain relaxation, the second important factor that determines the orientation achieved, is controlled by the frictional resistance to molecular motion. This is characterized by the friction coefficient and is involved in all chain relaxation processes. A higher friction coefficient implies greater hindrance to chain relaxation, which in turn results in greater final molecular orientation.

In a series of orientation studies of miscible polymer blends,[4–6] it was found that under the same experimental conditions—that is, at the same strain rate and at a normalized stretching temperature ($T - T_g$ = constant)—the orientation of the major component in the blend is greater than that of the homopolymer alone regardless of the chain flexibility of the second component. This observation has been explained by hypothesizing that the specific intermolecular interactions in these polymer systems, which are generally responsible for the observed miscibility, increase the friction coefficient and thereby hinder the relaxation of chain orientation during stretching.

However, other ways of interpreting these results must be considered. For, in at least one of the blends studied, namely, poly(methyl methacrylate)/poly(ethylene oxide) or PMMA/PEO,[6] the specific intermolecular interactions were shown to be very weak;[7,8] indeed, the Flory–Huggins interaction parameter, as determined recently by small-angle neutron scattering, was calculated to be close to zero.[9] As an alternative explanation, it is possible that a modification in entanglement spacing in the blend compared to that in the homopolymer may give rise to or contribute to an increase of chain orientation.

A similar issue was encountered in comparing chain orientation in polystyrene (PS) and in PMMA.[10] There it was concluded that the greater chain orientation observed in PMMA than in PS is due to either (a) the greater friction coefficient in the former that is induced by the local dipole–dipole interactions between the ester groups or (b) the smaller entanglement spacing indicated by the average molecular weight between entanglements as determined from viscoelastic experiments. It was not possible to decide which factor plays the dominant role in the observed orientation.

It would be of great interest to be able to evaluate the relative importance of the two factors by means of "model" polymers where the influence of the specific intermolecular interactions and that of the entanglement spacing on chain orientation is separable. For this purpose, we present in this paper the results of an infrared dichroic investigation of uniaxial orientation in a styrene-based random copolymer, poly[styrene-*co*-(methacrylic acid)] (S–MAA) and its metal cation neutralized product, termed ionomer. S–MAA is a polymer where one of the specific interactions responsible for miscibility in polymer blends, namely, hydrogen bonding, is present through the carboxylic acid groups.[11] In the ionomers, it is well-known that ionic aggregates act as transient cross-links,[12,13] thus modifying the network density. It will be shown that useful information can be obtained from a comparison of chain orientation observed in PS, the S–MAA's of different methacrylic acid contents, and ionomers of varying ion contents and counterions. Orientation is induced through uniaxial stretching and is determined by dichroism measurements using Fourier transform infrared spectroscopy (FTIR).

Experimental Section

Sample Preparation. The S–MAA's of different methacrylic acid contents were prepared and characterized as described in the literature.[12] Molecular weights were determined by GPC. To form the ionomer, the copolymers were partially or completely neutralized in benzene/methanol solutions by adding calculated amounts of NaOH and CsOH in methanol. The characteristics of the polymers used are given in Table I. The acronyms used for the samples indicate from left to right the major component of the polymer, followed by the minor component and its mole fraction, followed in the case of the ionomer by the neutralizing cation (along with extent of neutralization when not 100%). The PS sample is a commercial atactic polystyrene (Aldrich).

Thin films of about 40 μm thick were obtained by casting a chloroform solution of about 4% polymer onto glass plates. The films were dried under vacuum at room temperature for 1 day and then at 140 °C for 2 days in order to remove residual solvent and internal stress. Stretching of the films (20 mm in length and 5 mm in width) was performed by using an apparatus, constructed in the laboratory, that allows linear deformation at a constant rate and a controlled temperature (±1 °C). Following stretching, the samples were quenched to room temperature in order to freeze the chain orientation.

Orientation Measurements. Infrared dichroism measurements allow the determination of the second moment of the orientation distribution function, $\langle P_2(\cos\theta)\rangle$, which is defined as

$$\langle P_2(\cos\theta)\rangle = (3\langle\cos^2\theta\rangle - 1)/2$$

where θ is the angle between the chain axis and the stretching direction. This orientation parameter is related to the dichroic ratio, R, by the following expression:

$$\langle P_2(\cos\theta)\rangle = (R - 1)(R_0 + 2)/(R + 2)(R_0 - 1)$$

in which $R_0 = 2\cot^2\alpha$ where α is the angle between the dipole moment vector of the vibration considered and the chain axis and $R = A_\parallel/A_\perp$ ($A_\parallel$ and $A_\perp$ being the measured absorbances for the electric vector parallel and perpendicular, respectively, to the stretching direction).

The determination of $\langle P_2(\cos\theta)\rangle$ of PS through infrared dichroism measurements is documented.[14] The absorption band

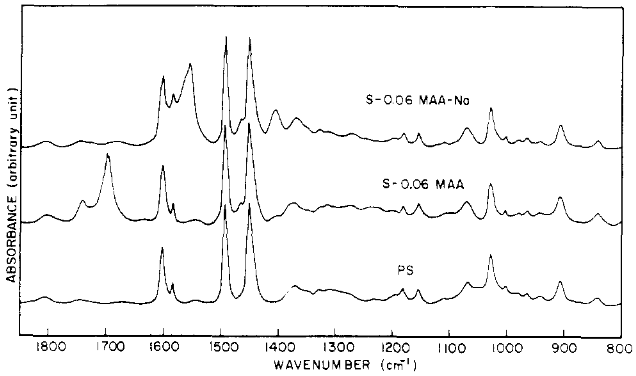

Figure 1. Infrared spectra of polystyrene (PS), of poly[styrene-*co*-(methacrylic acid)] containing 6 mol % acid groups (S-0.06MAA), and of its 100% neutralized sodium salt (S-0.06MAA-Na).

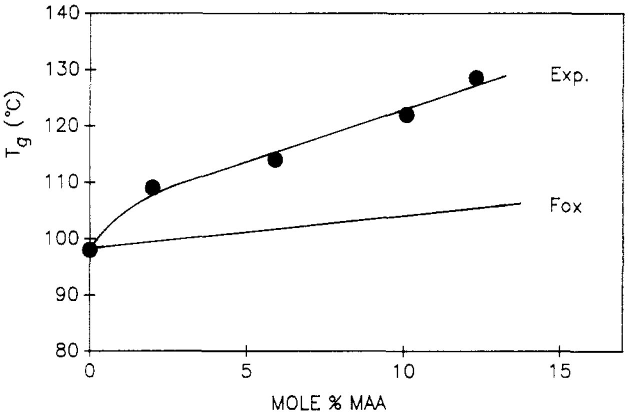

Figure 2. Glass transition temperatures of the copolymers as a function of mole percent acid content: experimental and theoretical (as predicted by the Fox equation).

at 1028 cm^{-1}, which does not overlap with any absorption bands of the methacrylic acid species, was used in this study. With this band, which is assigned to the ν_{18a} in-plane CH bending mode of the aromatic ring with the dipolar transition moment perpendicular to the chain axis, $\langle P_2(\cos\theta)\rangle$ can be calculated according to[14]

$$\langle P_2(\cos\theta)\rangle = -2(R-1)/(R+2)$$

It should be pointed out that in the case of the random copolymer S-MAA, $\langle P_2(\cos\theta)\rangle$ calculated from the 1028-cm^{-1} band gives the chain orientation averaged over all segments, since for a random AB copolymer the average orientation of segments A and segments B is necessarily the same.[10]

The polarized infrared spectra were recorded on a Mattson FTIR spectrometer at a resolution of 2 cm^{-1} from a total of 50 interferograms. Polarization of the infrared beam was effected by a wire-grid polarizer with the sample rotated 90° in order to obtain the two polarization measurements.

DSC Measurements. The glass transition temperatures (T_g) of the thin films were determined on 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.

Results

The infrared spectra in the 800–1800-cm^{-1} region of PS, S-0.06MAA and S-0.06MAA-Na are shown in Figure 1. The presence of the methacrylic acid units in PS is indicated by the characteristic bands at 1700 and 1745 cm^{-1} (C=O stretching vibration), which are assigned to the intermolecular hydrogen-bonded dimer and the free acid groups, respectively.[11] In the 100% neutralized ionomer, those two bands are absent, and two new bands appear at about 1560 and 1405 cm^{-1}; these are assigned to the asymmetrical and symmetrical COO$^-$ stretching vibrations, respectively.[12]

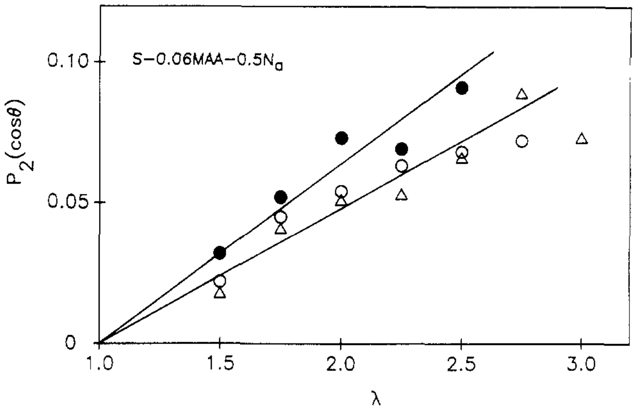

Figure 3. Orientation function of a S-0.06MAA-0.5Na ionomer versus draw ratio at two elongation temperatures (T) and draw rates (*V*): (●) *T* = 132 °C, *V* = 8 cm/min; (○) *T* = 138 °C, *V* = 8 cm/min; (△) *T* = 132 °C, *V* = 4 cm/min.

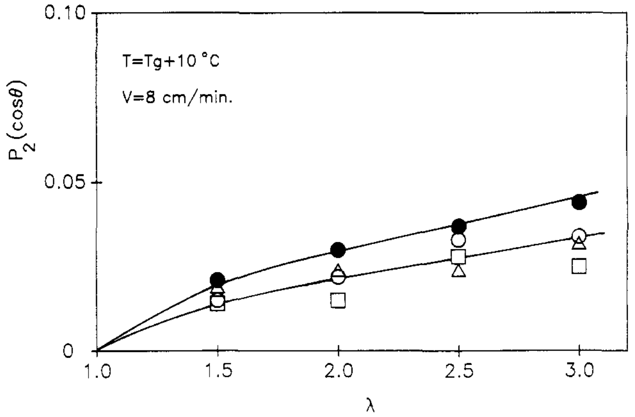

Figure 4. Orientation function versus draw ratio for PS (●) and S-MAA copolymers of different MAA contents: (○) 2; (□) 6; (△) 10 mol % MAA.

The effects of intermolecular hydrogen bonding interactions in the copolymers are also evident from the increase of the glass transition temperature as a function of acid content. As depicted in Figure 2, the observed T_g's (Table I) show a strong positive deviation from the values predicted by the Fox equation[15] with a T_g of 98 °C for PS (as determined by DSC) and 185 °C for poly(methacrylic acid).[16] For the ionomers, it is evident from Table I that their T_g's increase with increasing degree of ion content, consistent with literature results,[12] and that their increase is similar for the sodium and cesium salts.

Before comparing the orientation observed in the different types of polymers, that observed in the ionomer under the experimental conditions of study should be characterized. As an example of the results obtained, the orientation function, $\langle P_2(\cos\theta)\rangle$, of the ionomer S-0.06MAA-0.50Na is plotted in Figure 3 as a function of the draw ratio $\lambda = l/l_0$ (l_0 and l being the sample length before and after stretching, respectively). As previously observed for nonionized amorphous polymers,[17] orientation increases both with decreasing stretching temperature at a given draw rate and with increasing draw rate at a given temperature. This reflects the phenomenon of chain relaxation that occurs during stretching; it is favored at higher temperatures where there is greater chain mobility and at lower draw rates which allow more time for the relaxation of the chains.

Comparison of the orientation functions of polystyrene and three copolymers containing 2, 6, and 10 mol % of the acid groups are given in Figure 4. Stretching was performed at a reference temperature, *T*, of T_g + 10 °C and

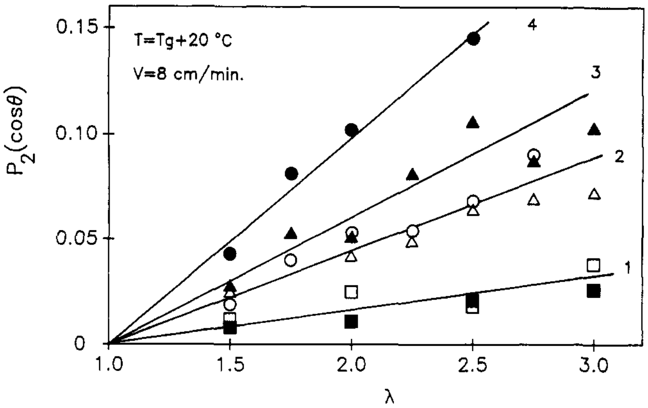

Figure 5. Orientation function versus draw ratio for PS, S–MAA copolymers, and ionomers: (1) PS (□) and S–0.06MAA (■); (2) S–0.06MAA–0.5Na (○) and S–0.06MAA–0.5Cs (△); (3) S–0.06MAA–Cs (▲); (4) S–0.06MAA–Na (●).

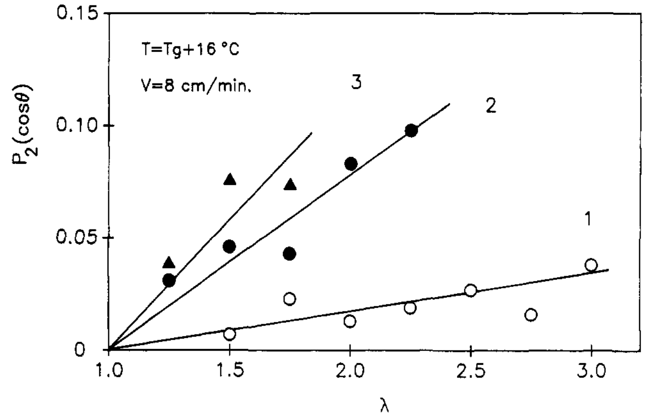

Figure 6. Orientation function versus draw ratio for (1) S–0.12MAA (○), (2) S–0.12MAA–0.25Na (●), and (3) S–0.12MAA–0.5Na (▲).

at a constant draw rate, V, of 8 cm/min. In spite of the intermolecular hydrogen bonding, which would be expected to be greater at higher carboxylic acid contents, no increase in chain orientation in the copolymers is observed. Within experimental error, the results for all the copolymers are the same and, compared to polystyrene, their orientation is slightly smaller, probably due to a somewhat smaller molar mass for the copolymers than for PS (Table I).

The orientation functions obtained for the ionomers, under stretching conditions of $T = T_g + 20$ °C and $V = 8$ cm/min, are shown in Figure 5. Once again, there is no increase in chain orientation for the copolymer S–0.06MAA as compared with PS; however, both the sodium and cesium salts at two degrees of neutralization, 50% and 100%, show significant increases in orientation. Two observations can be made. First, the orientation function increases with increasing degree of neutralization; that is, the higher the ion content in the copolymers, the greater the chain orientation achieved. Second, there is no difference in orientation between the partially neutralized sodium and cesium ionomers, whereas for the 100% neutralized salts, the orientation in the sodium ionomer is greater than that in the cesium ionomer.

The strong increase in chain orientation in the ionomer is also shown in Figure 6, where the orientation functions of another copolymer with a higher methacrylic acid content, 12.3 mol %, and its sodium salts, stretched at $T = T_g + 16$ °C and $V = 8$ cm/min, are compared. The orientation function of the 25% neutralized ionomer is much greater than that of the nonionized sample but lower than that of the 50% neutralized ionomer.

Discussion

The presence in the styrene–methacrylic acid copolymers of randomly distributed intermolecular hydrogen bonds that do not exist in PS justifies the comparison of the two materials for the purpose of clarifying the influence of the specific intermolecular interactions on chain orientation. In other words, greater frictional resistance to chain relaxation, and hence greater orientation, might be expected in the copolymer than in the homopolymer. However, the evidence presented in Figure 4 shows that for samples stretched at temperatures normalized to their T_g and at the same draw rate, the chain orientation in copolymers of different acid contents, and hence of different hydrogen bonding densities, is not greater than that in PS. This result indicates that under the experimental conditions of study, the intermolecular hydrogen bonding interactions do not lead to greater hindrance to the relaxation of chain orientation during stretching.

The particular hydrogen bond in these copolymers is not necessarily representative of all the types of specific interactions that may be found in polymers and that may contribute to frictional resistance and hence affect chain relaxation. However, its behavior in the oriented copolymers gives some insight into the latter process. In fact, the intermolecular carboxylic acid dimer is considered to be a hydrogen bond of intermediate strength.[11] The anomalous increase of T_g with acid content in the copolymer (Figure 2) is another indication that this bond is among the stronger of the specific interactions found in usual polymer blends. Furthermore, since thermal dissociation of the hydrogen bonds is not significant at the temperatures (<140 °C) at which the samples were stretched,[18] the majority of the hydrogen bonds must be considered to be involved in intermolecular interactions during stretching. Therefore, the fact that no increase of chain orientation was found in the copolymers as compared to PS would suggest that, relative to T_g, specific intermolecular interactions do not, in general, lead to a sufficient increase of the friction coefficient such that there is a detectable decrease in relaxation of chain orientation during stretching.

Neutralization of the acid groups, on the other hand, as shown in Figures 5 and 6, does bring about a dramatic increase in chain orientation. This can be associated with the cross-linking effect of the ionic aggregates in the ionomers. For it is generally accepted that two types of ion-containing aggregates are present in microphase-separated ionomers: the so-called multiplets, defined as groups of ion pairs with no hydrocarbon content, and clusters, which may be thought of as associations of multiplets and which contain polymeric chain material. Although the details of the microstructure remain largely unresolved, the effectiveness of the aggregates as cross-link regions is uncontested. In the case of the styrene-based ionomers used in the present study, for example, Eisenberg and Navratil[12] have shown from viscoelastic investigations that there is a distinct increase in the modulus of the rubberlike plateau with increasing salt group content. At the lower ion contents, this has been attributed to the multiplets acting as transient ionic cross-links. In other words, there is an increase in the effective network density, in that the plateau modulus of an amorphous polymer is inversely proportional to the molecular weight between entanglements.[19] At higher ion contents (greater than about 6 mol %), where the clusters apparently dominate the physical properties, the situation is less easy to interpret, since we are dealing with microphase-separated regions rather than simple cross-linking sites. Nevertheless, in a qualitative sense, they too may be considered to be contributing to an effective network.

It is important at this point to clarify that the ionic domains indeed act as physical cross-links in the time scale of the experiments of the present study and not as interactions that slow down chain relaxation. For, as stated in the introduction to this paper, the orientation observed under given experimental conditions reflects the contributions both from the chain extension due to the sample deformation itself and from the relaxation processes that occur during deformation. In ionomers, it has been shown that the ionic domains do retard chain diffusion,[12,13] and it could thus be contested that the increased orientation in ionomers is due to a higher friction coefficient, and hence decreased chain relaxation, caused by the time-dependent ionic cross-links. However, the time scale of the present study is sufficiently short that only local relaxation modes, or short relaxation times, are relevant. The effect of long-time chain diffusion is probably inconsequential. This is consistent with the aforementioned stress relaxation data on the system of the present study, which show a pseudorubbery plateau in an intermediate time scale. Therefore, it is valid to attribute the high orientation observed in the ionomers, compared with the copolymers and polystyrene to the ionic domains acting as effective physical cross-links.

Qualitatively, then, the increase in orientation with increasing ion content has been explained as being due to an increase in the effective number of effective cross-link regions. It is more difficult to explain the differences observed in orientation between complete and partial neutralization for the Na and Cs salts. It is perhaps simplest to interpret the greater orientation of the Na salt compared to the Cs salt at complete neutralization as a reflection of a greater effective cross-link density in the former than in the latter. This may be related in some way to the larger size of the Cs compared to the Na ion, leading to weaker aggregates, the results of which are also seen in the weaker mechanical properties of the former compared to the latter.[20] Perhaps fewer of the Cs ionized groups are implicated in aggregates or perhaps the aggregate structure (e.g., different sizes of aggregates and/or a different distribution between multiplets and clusters) somehow leads to fewer effective cross-links. On the other hand, it cannot be ruled out that some relaxation times of the Cs-ionized domains, which are shorter than those of the Na-ionized domains (as reflected in the mechanical properties), are sufficiently short to contribute to a decrease in orientation in the time scale of the experiments. That there is no apparent difference in measured orientation between the two cations for the 50% neutralized ionomers may be real or may be due to the experimental error being equal to or larger than the difference. If there is truly no difference in orientation, it is possible that the influence of the hydrogen-bonded groups on the ionic aggregates, which is to weaken them,[20] may swamp out the effect of cation size. In any case, the orientation behavior observed in the Cs-neutralized ionomers confirms the results for the Na-neutralized ionomers; furthermore, the differences in orientation between the two neutralized forms are explainable in the context of the interpretation given above for the data for the copolymers and the Na ionomers.

As a final point of discussion, the possible implications of the present study to studies of strain-oriented miscible blends such as those referred to the Introduction should be considered briefly. The present study shows the greater importance of an increase in the temporary network density compared to that of an increase in specific intermolecular interactions in increasing the chain orientation in amorphous polymers. This suggests that for the miscible polymer blends of ref 4–6, the possible role of a modification of entanglement spacing upon mixing merits further investigation. On the other hand, it is recognized that the situation in these miscible blends is certainly more complex than that in the "model" polymers employed in the present investigation. In addition to specific intermolecular interactions, such as hydrogen bonding, other types of interactions between the dissimilar chains in a blend are expected to be present. For example, a cooperative effect of interactions between PMMA and PEO chains has been tentatively proposed[6] to explain the influence of PEO molecular weight on the chain orientation of PMMA. Another aspect that may well influence chain orientation in miscible polymer blends is the free volume evolution above T_g, which may not be the same in the blends as in the respective homopolymers. A different free volume evolution upon mixing would lead to a modification in the friction coefficient in the blends and thereby result in an increase in chain orientation.

Thus, the present study, although it does not resolve the question concerning the reasons for the increased orientation observed in miscible polymer blends compared to that in the homopolymers alone, does clarify one aspect of that question. Namely, it indicates that the existence of a rubberlike network plays a greater role in enhancing strain-induced orientation than does the existence of specific interactions at least of the type found in the system of this study.

Conclusion

It can be concluded from the above that the ionic domains in styrene-based ionomers act as effective cross-links, and that, as such, they lead to higher chain orientation in materials subject to uniaxial elongation than is achieved in the absence of cross-links. Furthermore, the higher the ion content, the higher the effective cross-link density, and the higher the observed orientation. In contrast, the intermolecular hydrogen bonding interactions in the (styrene–methacrylic acid) copolymers, which are expected to contribute to a significant increase in the friction coefficient and thus hinder chain relaxation, cause *no observable increase of chain orientation in the system* studied. These results demonstrate the relative importance of a network structure compared to that of specific intermolecular interactions for chain orientation in amorphous polymers such as polystyrene. This should be taken into consideration in interpreting the increase of chain orientation observed in the polymer blends mentioned in the introduction.

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Registry No. PS, 9003-53-6; (S)(MAA) (copolymer), 9010-92-8; (S)(MAA)·Na (copolymer), 31227-13-1; (S)(MAA)·Cs (copolymer), 70850-09-8.

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Self-Diffusion and Tracer-Diffusion Coefficient and Viscosity of Concentrated Solutions of Linear Polystyrenes in Dibutyl Phthalate[†]

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ABSTRACT: The slow chain dynamics of linear macromolecules in the concentrated regime has been studied from measurements of the steady viscosity η and the self-diffusion coefficient D_s of seven polystyrene (PS) samples with weight-average molecular weight (M_w) from 43 900 to 2 890 000 in 40 wt % PS–dibutyl phthalate (DBP) solutions and also from measurements of the tracer-diffusion coefficient D_{tr} of 11 PS samples with probe molecular weight (M_N) from 2800 to 2 890 000 in 40 wt % DBP solutions of PSs with matrix molecular weight (M_P) varying from 43 900 to 8 420 000. The viscosity of the solutions was found to follow the well-established relation $\eta \propto M_w^{3.5\pm0.1}$ above $M_w = 102\,000$. The M dependence of D_s was approximately expressed by the power law $D_s \propto M_w^{-2.6\pm0.2}$ over the whole molecular weight range investigated. The product of D_s and η became approximately proportional to M in the highly entangled region, indicating that both viscosity and self-diffusion behavior can be related to the slowest chain motion with the same characteristic relaxation time τ_m. D_{tr} data in the unentangled 40 wt % DBP solution of PS with $M_P = 43\,900$ showed a gradual transition from the Rouse type of free-draining chain to the Einstein-Stokes type of impermeable sphere diffusion in the highest M_N end with increasing M_N. In entanglement networks with molecular weight between entanglements $M_e = 42\,300$ at $c = 40$ wt %, D_{tr} decreased with increase in M_P and assymptotically approached D_{tr}^∞ independent of M_P for $M_P > 5M_N$. D_{tr}^∞ was found to be proportional to M_N^{-1} in the range of $2800 \le M_N \le 10\,000$ and then to $M_N^{-2.5\pm0.1}$ for $43\,900 \le M_N \le 1\,260\,000$. The exponent 2.5 is appreciably larger than 2, either predicted by the reptation theory or observed for PS melts.

Introduction

Slow chain dynamics of a linear flexible polymer in solutions as well as in melts is greatly affected by the intermolecular interaction with surrounding polymer chains. Variables such as self- (or tracer-) diffusion coefficient D_s (or D_{tr}) and steady viscosity η are quantities suitable for a study on the topological interaction in extensively overlapped polymeric systems, that is, for a study of the entanglement effect.

Quite recently, we showed that D_s in melts as well as in concentrated solutions could be expressed by the product of two seperate contributions, f_2 and g_2, as is given in eq 1.[1,2] Here ζ is the segment friction constant, and C and

$$D_s = f_2(\zeta)g_2(C,M) \tag{1}$$

M are the concentration and molecular weight of the polymer, respectively. An analogous expression for viscosity is well established.[3]

$$\eta = f_1(\zeta)g_1(C,M) \tag{2}$$

$$\begin{aligned} g_1(C,M) &= CM && M < M_c \\ &= (CM)^{3.5\pm0.2} && M > M_c \end{aligned} \tag{3}$$

$f_i(\zeta)$ (i = 1, 2) represents a contribution from micro-Brownian motion of a segment, that is, local one in nature, being independent of the polymer molecular weight at high M. $f_1(\zeta)$ to η is a function simply proportional to ζ, while f_2 to D_s is inversely proportional to ζ as

$$f_2(\zeta) = k_BT/\zeta \tag{4}$$

Here k_B is the Boltzmann consant and T is the absolute temperature. The function g_i (i = 1, 2) represents the effect of the topological interaction with surrounding chains, and the dependence of g_1 on C and M is given by eq 3, which is verified for the viscosity of many polymer–solvent systems. On the other hand, the functional form of g_2 is presently in question. For example, M dependence of g_2 looks different between polymer melts and the semidilute regime.[4-14] That is, if the dependence of g_2 on M is expressed by the power law as $g_2 \propto M^{-\alpha}$, the exponent α ranges from 2 to 3 in the semidilute regime, while α is 2 in highly entangled polymer melts. It may be noted that the reptation theory predicts $\alpha = 2$ for entanglement networks independently of polymer concentration studied.[15]

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