Study of the Orientation of Poly(styrene)/Poly(vinyl methyl ether) Blends Relative to the Glass Transition Temperature

Essaid Abtal and Robert E. Prud'homme*

Centre de recherche en sciences et ingénierie des macromolécules, Chemistry Department, Laval University, Québec (Qué), Canada G1K 7P4

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ABSTRACT: Molecular orientation and mechanical properties of poly(styrene)/poly(vinyl methyl ether) (PS/PVME) miscible blends are studied, in a broad range of compositions, taking as a reference the temperature of the glass transition. The PS orientation is directly measured using Fourier transform infrared spectroscopy (FTIR), whereas the orientation of PVME is characterized by coupling FTIR and birefringence techniques. It is observed that the overall and individual orientations, as well as Young's modulus of the blends, remain constant up to 30% PVME. Above this concentration, these properties are found to be strongly composition dependent and to increase at the 50% PVME composition by a factor of 6 (PS orientation), 4 (overall birefringence), and 10 (modulus) as compared to the corresponding values below 30%. This behavior is interpreted in terms of a change in the strength of specific interactions between the dissimilar chains with the blend composition and is analyzed with a simple version of the Doi-Edwards theory.

Introduction

The orientation behavior of polymer blends is complex as compared to that of homopolymers. For instance, several studies of Cooper et al.[1,2] on poly(caprolactone)/poly(vinyl chloride)-based blends and subsequent investigations by Jasse, Monnerie, and collaborators[3-6] on various miscible blends have shown that dissimilar chains orient differently, despite the miscible nature of the systems. For example, in poly(styrene)/poly(phenylene oxide) (PS/PPO) blends, the orientation function of PPO, the component with the higher T_g, is larger than that of PS and remains almost constant over a broad range of composition, while, in poly(styrene)/poly(vinyl methyl ether) (PS/PVME) mixtures, the component with the lower T_g (PVME) remains practically unoriented. On the other hand, Inoue et al.[7,8] have investigated the orientation relaxation of some miscible blends and suggested that the two polymers relax similarily and cooperatively even if their initial orientation may be different. Several interpretations of the orientation behavior of polymer blends have been proposed in terms of free volume, entanglement density, specific interactions, chain stiffness, etc. However, it is clear from these studies, that a unified view, taking into account the individual contributions of these parameters to the global and individual orientations, is still to be developed.

Investigations of the orientation of polymer blends over the full range of compositions are made difficult by the fact that any change of the concentration of the two components usually leads to a simultaneous change of parameters such as T_g, free volume, strength and number of specific interactions, chain entanglements, etc., which control closely the local dynamics of chain relaxation. Such analysis requires then a reference state, as widely discussed by Stadler et al.,[9] but this choice is difficult since these parameters are not completely independent. For example, the free volume fraction depends closely upon the distance to T_g[10] and strong specific interactions may reduce dramatically this fraction.[11] Moreover, these interactions may play the role of effective cross-links, thereby modifying the density of chain entanglements.[12]

The general objective of the present work is to gain further understanding of the orientation behavior and the molecular mechanisms of deformation in polymer blends through the analysis of the PS/PVME system. This blend, which is miscible at the T_g level (at least), represents an excellent model since it is completely amorphous and, in addition, it exhibits phase separation at high temperature, which allows the possibility of comparing the orientation behavior in the miscible and heterogeneous states. Also of interest are the correlations between the mechanical properties of the blends and their state of overall and individual orientations.

In a previous paper,[13] we have pointed out that if the same state of specific interactions is taken as a reference, the distance to T_g and, consequently, the fractional free volume are necessarily modified. Under those conditions, the orientation behavior of the blend is completely governed by these two parameters which control the local dynamics of chain relaxation. In order to compensate for the free volume variations with the distance to T_g, the orientation behavior of PS/PVME blends is investigated in this article, in a broad range of compositions, by taking as a reference the glass transition temperature.

Theory

The uniaxial orientation of a structural unit of a polymer chain can be described by an orientation function f(θ),[14] θ being the angle between the structural unit axis and the stretching direction. The orientation function can be developed as a series of Legendre polynomials in cos θ:

$$\mathrm{f}(\theta) = \sum_{n=0}^{\infty}(n + {}^1/_2)\langle P_n(\cos\theta)\rangle P_n(\cos\theta) \qquad (1)$$

where

$$\langle P_n(\cos\theta)\rangle = \int \mathrm{f}(\theta) P_n(\cos\theta)\sin\theta\, d\theta \qquad (2)$$

To evaluate precisely f(θ), the different moments $\langle P_n(\cos\theta)\rangle$ of the orientation function must be determined. However, for a simple deformation process, the second moment $\langle P_2(\cos\theta)\rangle$ is adequate to describe properly the state of orientation.[15]

Different techniques have been used to measure $\langle P_2(\cos\theta)\rangle$. Among them, birefringence and infrared dichroism are usually used as complementary methods to analyze the molecular orientation of multicomponent blends. In the case of an amorphous homopolymer, the birefringence

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Δ is directly related to $\langle P_2(\cos\theta)\rangle$ by[14,16]

$$\Delta = \Delta o \langle P_2(\cos\theta)\rangle \quad (3)$$

where Δo is the intrinsic birefringence of the material. For a binary mixture, the measured birefringence can be written

$$\Delta = \phi_1 \Delta o_1 \langle P_2(\cos\theta_1)\rangle + \phi_2 \Delta o_2 \langle P_2(\cos\theta_2)\rangle + \Delta f \quad (4)$$

where $\langle P_2(\cos\theta_i)\rangle$, Δo_i, and ϕ_i are the second moment of the orientation function, the intrinsic birefringence, and the volume fraction of the ith component, respectively. Δf is the form birefringence related to the difference of refractive index at the interphase between the two polymers. However, in the case of miscible blends, this term can be neglected.[17,18]

The second moment of the orientation function can also be calculated from FTIR measurements. The dichroic ratio D of any infrared absorption band is related to $\langle P_2(\cos\theta)\rangle$ by[14]

$$\langle P_2(\cos\theta)\rangle = (D-1)(D_0+2)/(D+2)(D_0-1) \quad (5)$$

where $D = A_{\parallel}/A_{\perp}$ is the ratio of the absorbance for the electric vector of the incident radiation polarized parallel and perpendicular to the stretching direction, respectively. $D_0 = 2\cot^2\alpha$, α being the angle between the transition moment vector of the vibration under consideration and the local chain axis. For polymer blends, the orientation of each component can be determined provided that specific bands, corresponding to vibration modes with well-defined transition moment vectors, are observed for the two polymers. This is not the case for the PS/PVME system. However, combining FTIR and birefringence measurements allow one to characterize the individual orientation of the two chains, as will be explained later.

Experimental Section

Materials. Atactic poly(styrene) (PS) obtained from Pressure Chemicals and poly(vinyl methyl ether) (PVME) obtained from Polysciences were used in this study. PS had a M_w of 300 000 and a polydispersity index of 1.06. PVME had a M_w of 44 000 and a polydispersity of 2.3. These values were determined by size exclusion chromatography in tetrahydrofuran, at 298 K, using PS standards.

Films of different compositions and thicknesses were cast from benzene solutions onto a glass plate. They were first air-dried for 1 day, and then the last traces of solvent were removed under vacuum at $T_g + 30$ for 36 h.

Birefringence and Mechanical Property Measurements. Birefringence and mechanical property measurements were conducted using an Instron tensile tester, Model 1130, with a controlled temperature sample compartment constructed in our laboratory. For the birefringence measurements, a He/Ne laser source was placed at the back of the sample compartment and a Soleil-Babinet compensator at the front. Therefore, it was possible to measure the birefringence and the stress–strain curves simultaneously, at a fixed temperature. The samples, having an initial thickness of 200 μm, a width of 3.5 mm, and a length of 45 mm (32 mm between the jaws), were stretched at a strain rate of 5 cm/min. The birefringence measurements required a pause time which, however, did not exceed 100 s.

Infrared Dichroism Measurements. FTIR measurements were carried out using a Mattson Sirius 100 spectrophotometer with a rotating wire-grid polarizer (Specac U.K.). An infrared cell, constructed in our laboratory and adapted to the sample compartment of the spectrophotometer, allowed the sample to be heated to a given temperature and to be stretched at a constant strain rate of 5.0 cm/min. The sample was stretched to the desired draw ratio and the stretching process was then interrupted for a period of time of about 100 s while the two polarized spectra were recorded. For each polarization, the phase correction was executed separately, and 30 scans were co-added with a maximum optical retardation of 0.52 cm and triangularly apodized to yield a resolution of 4 cm^{-1}. Infrared dichroism was calculated from the peak height intensity measured in absorbance. All spectral manipulations were executed with software provided by Mattson. The samples had an initial width of 5.0 mm and initial length of 20 mm. The thickness was adjusted between 40 and 100 μm, depending on blend composition, in order to maintain the infrared absorbance below unity and to avoid deviations from the Beer–Lambert law.

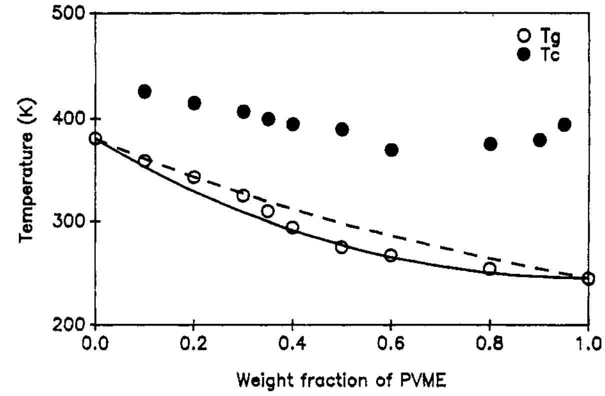

Figure 1. Phase diagram of the PS/PVME blend. (---) Fox equation: $T_g = T_{g_1}T_{g_2}/(w_1T_{g_2} + w_2T_{g_1})$. (—) Kwei equation: $T_g = T_{g_1}T_{g_2}/(w_1T_{g_2} + w_2T_{g_1}) + qw_1w_2$; $q = -85$ K.

For both birefringence and IR experiments, values of the orientation function reported in this paper are averages of at least three measurements on different samples with a reproducibility estimated to about 10%.

T_g and T_c Measurements. To construct the PS/PVME phase diagram, T_g was determined with a Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a thermal analysis data station and calibrated with indium, at a heating rate of 20 K/min; T_c was determined using a Zeiss optical microscope, a Zeiss photometer, and a Mettler hot stage. The samples were heated from room temperature to the phase-separated state, at a heating rate of 2 K/min. T_c was then taken as the temperature where the intensity begins to increase (cloud point).

As can be seen in Figure 1, a single T_g intermediate to those of the pure components is observed at each composition, indicating the miscibility of the system in the entire range of composition. On the other hand, the variation of T_c with composition is monotonous and almost linear in a broad range of composition, with a minimum at a PVME weight fraction of about 0.75 and at a temperature of 370 K, in good agreement with the data of Hashimoto et al.[14] Furthermore, the miscibility window, i.e., the interval between T_g and T_c, increases from 60 K, at low PVME content, to about 120 K, at high PVME concentration.

Results and Analysis

Overall Orientation and Modulus. The overall orientation of PS/PVME blends was characterized using birefringence measurements. The change of birefringence as a function of the draw ratio λ, for different compositions at $T_g + 10$, is depicted in Figure 2. It can be seen that the birefringence values of the blends are negative and above those of pure PS. The composition dependence of the overall orientation is illustrated in Figure 3, where the initial slope of the birefringence data ($d\Delta/d\lambda$) is plotted as a function of the PVME weight fraction (w_2). It can be seen that the overall orientation remains constant and similar to that of pure PS, up to $w_2 \sim 0.3$; above this value, a dramatic increase is observed in the overall orientation, which goes through a maximum at $w_2 \sim 0.5$ and decreases afterward.

Young's modulus (E), for different compositions, was calculated from the initial slope of the stress–strain curves. These values, when plotted as a function of the PVME blend concentration, exhibit the same variation as the

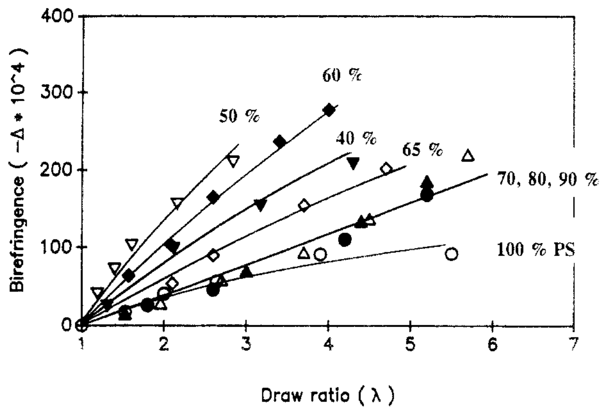

Figure 2. Birefringence Δ as a function of the draw ratio λ for different blend compositions, at a stretching rate of 5 cm/min.

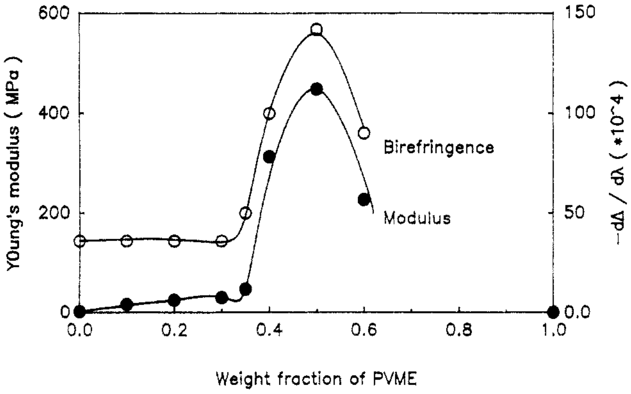

Figure 3. Initial slope of the Δ–λ curves (Figure 2) and Young's modulus E as a function of the weight fraction of PVME.

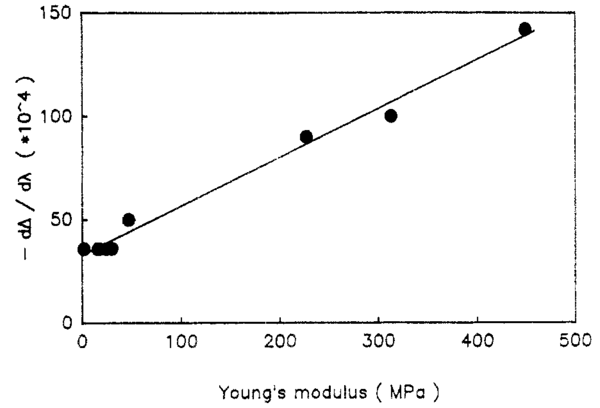

Figure 4. Initial slope of the Δ–λ curves (Figure 2) as a function of Young's modulus E, for different blend compositions.

overall orientation (Figure 3). This similar behavior leads to a linear relationship between $-d\Delta/d\lambda$ and E, as illustrated in Figure 4.

PS and PVME Orientation. The significant increase observed in birefringence and Young's modulus may be, a priori, related to an overall increase of orientation of the two components, or to a preferential increase in orientation of one of them. In order to verify this point, FTIR analysis of the PS orientation in the blend was made using the well-isolated 1028 cm^{-1} band, corresponding to the ν_{18a} vibration of the in-plane stretching mode of the C—H groups of the aromatic cycle. This vibration is conformationally insensitive, with a transition moment vector perpendicular to the chain axis.[3]

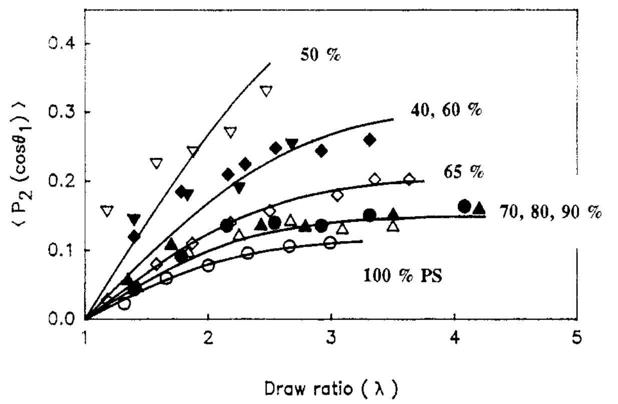

Figure 5. Orientation function $\langle P_2(\cos\theta)\rangle$ of PS as a function of the draw ratio λ, for different blend compositions, at a stretching rate of 5 cm/min. Continuous lines are drawn using eq 7.

Figure 5 shows the variation of $\langle P_2(\cos\theta_1)\rangle$ of PS with the draw ratio, for different compositions. As it was observed for the birefringence and Young's modulus, the PS orientation remains constant, but slightly superior to that of the pure PS up to $w_2 \sim 3$. It increases significantly above this value, reaches a maximum at $w_2 \sim 0.5$, and decreases subsequently (Figure 5).

As pointed out in a previous work,[13] the FTIR determination of PVME orientation is not possible since the infrared spectrum of the blend exhibits an overlap of a large number of PS and PVME bands. Only two bands at 1100 and 2820 cm^{-1}, attributed to the side chain groups —OCH$_3$ whose real conformation in the blend is not known,[4] are well-isolated for PVME. However, qualitative information about the state of orientation of this polymer may be obtained from the calculation of the dichroic ratio D. In the range of composition and temperature investigated, only small variations of D, which ranges between 1 and 0.98, have been observed, indicating a weak orientation of PVME in the blend.

The PVME orientation can be characterized more accurately by coupling FTIR and birefringence techniques. The contribution $\Delta o_2\langle P_2(\cos\theta_2)\rangle$ of PVME to the total birefringence is directly related to its state of orientation. According to eq 4, and neglecting the small difference between the density of the two polymers, i.e., $\phi_i = w_i$, this quantity can be expressed as

$$\Delta o_2\langle P_2(\cos\theta_2)\rangle = (\Delta - w_1\Delta o_1\langle P_2(\cos\theta_1)\rangle)/w_2 \qquad (6)$$

To calculate the PVME contribution, we have used the experimental values of Δ and the $\langle P_2(\cos\theta_1)\rangle$ values reported in Figures 2 and 5, whereas Δo_1 was derived from FTIR and birefringence data of the pure PS, according to eq 3. The orientation of PVME, illustrated in Figure 6, is more complex than that of PS. Above $w_2 \sim 0.3$, assuming a negative intrinsic birefringence Δo_2 for this polymer, its orientation behavior is similar to that observed for PS. Before this concentration, we must assume a positive sign for Δo_2, since a negative value of $\langle P_2(\cos\theta_2)\rangle$ and, consequently, an orientation of the PVME perpendicular to the stretching axis, is highly improbable. The change of sign of the intrinsic birefringence of polymers has been reported by several authors. Stein[19] demonstrated that the intrinsic birefringence of PS depends on the angle between the perpendicular to the plane of the benzene ring and the chain axis. Also, Read[20] and Hong and Chung[21] showed that the intrinsic birefringence of poly(methyl methacrylate) may be positive or negative, depending on the —COOCH$_3$ lateral group conformation. Therefore, the variations of the PVME contribution to the total birefringence, observed in this range of composi-

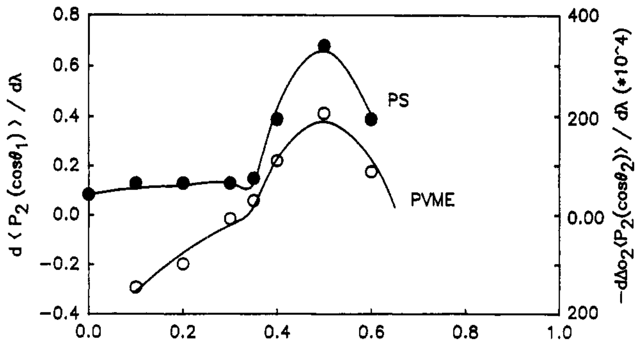

Figure 6. Initial slope of the $[\langle P_2(\cos\theta)\rangle - \lambda]$ and $[\Delta o\langle P_2(\cos\theta)\rangle - \lambda]$ curves of PS and PVME, respectively, as a function of the weight fraction of PVME.

tions, may indicate a progressive change of its intrinsic birefringence, as will be discussed later.

Analysis of Orientation Using the Doi–Edwards Theory. The molecular theory recently proposed by Doi and Edwards for simple systems, with highly entangled chains, offers a simple description of relaxation motions, using a relatively small number of parameters.[22–24] The relaxation of a suddenly deformed chain is described in terms of three different steps, occurring on various time scales. At short times, the relaxation process (step A) consists of a Rouse motion of a fraction of the chain between two entanglement points. The second process (step B) is a retraction of the chain inside its deformed tube to recover its equilibrium curvilinear length. The last relaxation step (step C) corresponds to the reptation of the chain outside its deformed tube in order to reach an equilibrium isotropic conformation.

In a previous study,[13] this topological model was extended to analyze the orientation behavior of PS/PVME blends, at Tc-62, assuming that the PS chain relaxation proceeds from the three steps of relaxation proposed by the Doi–Edwards model and that specific interactions just introduce additional entanglements in the PS network. Taking into account these assumptions, the following expression of the second moment of the orientation function has been derived:

$$P_2(\lambda) = c\sum_{i=1}^{3}\left\{F_i(\lambda)\mu_i((\lambda - 1)/\dot{\epsilon}) + \int_1^{\lambda} F_i(\lambda/\lambda')\frac{\partial}{\partial\lambda'}[\mu_i((\lambda - \lambda')/\dot{\epsilon})]\,\mathrm{d}\lambda'\right\} \tag{7}$$

where $\dot{\epsilon}$ is the strain rate and c is a parameter related to the chain density of entanglements. $F_i(\lambda)$ and $\mu_i(t)$ are given by

$$F_1(\lambda) = (1/3\alpha^2)(\lambda^2 - 1/\lambda) \tag{8}$$

$$\mu_1(t) = \mu_A(t)\mu_C(t) \tag{9}$$

$$F_2(\lambda) = (2/3\alpha^2)(\alpha - 1)(\lambda^2 - 1/\lambda) \tag{10}$$

$$\mu_2(t) = \mu_A(t)\mu_B(t)\mu_C(t) \tag{11}$$

$$F_3(\lambda) = (1/3)(1 - 1/\alpha)^2(\lambda^2 - 1/\lambda) \tag{12}$$

$$\mu_3(t) = \mu_A(t)\mu^2_B(t)\mu_C(t) \tag{13}$$

with

$$\alpha = (\lambda + \sinh^{-1} X/(X\lambda^{1/2}))/2 \tag{14}$$

and

$$X = (\lambda^3 - 1)^{1/2} \tag{15}$$

The relaxation functions $\mu_A(t)$, $\mu_B(t)$, and $\mu_C(t)$ correspond respectively to steps A, B, and C:

$$\mu_A(t) = 1 + \sum_{k=1}^{N_s} \exp(-tk^2/\tau_A) \tag{16}$$

$$\mu_B(t) = \sum_{p=\mathrm{odd}} (8/p^2\pi^2)\exp(-tp^2/\tau_B) \tag{17}$$

$$\mu_C(t) = \sum_{p=\mathrm{odd}} (8/p^2\pi^2)\exp(-tp^2/\tau_C) \tag{18}$$

where τ_A, τ_B, and τ_C are respectively the characteristic times of relaxation of the A, B, and C processes, given by

$$\tau_A = (\xi b^2 N_s^2/6\pi^2 k_B T)^2 \tag{19}$$

$$\tau_B = 2(N_c/Ne)^2\tau_A \tag{20}$$

$$\tau_c = 6(N_c/Ne)^3\tau_A \tag{21}$$

where ξ is the Rouse segment friction coefficient and b is the length of the repeat unit. N_c and Ne are respectively the number of repeat units per chain and between entanglements, N_s is the number of Rouse segments between entanglements, k_B is the Boltzmann constant, and T is the temperature.

It is difficult to model the experimental data using the general constitutive eq 7 since, for a given value of λ, $P_2(\lambda)$ depends upon four adjustable parameters c, τ_A, τ_B, and τ_C, $\dot{\epsilon}$ being fixed by the experimental conditions. In other words, the set (c,τ_A,τ_B,τ_C) is not unique, for a given composition. However, it can be shown that eq 7 is sensitive to a specific relaxation time τ_i only if the corresponding $\dot{\epsilon}\tau_i$ lies between 0.25 and 25, as has been checked numerically,[13] which corresponds to τ_i values between 10^2 and 10^4 s using an effective strain rate $\dot{\epsilon}$ of 0.0025 s^{-1}. Outside these limits, the relative variation of $\langle P_2(\cos\theta)\rangle$ is well below 10%, which is the limit of sensitivity of the experimental results. In other words, if τ_i is out of this range, the relaxation process is either too fast or too slow, as compared to the experimental time scale, to be detected in the orientation measurements. For pure PS, at T_g + 10, only τ_B is expected to verify this condition. Actually, from the literature data, τ_A ranges between 0.5 and 7 s, τ_B ranges between 290 and 3900 s, whereas τ_C goes from 1.5×10^4 to 19×10^4 s.[13,25–28]

Assuming that the relaxation times of the PS chains in the blend are of the same order of magnitude as those in pure PS, at the same reference temperature T_g + 10, the variation of $\langle P_2(\cos\theta)\rangle$ of PS with λ has been fitted using only two adjustable parameters, namely c and τ_B (Figure 5). It should be noted that the shape of the curve depends on the relaxation time whereas the parameter c, which is a multiplicative constant in eq 7, affects only the magnitude of $\langle P_2(\cos\theta)\rangle$. Therefore, this analysis gives the charac-

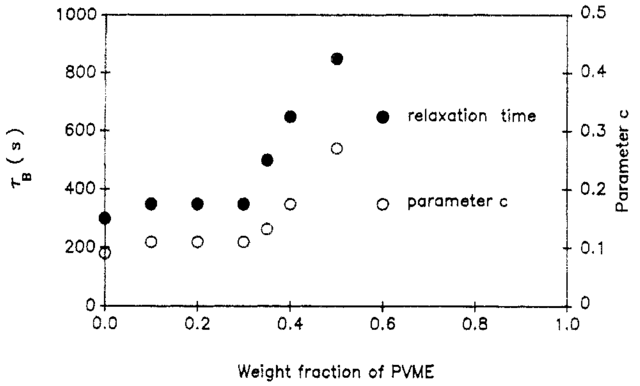

Figure 7. Relaxation time τ_B and c parameter of PS chains in the blend, as a function of the weight fraction of PVME.

teristic parameters c and τ_B of the PS chains, which are plotted in Figure 7 as a function of the blend composition. The parameters exhibit the same behavior as the orientation and modulus (Figure 6). In particular, it can be observed that the relaxation time of PS in the 50% PS blend is 3 times larger than that in pure PS.

The analysis of the orientation in terms of the Doi–Edwards theory provides further insight about the orientation process in PS/PVME blends. Up to $w_2 \sim 0.3$, the characteristics of the PS network differ slightly from those of pure PS due to weak interactions between PS and PVME. Thus, the small changes observed in PS orientation and Young's modulus result from a slight increase of entanglement density and relaxation times of PS chains. Above this critical value, specific interactions become strong and the dissimilar chains orient significantly by a cooperative mechanism of orientation. On the one hand, they may act as temporary "cross-links", increasing the density of the PS network and reducing the tube diameter of the chains, which leads to an increase of the intrinsic orientation. On the other hand, they increase the mutual friction coefficient between the dissimilar chains and hinder their relaxation motions, thereby increasing the orientation achieved by the two polymers. Beyond a PVME weight fraction of ~0.5, both the density of entanglements and the mutual friction coefficient decrease due to the reduction of the number of heteromolecular contacts, resulting in a decrease of chain orientation.

These remarkable variations of molecular orientation and relaxation times are similar to several experimental results recently reported in the literature. For instance, Zawada et al.[29] analyzed the relaxation dynamics of poly(methyl methacrylate)/poly(ethylene oxide) (PMMA/PEO) miscible blends in the melt state, using rheo-optical methods. For a given $T - T_g$ temperature, the relaxation time of PEO was found to increase by 2 orders of magnitude, passing through a maximum at 60% PEO. This trend was attributed to two competing effects, each dominating the relaxation dynamics in a separate concentration domain. On the one hand, it was argued that specific interactions cause PEO to preferentially adopt a trans conformation in the blend as compared to the primarily helical structure that PEO takes on in the pure state. This conformation change may cause a reduction in mobility and hinder the PEO relaxation. On the other hand, the tube diameter of the chains in the blend is expected to increase with the PMMA content since PMMA experiences fewer entanglements than PEO; the tube broadening is assumed to account for the decrease of the relaxation time in PMMA-rich blends.

A similar behavior was reported by Composto, Kramer, and White[30] about the monomeric friction coefficient in PS/PPO. As a function of blend composition, the PS friction coefficient exhibits an increase of about 2 orders of magnitude, passing trough a maximum at $w_{PPO} \sim 0.25$. This result is analogous to that of Zawada et al. since the friction coefficient is directly proportional to the relaxation time, as can be seen from eq 19. The Brochard–Wyart theory[31] for chain friction in blends suggests that the monomeric friction coefficients of the two polymers are given by the general equation

$$\xi_{oi} = \phi_i\xi_{ii} + \phi_j\xi_{ij} \tag{22}$$

where ξ_{oi} is the observed monomeric coefficient of the ith component in the blend, and ξ_{ii} and ξ_{ij} are the friction coefficients of the i–i and i–j contacts, respectively. As pointed out by Composto et al.[30] and Zawada et al.,[29] this equation fails to describe the composition dependence of the chain friction of the two components of a blend. From our results, the variation of this coefficient with blend composition may be more properly described by an equation such as

$$\xi_{oi} = \xi_{ii}\phi_i^2 + 2\xi_{ij}\phi_i\phi_j + \xi_{i1}\phi_j^2 \tag{23}$$

where ξ_{i1} is introduced to take into account the fact that ξ_{oi} does not vanish when ϕ_i tends toward zero, as illustrated by the results of Composto, Kramer, and White (it does not represent the contribution of the j–j contacts to the friction coefficient of the ith component). A similar equation, using ln ξ instead of ξ, has been proposed by Wu.[32]

Discussion

For amorphous miscible blends, deformation mechanisms and molecular orientation are intimately related to both relaxation motions and the characteristics of the temporary network formed by the two dissimilar chains. Changes with composition of parameters such as glass transition temperature, density of entanglements, free volume distribution, specific interactions, etc., which control the local dynamics of relaxation and the properties of the network, require the choice of a reference state for orientation investigations over a broad range of compositions. When the stretching temperature is kept constant relative to T_g, the present study shows clearly that specific interactions, responsible for the miscibility, play a crucial role in the orientation process, as pointed out by numerous studies.[3-5] Moreover, the analysis of the results suggests that both the strength and number of the 1–2 contacts should be taken into account. If specific interactions are weak, i.e. at low PS concentrations, the local environment of the two dissimilar chains is slightly perturbed, and the two polymers may orient independently, with an orientation which differs slightly from that of the pure components. In contrast, when these interactions are strong, i.e. in the intermediate range of composition, they may play a role of actual "cross-links", increasing the entanglement density of the chains and, consequently, their intrinsic orientation. These 1–2 contacts increase the interchain friction, and the dynamics of the dissimilar chains relaxation is mutually hindered, leading thereby to an increase of the two polymers orientation by a cooperative process of orientation.

In this context, the dependence on composition of the thermodynamic interaction parameter of miscible blends has been pointed out in several studies.[33-36] For instance, the data of Han et al.[34,35] and Qian et al.[36] reveal a strong dependence on composition of the χ_{12} interaction parameter of miscible PS/PVME blends (Figure 8). Further-

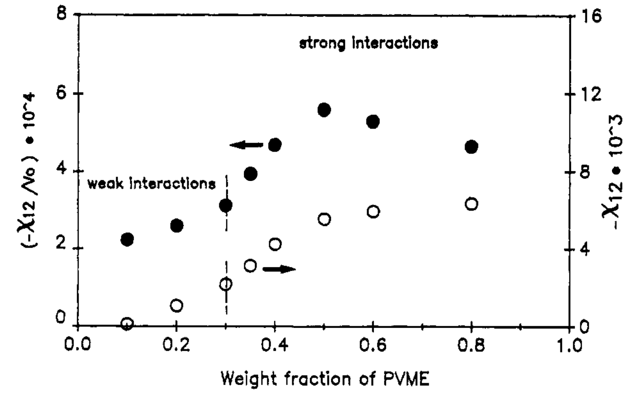

Figure 8. Variation of the χ_{12} interaction parameter of PS/PVME blends, at $T_g + 10$, as a function of the PVME weight fraction. The filled circles are the data of Han et al.,[34,35] and the open circles, those of Qian et al.[36] In the former case, v_0 is the molar volume of the reference unit cell.

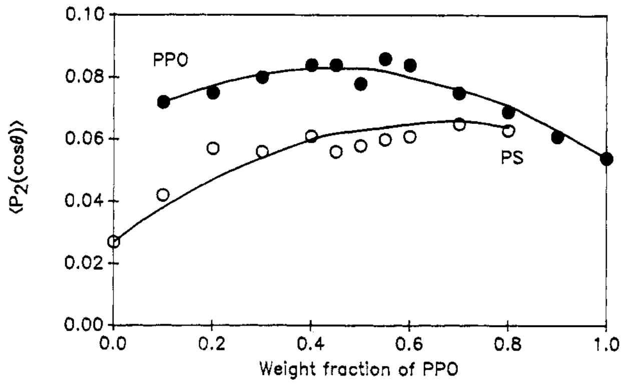

Figure 9. Variation with composition of $\langle P_2(\cos\theta)\rangle$ of PPO and PS in PPO/PS blends. Experimental data are taken from ref 5.

more, it can be seen that, below $w_2 \sim 0.3$, χ_{12} values are relatively small, as compared to those above this concentration, which indicates weaker interactions in this range of composition. In particular, the data of Han et al. show the same variation of χ_{12} with respect to the blend composition as the orientation and mechanical property measurements (Figures 3 and 6); in the data Qian et al., the maximum is not defined but the general tendency is the same. These results are in line with the study of Tran-Cong et al.[37] who showed that, for this system, the amplitude of the critical concentration fluctuations in the homogeneous state goes through a maximum at ~35% PVME and decreases dramatically above this composition, indicating an increased stability of the miscible state. This is in agreement with our results which suggests that, at a critical composition, close to 30% of PVME, the system changes from a weak to a strong interaction state, modifying completely its viscoelastic and mechanical response. Similarly, Byoungchul[38] reported that the PS/PVME blends change from a craze to a shear-controlled mode of deformation at 35% PVME; this transition was explained as being due to increased interactions between PS and PVME which are predicted to suppress crazing, as suggested by Wellinghoff and Baer.[39]

It is also interesting to compare the PS/PVME orientation behavior to that of other amorphous miscible blends and, in particular, to that of PS/PPO, which has been extensively studied[3,5] and which exhibits a different behavior, as illustrated in Figure 9. For both PS and PPO rich blends, the major component exhibits a progressive increase of its orientation when adding the second polymer whereas the minor component orients significantly even when its concentration in the blend is neglegibly small, as has been shown for PPO by Zhao and Prud'homme.[40] In the intermediate range of concentration, only small variations of orientation are observed without the transition behavior observed in PS/PVME.

Further evidence of the difference in the local chain dynamics in miscible blends is given by the study of Le Menestrel et al.[41] The motional behavior of PS in PS/PVME was found to be governed by intramolecular constraints and to be different from that of PVME which is controlled by both intramolecular constraints and intermolecular interactions. Schmidt-Rohr et al.[42] attributed this difference in the local dynamics of the two dissimilar chains to the fact that PS/PVME blends are heterogeneous on the nanometer scale, with an average diameter of heterogeneities of 3.5 nm, which corresponds to two or three statistical segments. In other words, different parts of the same chain may have different local environments and different relaxation behaviors, as suggested before. On the other hand, it is expected that the molecular weight will play a crucial role in the relaxation motions of the two polymers. Indeed, according to the Doi–Edwards theory, the polymer with the lowest molecular weight is expected to relax faster.

In this context, obtaining the same orientation for the two components seems to be rather an exception. This would be the case with strong segment-to-segment specific interactions, which is an ideal situation, or if the friction coefficients, density of entanglements, and molecular weights were similar for the two polymers.

Finally, it must be realized that this interpretation of the molecular orientation assumes implicitly that specific interactions are strong enough to induce an effective coupling of the dissimilar chain dynamics. For weak interacting systems, the two polymers are expected to orient independently.

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