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Infrared Dichroism Study of Orientation and Relaxation in Miscible Polymer Blends Containing a Small Amount of Poly(2,6-dimethyl-1,4-phenylene oxide)

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ABSTRACT: Infrared dichroism has been used to study the strain-induced orientation and orientation relaxation of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) diluted to 1 and 2 wt % in several polymer matrices with which it is miscible. The much higher orientation of PPO than polystyrene (PS) in the blends is attributed to a high entanglement density of the isolated PPO chains with surrounding PS chains compared to that of PS chains with themselves. Relaxation coupling between the PPO chains and PS chains was observed in the PS/PPO blends when comparing two monodisperse PS matrices of very different molecular weights. In blends where the matrix is a random copolymer of poly(styrene-*co*-methacrylic acid) containing 6 mol % of the acid counits (S-0.06MAA) or its sodium-neutralized ionomer (S-0.06MAA-Na), the orientation and orientation relaxation of PPO are not affected by the differing orientations of the two matrices. An analysis in terms of a variation of entanglements with composition is proposed to explain the orientation behavior previously observed in PS/PPO blends. In particular, it is shown that a decrease in the M_e (average molecular weight between entanglements) of one component does not necessarily result in an increase in the M_e of the other component.

Introduction

A number of spectroscopic techniques are useful for studying molecular deformation and relaxation in strained polymers by allowing measurements of chain segment orientation. These techniques include fluorescence polarization,[1,2] deuterium nuclear magnetic resonance,[3,4] and infrared dichroism (IRD).[5-7] Fluorescence polarization is *the* technique, to date, used to make orientation measurements of diluted polymer chains (ca. 0.5 wt %) in a polymer matrix.[1] However, this method requires attaching a chromophore to the diluted chains.

Under certain circumstances, IRD can also be utilized for orientation measurements of diluted polymers. This is made possible by the fact that many polymers exhibit one or more very intense absorption bands. Normally, for IRD measurements in bulk polymers[5,6] or in blends at the compositions usually studied,[7-9] these bands are undesirable and unusable. However, in a miscible blend, sufficient dilution of a polymer possessing such a band can reduce the absorbance values of the band to a level suitable for orientation measurements, i.e., to an absorbance of less than 0.7 for a sample thickness of about 50 μm.[10] In this paper, we exploit this situation. In particular, we present results of a study of a polymer blend system in which there are no interactions among the chains of the diluted polymer and where the matrix polymer behaves essentially as it would in the bulk. Under these conditions, it is obvious that the strain-induced orientation and orientation relaxation of the dilute chains will reflect only their interactions with the matrix chains. This allows the influence of the matrix on the diluted chains to be readily observed.

For this study, 1-2 wt % poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is used as the diluted polymer. The matrix polymers are monodisperse polystyrene (PS) of two very different molecular weights, poly(styrene-*co*-methacrylic acid) containing 6 mol % acid units (S-0.06MAA) and its sodium-neutralized ionomer, poly(styrene-*co*-sodium methacrylate) (S-0.06MAA-Na). Strain-induced orientation and relaxation of both PPO and the different matrices were measured by Fourier transform infrared dichroism. It will be shown, on the one hand, that some chain relaxation phenomena previously observed in homopolymers are also evident in the miscible blends, and, on the other hand, that useful information about the orientation and relaxation in miscible blends can be obtained. Supported by the results obtained in this study, we also propose an explanation in terms of entanglement interactions for the orientation behavior as a function of blend composition observed in the PS/PPO blends.[7,11,12]

Experimental Section

Sample Preparation. The characteristics of the polymers used are given in Table I. The two monodisperse PS samples were purchased from Pressure Chemical Co., and the PPO was purchased from Aldrich. The random copolymer, S-0.06MAA, was synthesized in our laboratory following the procedure described in the literature.[13] The corresponding sodium ionomer, S-0.06MAA-Na, was prepared from complete neutralization of the copolymer in a benzene/methanol solution by adding a calculated amount of NaOH in methanol.

Thin films for infrared measurements were obtained by casting a chloroform solution of 5% blended polymer onto glass plates. The films, ca. 40 μm thick, were dried under vacuum at room temperature for 1 day and then at 140 °C for 3 days, thereby ensuring the complete removal of residual solvent as well as internal stress.

The glass transition temperatures (T_g) of the dried films were determined by using a Perkin-Elmer DSC-4 apparatus at a heating rate of 20 °C/min and a sample weight of ca. 15 mg. The T_g values of the different blends with PPO are given in Table II; they are unaltered from the T_g's of the matrices without the PPO.

Molecular orientation was induced through uniaxial extension above the T_g. Stretching of the films (20 mm in length and 5 mm in width) was performed by using an apparatus, constructed in our laboratory, that allows linear deformation at a constant rate and a controlled temperature (±1 °C). Unless otherwise noted, a draw rate of 90 mm/min was used.

For measurements of orientation as a function of the draw ratio λ (where λ is defined as $\lambda = l/l_0$, l_0 and l being the sample length before and after stretching, respectively), the samples were quenched to room temperature immediately following stretching, in order to effectively freeze the molecular orientation. For

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Table I
Characteristics of the Polymers Used

polymer	sample	M_n	M_w/M_n
polystyrene	PS100	110 000	<1.04
	PS2000	2 000 000	<1.3
poly(styrene-*co*-methacrylic acid)	S-0.06MAA	101 000	1.9
poly(styrene-*co*-sodium methacrylate)	S-0.06MAA-Na	101 000	1.9
poly(2,6-dimethyl-1,4-phenylene oxide)	PPO	21 000	2.3

Table II
Glass Transition Temperature of the Blends

blend	PPO, wt %	T_g, °C
PS100/PPO	1	105
	2	105
PS2000/PPO	1	105
S-0.06MAA/PPO	2	114
S-0.06MAA-Na/PPO	2	120

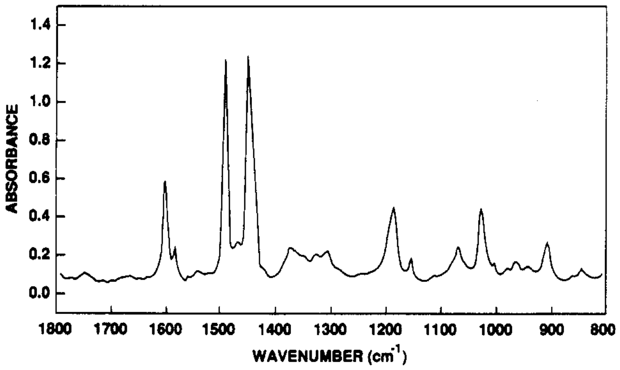

Figure 1. Infrared spectrum of the PS100/PPO(2%) blend film of ca. 40-μm thickness.

measurements of orientation relaxation with time, the samples were held, after stretching, at a fixed strain and a constant temperature for the desired aging (relaxation) time, followed by quenching to room temperature. The local macroscopic deformation upon stretching was measured from small successive equidistant ink lines perpendicular to the stretching direction that were traced before stretching; this ensured that the infrared measurements were taken at the desired draw ratio for each sample. In the relaxation experiments, each reported point is the average value of measurements on three different samples.

Orientation Measurements. The second moment of the orientation distribution function (Hermans' orientation function) $\langle P_2(\cos\theta)\rangle$, hereafter referred to as P_2, is obtained from infrared dichroism through the relation

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

in which θ is the angle between the chain axis and the stretching direction, $R_0 = 2\cot^2\alpha$, where α is the angle between the dipole moment vector of the vibration considered and the chain axis, and R is the infrared dichroic ratio defined as $R = A_{\parallel}/A_{\perp}$ where $A_{\parallel}$ and $A_{\perp}$ are the measured absorbances of the electric vector parallel and perpendicular, respectively, to the stretching direction. P_2 represents the average orientation of all the chain segments involved.

The orientation function of small amounts of PPO in miscible blends can be measured from the very intense absorption band at about 1186 cm^{-1}. This band is attributed to the asymmetrical ether stretching vibration for which α = 20.6°.[11] The infrared spectrum, in the 800–1800-cm^{-1} region, of a PS100/PPO(2%) blend film of 40-μm thickness is given in Figure 1; it shows the 1186-cm^{-1} band with an absorbance value of ca. 0.34, which is suitable for the orientation measurements. The orientation function P_2 of PPO, using this band, has been determined as:[11]

$$P_2 = 1.23(R - 1)/(R + 2) \qquad (2)$$

This band overlaps a very weak PS band at 1196 cm^{-1}, which can normally be neglected.[11,14] In the case of the PS/PPO blends with 1% PPO, the overlap affects the absolute P_2 values of PPO somewhat, but since this is a systematic error, it does not influence the comparisons of orientation and relaxation in these blends.

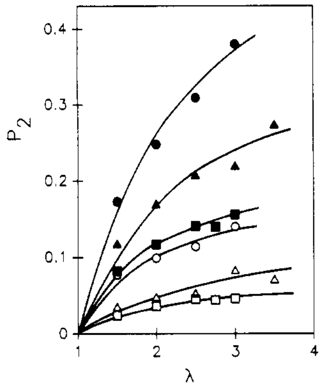

Figure 2. Orientation function vs draw ratio for the PS100/PPO(2%) blend at three stretching temperatures (T): (1) PPO (●) and PS (○) at T = 113 °C; (2) PPO (▲) and PS (△) at T = 120 °C; (3) PPO (■) and PS (□) at T = 125 °C.

The orientation functions of the matrices (PS, S-0.06MAA, and S-0.06MAA-Na) were measured by using the absorption band at 906 cm^{-1}, which does not overlap any PPO absorption band.[11] This band is known to correspond to the out-of-plane ν_{17b} mode of the benzene ring with an angle α of 35°.[15] P_2 can be calculated from

$$P_2 = 1.97(R - 1)/(R + 2) \qquad (3)$$

For the blends with 1% PPO, the effect of PPO absorption around 1030 cm^{-1} is very small; thus, the orientation relaxations measured for the matrix were confirmed by using the PS band at 1028 cm^{-1}. This band corresponds to the ν_{18a} in-plane CH bending mode of the benzene ring which has an angle α of 90°,[15] giving

$$P_2 = -2(R - 1)/(R + 2) \qquad (4)$$

The polarized infrared spectra were recorded by using a Mattson Fourier transform IR spectrometer at a resolution of 4 cm^{-1} from a total of 300 interferograms. Polarization of the infrared beam was effected by a wire-grid polarizer with the sample rotated 90° between the two polarization measurements.

Results and Discussion

Orientation and Relaxation in the PS100/PPO(2%) Blend. The orientation functions of PS and PPO in the PS100/PPO(2%) blend are shown in Figure 2 as a function of draw ratio at three stretching temperatures. The orientation of both PS and PPO clearly decreases with increasing temperature, reflecting the chain relaxation which occurs during stretching and which is favored at higher temperatures because of greater chain mobility. It is noteworthy that the effect of temperature on the orientation measured is similar for the two types of polymer chains.

Figure 3 shows the rates of orientation *relaxation* of the PS and PPO chains in the blend at 115 °C and at a strain of λ = 3.5 during a period of 5 min. The orientation function, $P_2(t)$, measured after an aging time, t, is normalized to the orientation function, $P_2(0)$, obtained when the sample is quenched immediately after stretching. As was observed for a PS/PPO blend containing 10% PPO,[11] the relaxation of the two types of chains is obviously similar; that is, there is a rapid decay of orientation in the first 2 min, followed by a slow decay tending toward a constant relaxation rate. At the relatively longer aging times, the relaxation of PS is slightly more rapid than that of PPO.

These results indicate that the characteristic relaxation time of the PPO chains is of the same order of magnitude

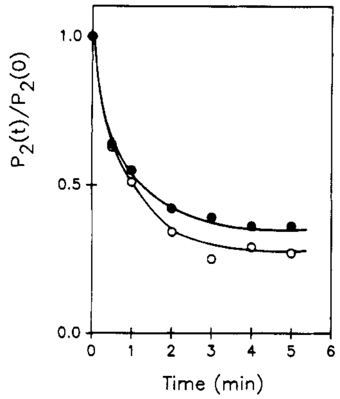

Figure 3. Normalized orientation function vs time for the PS100/PPO(2%) blend at a stretching temperature of 110 °C and a strain of $\lambda = 3.5$: PPO (●) and PS (○).

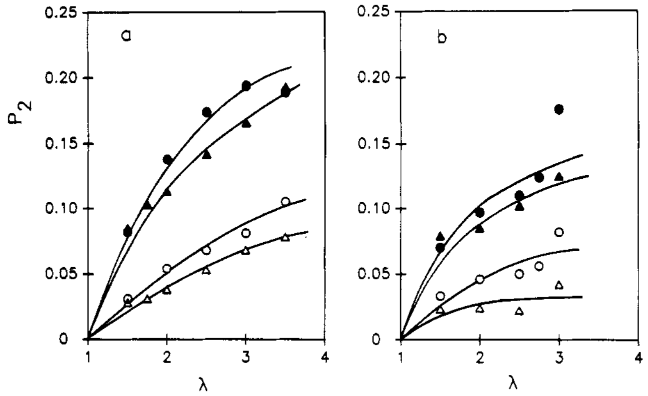

Figure 4. Orientation function vs draw ratio for the PS100/PPO(1%) and PS2000/PPO(1%) blends at a stretching temperature of 120 °C and two draw rates (V): (a) V = 90 mm/min, (b) V = 10 mm/min. PPO in PS2000 (●) and in PS100 (▲), matrices PS2000 (○) and PS100 (△).

as that for PS chains and is in the experimental time range. This is a necessary condition for observing the influence of the matrix on the relaxation of the diluted chains (see the following section). It should be noted that the molecular weight of the PPO used (M_n = 21 000) is much smaller than that of PS100 (M_n = 110 000).

In contrast to the relaxation behavior, which is similar for the two blend components, Figure 2 shows that the *orientation* of the 2% PPO is much greater than that of the PS matrix. This is in agreement with literature results for higher PPO concentrations.[7,11] Since PPO and PS relax in a similar way, the high orientation of PPO cannot be attributed to a slower relaxation of its chains during stretching compared to those of PS; rather, this must reflect a higher intrinsic orientation of PPO chains compared to PS chains, i.e., a higher orientation induced by the extensional forces. It will be shown shortly that this can be explained by entanglement interactions of the dilute PPO chains with the matrix chains.

First, it is appropriate to briefly review, in terms of the Doi–Edwards tube or slip-link model,[16,17] the mechanism of chain relaxation in an entangled, amorphous polymer melt under constant strain after rapid deformation. According to this model, a chain relaxes through three distinct processes with well-separated characteristic times. The first is the relaxation of the chain segments between entanglements, with the Rouse time as the characteristic time and which is independent of the molecular weight of the chain. The second is the retraction of the deformed chain inside its deformed tube, for which the characteristic time scales as the square of the molecular weight of the chain. The third is the reptation of the chain through its deformed tube, with a characteristic time that scales as the cube of the molecular weight of the chain. At the end of the first relaxation process, according to this model, an entangled, amorphous polymer is temporarily similar to a rubber in equilibrium, for which the orientation function is given by[18]

$$P_2 = (\lambda^2 - \lambda^{-1})/5n_k \qquad (5)$$

where n_k is the number of statistical Kuhn segments between entanglements. This means that extension results in greater intrinsic chain orientation in an entangled polymer having a higher density of entanglement interactions, i.e., having a smaller molecular weight, M_e, between entanglements.

Now, in the bulk, PPO exhibits a very small M_e, 3620, compared with PS, whose M_e is about 18 700.[19,20] With the values of the characteristic ratio, C_∞, reported in the literature (3.2 and 10.8 for PPO and PS, respectively),[19,20] n_k can be estimated to be about 9 for PPO and 33 for PS.[21] From eq 5, this indicates that the orientation induced by the extensional forces, at a given draw ratio, should be expected to be much greater in bulk PPO than in bulk PS.

However, this still does not explain how the *diluted* PPO chains, which cannot form entanglement interactions among themselves, also show greater orientation than the PS chains of the matrix. For this, the role of the characteristic ratio, C_∞, must be emphasized. In fact, it has been shown to be related to M_e and is a measure of the chain *tortuosity*.[19,20] That PPO has a small C_∞, as noted above, means that it has a high tortuosity, much higher than that of PS. With this in mind, it is easy to picture that when diluted in the PS matrix with which it is miscible, each isolated PPO chain interacts with surrounding PS chains. Moreover, in keeping with the higher chain tortuosity of PPO than PS, the PPO chains must form more numerous entanglement couplings with the PS chains than do the PS chains among themselves (at 2% PPO concentration, the average entanglement spacing of the matrix PS chains should be essentially the same as that in the bulk). We propose that this is the origin of the high PPO orientation induced by stretching in the PS/PPO(2%) blend. The state of entanglements in the PS/PPO blends will be further discussed later in connection with interpreting the change in orientation with composition in these blends[7,11,12] in terms of a variation in the entanglement density.

Influence of the Matrix Molecular Weight. The orientation and relaxation behavior of 1% PPO diluted in two monodisperse PS matrices of very different molecular weights (PS100 and PS2000) were investigated in order to determine the influence of matrix relaxation on the relaxation of the diluted PPO chains. There should be no difference between the two blends in the entanglement coupling of PS–PS and PS–PPO chains or in the specific interactions between PS and PPO. In other words, stretching should induce the same intrinsic orientation for the PPO and the PS chains in the two blends. Consequently, any difference in orientation of either PPO or PS in the two blends arises from a difference in relaxation.

The orientation measured as a function of draw ratio for PS and PPO in the two blends, stretched at 120 °C and two draw rates, is shown in Figure 4. Several observations can be made. First, there is the obvious effect of draw rate. Smaller orientations for both PPO and PS were obtained in the two blends at the lower draw rate (Figure 4b). This is easily explained by the greater amount of

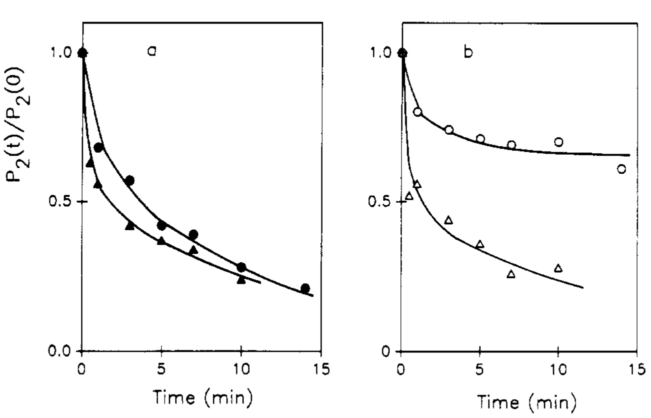

Figure 5. Normalized orientation function vs time for the PS100/PPO(1%) and PS2000/PPO(1%) blends at a stretching temperature of 110 °C and a fixed strain of $\lambda = 3$: (a) PPO in PS2000 (●) and in PS100 (▲), (b) matrices PS2000 (○) and PS100 (△).

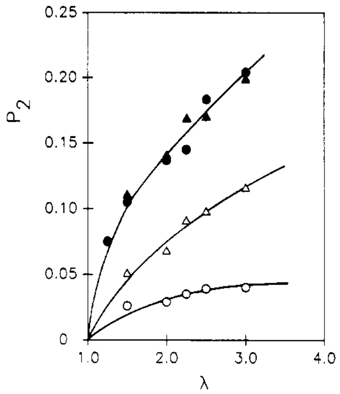

Figure 6. Orientation function vs draw ratio for the S-0.06MAA/PPO(2%) and S-0.06MAA-Na/PPO(2%) blends at a stretching temperature $T = T_g + 20$ °C: (1) PPO in S-0.06MAA-Na (▲) and in S-0.06MAA (●), (2) matrix S-0.06MAA-Na (△), (3) matrix S-0.06MAA (○).

chain relaxation that takes place during stretching because of the longer time available. Second, the orientation of PS2000 is greater than that of PS100, indicating more relaxation of the lower molecular weight chains during stretching. This is consistent with the molecular theory[16,17] described above, which predicts a characteristic relaxation time that is proportional to the square, at intermediate times, or to the cube, at long times, of the molecular weight of the chain. It should be noted that the weaker effect of draw rate on the orientation of PS2000, in Figure 4, is due to its very high molecular weight; this accentuates the difference in orientation between PS2000 and PS100 at the lower draw rate. Finally, and most significantly, Figure 4 shows the influence of the molecular weight of the PS matrix on the orientation of PPO. The orientation of PPO is clearly greater in PS2000 than in PS100. Moreover, this effect seems more pronounced at the higher draw rate, despite the smaller difference in orientation between the two PS matrices. This result suggests that there is relaxation coupling between the diluted PPO chains and the surrounding PS chains. If not, the PPO chains in the two PS matrices should relax in the same way during stretching, resulting in the same measured orientation, since their molecular weight is the same and the specific interactions with the matrix chains are unchanged (recalling, here, that unchanged specific interactions imply a constant friction coefficient, ξ, which characterizes the frictional resistance to chain relaxation and which is involved in all relaxation processes).

The relaxation coupling was further confirmed through relaxation experiments, depicted in Figure 5, where the rates of orientation relaxation of both PPO and the matrix are plotted as a function of aging time. It is observed that the PPO chains relax more slowly in PS2000 than in PS100 (Figure 5a), accompanied by a much slower relaxation of the PS2000 matrix compared to the PS100 matrix (Figure 5b). This relaxation coupling can be explained in the same way as for diluted, labeled PS in a PS matrix, which was studied using fluorescence polarization.[1] In that study, it was observed that the orientation of the labeled PS chains is dependent on the molecular weight of the PS matrix. This was attributed to the entanglement interactions between the labeled chains and the matrix chains, which cause the relaxation motion of the matrix chains to influence that of the labeled chains. In the case of the PS/PPO blend, it has already been pointed out above that the high orientation of the diluted PPO chains is a consequence of a high degree of entanglement coupling with the surrounding PS chains. Therefore, a more rapid relaxation of those matrix chains that are entangled with PPO chains results in a greater loss of topological constraints acting on the PPO chains. This, in turn, leads to greater relaxation, and thus to a higher rate of orientational decay, of the PPO chains in the PS100 matrix compared to the PS2000 matrix.

In all of the experiments, complete recovery of sample deformation was obtained when annealing above T_g. This indicates that the longest relaxation times (reptation) were not reached in the present experimental conditions. Rather, the relaxation taking place is restricted to the first (Rouse motion) and second (chain retraction) of the three relaxation processes described above. The observed relaxation coupling occurs during the second process and has been described as "tube relaxation" by Viovy et al.[22]

Influence of the Matrix Orientation. PPO was diluted in the random copolymer S-0.06MAA and its corresponding ionomer S-0.06MAA-Na with the aim of isolating the effect of matrix orientation on the behavior of the isolated PPO chains. The choice of these two matrices is based on a previous study,[23] which showed that the strain-induced orientation in the ionomer is much greater than that in the nonionic copolymer owing to the ionic aggregates in the former that act as effective cross-links and thereby increase the temporary network density. A preliminary investigation of the miscibility of PPO with these two matrices indicates miscibility up to at least 15 wt % PPO (work is currently in progress in this laboratory to determine the phase behavior of PPO/PS ionomer blends for a complete range of compositions as well as several ion contents[24]). Thus, it can be safely concluded that 2% PPO is completely miscible in the two matrices.

The two blends with 2% PPO exhibit different T_g's (Table II), and thus orientation and relaxation were compared according to established procedures,[7,22] i.e., using the same draw rate and the same normalized stretching temperature ($T - T_g$ = constant). Figure 6 gives the results for the orientation of the two blends as a function of draw ratio at a temperature of $T = T_g + 20$ °C. As was observed in the previous study,[23] the orientation of the ionomer matrix is much greater than that of the copolymer matrix, due to their very different temporary network densities. The feature of interest in Figure 6 is that the orientation of the diluted PPO chains is unaffected by the different intrinsic orientations of the matrices. In other words, the orientation of PPO is independent of the matrix orientation as such, clearly indicating that there is no orientation coupling between the PPO chains and the surrounding matrix chains.

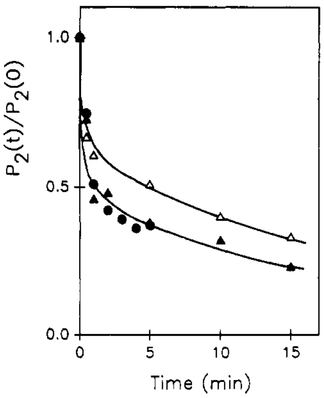

Figure 7. Normalized orientation function vs time for the S-0.06MAA/PPO(2%) and S-0.06MAA-Na/PPO(2%) blends at a stretching temperature $T = T_g + 20$ °C and a fixed strain of $\lambda = 3$: (1) PPO in S-0.06MAA-Na (▲) and in S-0.06MAA (●), (2) matrix S-0.06MAA-Na (△).

Figure 7 shows the rate of orientation relaxation of PPO in the two matrices at a temperature of $T = T_g + 20$ °C and a strain of $\lambda = 3$. Clearly, the PPO chain orientation decays at the same rate, within experimental error, in the two blends. In other words, the much more highly oriented ionomer matrix apparently causes no retardation in orientation relaxation of the PPO chains, compared with the less oriented copolymer matrix. The rate of orientation relaxation of the ionomer matrix is also given in Figure 7 (that of the copolymer could not be determined because of its very small orientation and correspondingly high relative error of measurement) and shows that the matrix has a significantly lower relaxation rate than PPO.

That no relaxation coupling is observed in Figure 7, in contrast to the situation for the two PS matrices (Figure 5), can be explained qualitatively as follows. First, it is to be noted that the two matrices, i.e., the copolymer and the ionomer, have the same molecular weight, which means that there is no molecular weight effect causing a difference in the relaxation times between the two types of matrix chains. Now, ionic interactions in the ionomer may slow down matrix chain relaxation relative to that of the copolymer; however, the effects of that may well be compensated for by the much smaller intrinsic orientation of the copolymer (compared to the ionomer), resulting in a relatively small amount of chain relaxation after stretching in this matrix, too. Consequently, the difference between the two matrices in the relaxation of the matrix chains, and the effect on the diluted PPO chains, is probably too insignificant to allow any relaxation coupling to be observed from Figure 7.

To account for the identical orientation of diluted PPO in the differently oriented matrices, it is postulated that PPO chains form approximately the same number of entanglement couplings with the surrounding chains in the two matrices. It is significant that the entanglement density of the PPO chains appears to be independent of the entanglement density, or temporary network, of the matrix chains.

Orientation Behavior in PS/PPO Blends. Chain orientation in PS/PPO blends has been extensively studied by Lefebvre et al.[7,11] for PPO concentrations up to 35 wt %. These studies were recently completed in the composition range where PPO is the major component.[12] The principal results are schematically shown in Figure 8. For the blends where PS is the major component, the PS orientation increases with increasing PPO content up to $C_1 \approx 25\%$ PPO, whereas the PPO orientation remains constant. Similarly, in the blends where PPO is the major component, PPO orientation increases with increasing PS content up to $C_2 \approx 35\%$ PS, while the PS orientation remains unchanged. This increase in chain orientation of the major component of the blend, compared to the bulk polymer, has been attributed to the specific interactions between the two blend components.[12] These interactions are considered to increase the friction coefficient in the blend and thus hinder the chain relaxation that occurs during stretching, thereby resulting in a higher measured orientation. The same explanation was given for other miscible polymer blends.[8,9]

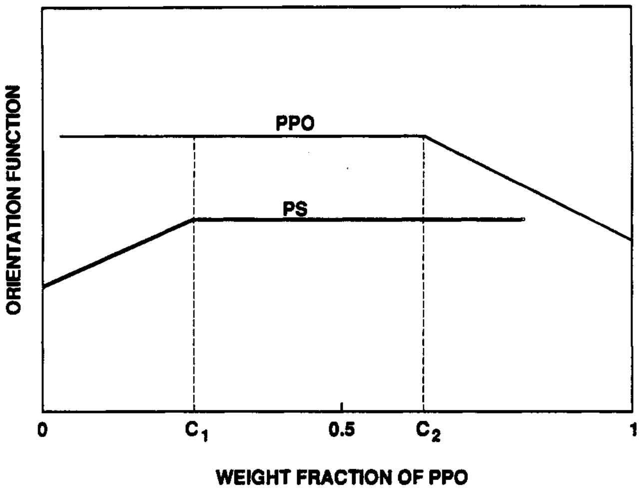

Figure 8. Schematic representation of the orientation behavior in PS/PPO blends, as reported in ref 12.

We believe, however, that the effects of the entanglement interactions on blend orientation behavior cannot be ignored. As in homopolymers, the effective temporary network density of each blend component determines its intrinsic orientation induced by stretching. This effective density is influenced by the entanglement interactions in the blend, both those between the same chains and those between dissimilar chains. The analyses in the preceding sections illustrate the key role played by entanglement coupling in the comparative orientations measured for the two blend components. To recapitulate, PPO chains diluted in a PS matrix are thought to form many more entanglements with the surrounding PS chains than do the PS chains with themselves due to the small C_∞ of PPO compared to that of PS: this is considered to account for the higher orientation of PPO than PS. Furthermore, the comparison of PPO orientation in the copolymer and in the ionomer matrices strongly suggests that it is not unusual that one blend component may maintain the same orientation while that of the other one changes, presumably because the effective entanglement density of the first is independent of that of the matrix. If entanglement coupling indeed plays such an important role, then it should also be considered for explaining the variation in orientation observed as a function of composition in the blends. This is all the more true in light of a previous study,[23] which suggests that the rubberlike network formed by entanglements and/or cross-links has a much stronger effect on the chain orientation measured than do specific interactions.

As far as the specific interactions are concerned, in a recent study,[25] no change was observed in the effective friction coefficient with composition in PS/PPO blends, and specific interactions in these blends apparently do not alter the linear viscoelastic properties of PS. Furthermore, an explanation based only on specific interactions clearly cannot account for the effect of PPO molecular

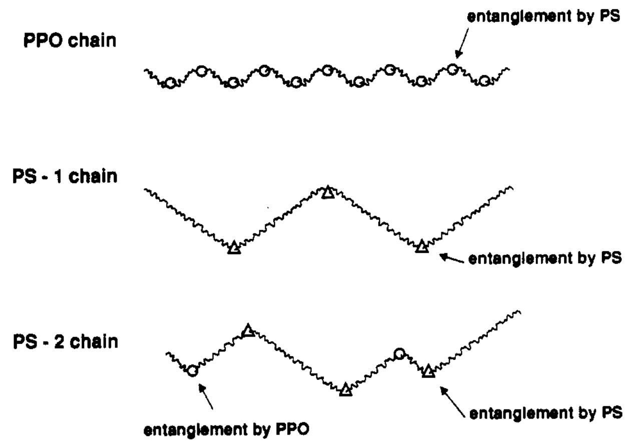

Figure 9. Schematic representation of the entanglement couplings in the PS/PPO blends of low PPO content.

weight on PS orientation,[7,26] since a change in molecular weight should not change the magnitude of interactions present. Finally, one of the results of the present study is that the orientation relaxation times of PS and PPO are similar, and observable, under the experimental conditions employed; therefore, the constant (and higher) orientation of PPO, where the (lower) PS orientation increases with composition up to C_1 (Figure 8), cannot be attributed to long relaxation times for PPO that are out of the experimental time scale (it should be noted that both our experimental conditions and the molecular weight of the PPO are similar to those used in the literature.[7,11,12])

Considering all of the above, we believe that what follows constitutes a plausible explanation, in terms of a variation of entanglement density with composition, for the orientation behavior observed in PS/PPO blends. We will focus first on the composition range where a very small amount of PPO (e.g., 1–2%, as in the present study) is diluted in the PS matrix. A schematic representation of the types of entanglement interactions that may exist in the blend at that composition range is shown in Figure 9. The PPO chains, which are isolated, form entanglements only with PS chains. For the PS chains, two situations can be envisaged. Given the small amount of PPO present, most of the PS chains will form entanglements only among themselves; this is pictured as PS-1 in Figure 9. The characteristic molecular weight between entanglements, M_e, for the PS-1 chains is similar to that in the bulk and much greater than that for the PPO chains. The second situation for PS chains is that pictured as PS-2 in Figure 9; these chains are those that interact with the PPO chains present. They form entanglements with both PS and PPO and therefore have a smaller M_e than the PS-1 chains.

Now, what is the effect of those entanglements as the PPO concentration in the blend increases? For PPO, it is obvious that up to a critical concentration, f_c, below which no self-entanglement of the PPO chains occurs, the situation remains unchanged from that represented in Figure 9 (f_c must not be confused with C_1, although it is possible that there may be a relationship). Moreover, M_e does not vary significantly since the conformation of each PPO chain should remain unaffected. For the PS chains, on the other hand, the amount of PS-2 chains increases at the expense of PS-1 chains with increasing PPO concentration. This implies a gradual decrease in the average M_e for the total of the PS chains. Consequently, in the applicable composition range, the strain-induced orientation as a function of PPO content should remain essentially constant for the PPO chains and increase for the PS chains, which is just what is observed on the left side of Figure 8.

When we temporarily focus on the PPO chains, the situation can be further clarified by two estimations: (1) the critical PPO concentration, f_c, at which PPO self-entanglements begin to take place and (2) the average molecular weight, M_e, between the PPO–PPO entanglements at f_c. In analogy to a similar determination for polymer solutions, f_c can be estimated from

$$f_c = M_c^0/M_n \tag{6}$$

where M_c^0 is the critical molecular weight in the bulk polymer and M_n is the molecular weight of the PPO used (21 000). In fact, M_n in eq 6 can be identified with M_c, the critical molecular weight at f_c. Thus, with M_c^0 of PPO ca. 7200[19,20] and with M_e being about half of M_c,[28] it can be estimated that, at a critical concentration of ca. 34% PPO in the blend, entanglements can form between different PPO chains with a M_e of about 10 500.

Now, to understand the essentially constant orientation in the intermediate concentration range (roughly between C_1 and C_2), it is to be emphasized that the M_e calculated from eq 6 is the average molecular weight between entanglements formed among PPO chains only. Over a significant range beyond f_c, this M_e is undoubtedly much larger than that between entanglements formed by PPO chains with PS chains. In other words, until well above f_c, perhaps up to C_2, it is still the entanglements of PPO with PS that dominate and that determine the effective M_e of PPO in the blend, and hence dominate its orientation behavior. Throughout this intermediate composition range, the average M_e for the PPO chains is thereby effectively controlled by the entanglement couplings of PS–PPO and remains essentially unchanged; therefore, the orientation measured is unchanged.

Once self-entanglements of PPO become dominant (at high PPO concentration, i.e., above C_2, right side of Figure 8), the situation is similar to that where PS is the major component, as discussed above; that is, the average M_e for the PPO chains is effectively determined by the entanglements of both PPO–PS and PPO–PPO, resulting in significant changes with composition in the average M_e of the total of the PPO chains. In this composition range, the PPO orientation decreases with decreasing PS content. This seems to indicate that the entanglement density of PPO in the blend is higher than that in the bulk. This may indeed be where the presence of specific interactions plays its role. For instance, a spectroscopic study[14] has indicated that blending PS with PPO leads to a conformational change for PPO and improves its packing efficiency by favoring interpenetration of the PPO chains.

The constant orientation of PS in the blend above C_1 can be explained similarly to that of PPO below C_2. That is, the entanglement density of the PS chains is effectively determined by the PS–PPO interactions both in the intermediate composition range and when the PS chains are diluted in the PPO matrix. As is the case for PPO below C_2, there is no significant change in PS network density with composition above C_1.

To summarize, the most important point of the above analysis is that, in miscible polymer blends, a decrease in the average M_e of one component does not necessarily result in an increase of the average M_e of the other component. Previously, an interpretation of the orientation behavior of PS/PPO blends in terms of a variation of entanglement density had been ruled out with the thought that an increase in entanglement density for PS should be accompanied by a decrease in entanglement density for PPO.[7,8] The discussion above shows that this is not necessarily the case. The following general statement may be made: when not masked by other factors, the orientation of a miscible component is composition-dependent when its entanglement spacing is influenced by entanglements both with chains of the same component and with chains of the other component; the orientation is essentially composition-independent when its entanglement spacing is effectively controlled by entanglements with the dissimilar chains.

It is recognized that such an analysis of the entanglement behavior in miscible polymer blends is probably an oversimplification of what is no doubt a complex situation. In particular, it does not explain why the orientation of PPO is higher than that of PS in the intermediate range. It is possible that this is related to a certain amount of self-entanglements that may always be present. Furthermore, it is noted that, because of the limited precision of the IRD technique, relatively small variations in orientation with composition cannot be detected unambiguously. For example, this may have the effect that a very slow variation, such as a shallow maximum in the intermediate concentration range, remains undetected. Despite such complications, the analysis presented here introduces what we believe are some new considerations and seems to encapsulate what is observed from orientation measurements using the IRD technique.

The analysis can be applied to the orientation behavior reported for other miscible blends. For PS/poly(vinyl methyl ether) (PS/PVME) blends,[8] the orientation of PS also increases with increasing PVME concentration (measured up to 25% PVME). No orientation was observed for PVME, attributed to a relaxation time shorter than the experimental time scale. Like PPO, the average M_e of PVME in the bulk is smaller (by ca. 5000) than that of PS,[29] and thus it is consistent that the PS orientation in the PS/PVME blends should increase as PVME is added, just as it does in the PS/PPO blends. Similarly, in poly(methyl methacrylate)/poly(ethylene oxide) (PMMA/PEO) blends,[9] PMMA orientation increases as PEO is added (until what is interpreted as a development of phase separation), consistent with the M_e for PMMA in the bulk (ca. 9000) being significantly larger than that of PEO (ca. 2200).[19,20] Finally, no change in orientation was observed for either component in blends of PS with poly(*o*-chlorostyrene),[30] in which M_e is similar for both components in the bulk.

Conclusions

Relaxation coupling was observed between diluted PPO chains and the matrix chains of PS by comparing the orientation relaxation of PPO in two PS matrices of very different molecular weights. The relaxation of the PPO chains in the PS100 matrix is more rapid than that in the PS2000 matrix. This is attributed to a greater loss of topological constraints acting on the PPO chains in the PS100 matrix, which relaxes more rapidly than the PS2000 matrix. This result demonstrates that such cooperative effects can influence the chain orientation achieved in miscible polymer blends.

From the measurements of orientation and relaxation in the two blends, S-0.06MAA/PPO and S-0.06MAA-Na/PPO, where the two matrices have very different orientation values, it can be concluded that the strain-induced orientation of PPO is not coupled with the orientation of the matrix chains as such but is determined essentially by its entanglement interactions with the matrix. That is, if the entanglement density of PPO in two different matrices is the same, its strain-induced orientation may also be the same, regardless of the entanglement situation, and hence the orientation, of the matrix chains. Furthermore, the much more oriented matrix (S-0.06MAA-Na) does not slow down the orientation relaxation of the PPO chains compared to the less oriented matrix (S-0.06MAA).

In comparison of the orientation of PS and of PPO, which is much higher for the latter even though the orientation relaxation rates of the two types of chains are similar, the results are again rationalized in terms of entanglement couplings with the surrounding matrix chains. The much higher tortuosity of PPO in the bulk (as characterized by a small characteristic ratio C_∞, or a small average molecular weight between entanglements) compared to PS in the bulk is considered to hold true also in the blend. This means that the (isolated) PPO chains have a greater average entanglement density with the PS chains than do the PS chains with themselves, thereby accounting for the greater chain orientation of PPO compared to PS.

On the basis of these results, a qualitative analysis in terms of a variation of the entanglement density with blend composition is presented to explain the overall orientation behavior observed in the PS/PPO blends.[7,11,12] This analysis shows that, in miscible polymer blends, a decrease in the average M_e for one component of the blend does not necessarily result in an increase in the average M_e for the other component. Furthermore, it is possible to understand why orientation may be insensitive to blend composition over a large composition range. That is, the average entanglement spacing is effectively determined by the entanglements formed between the dissimilar chains, such that there is no significant variation resulting in a change of the chain orientation measurable through infrared dichroism.

Finally, an important aspect of this study is the demonstration that infrared dichroism can be useful for investigating the molecular orientation and relaxation of a very small amount of polymer chains in a polymer matrix with which they are miscible, simply by analyzing a very intense absorption band.

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(21) The characteristic ratio C_∞ is defined as

$$C_\infty = \langle R_0{}^2\rangle / n\langle l^2\rangle \qquad \text{(R1)}$$

where $\langle R_0{}^2\rangle$ is the mean-square end-to-end distance of the chain, n is the number of real and/or virtual skeletal bonds in a chain, and $\langle l^2\rangle$ is the mean-square length of the real or virtual skeletal bond. In terms of the Kuhn chain, the chain contour length between entanglements, L_e, is given by

$$L_e = n_k l_k = n\langle l\rangle \qquad \text{(R2)}$$

where l_k is the length of a Kuhn segment, which is shown, in ref 20, to be

$$l_k = \langle l\rangle C_\infty \qquad \text{(R3)}$$

and n is calculated from

$$n = n_v(M_e/M_r) \qquad \text{(R4)}$$

where n_v is the number of real and/or virtual skeletal bonds in a repeat unit and M_r is the molecular weight of a repeat unit. Combining eqs R2–R4, we obtain:

$$n_k = n_v(M_e/M_r)/C_\infty \qquad \text{(R5)}$$

Taking $n_v = 2$, $M_e = 18\,700$, $M_r = 104$, and $C_\infty = 10.8$ for PS and $n_v = 1$, $M_e = 3600$, $M_r = 120$ and $C_\infty = 3.2$ for PPO, eq R5 yields $n_k \approx 33$ for PS and $n_k \approx 9$ for PPO.

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Registry No. PS, 9003-53-6; (MAA)(S) copolymer, 9010-92-8; (MAA-Na)(S) copolymer, 31227-13-1; PPO (SRU), 24938-67-8; PPO (homopolymer), 25134-01-4.