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Orientation of a Miscible Polymer Blend with Strong Interchain Hydrogen Bonds: Poly(vinylphenol)−Poly(ethylene oxide)

Sylvie Rinderknecht and Josée Brisson*

Department of Chemistry and CERSIM (Centre de recherche en sciences et ingénierie des macromolécules), Faculté des sciences et de génie, Université Laval, Québec, Québec, Canada G1K 7P4

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ABSTRACT: The orientation of miscible poly(vinylphenol) (PVPh)−poly(ethylene oxide) (PEO) blends for compositions of 20−35 wt % PEO and from $T_g + 10$ to $T_g + 18$ was studied using FTIR spectroscopy. In uniaxially deformed samples, both polymers were oriented for all compositions studied. For the POE component, a nonlinear relationship was observed between the orientation function $\langle P_2 \rangle$ and the draw ratio λ, which was ascribed to a rapid relaxation of this polymer. The fact that orientation does occur is noteworthy, since for the poly(methyl methacrylate)/PEO blend system studied by Zhao, Jasse, and Monnerie, PEO did not show any orientation, which was attributed to a fast relaxation. Hydrogen bonds are here proposed to hinder the relaxation process. A maximum in the orientation of the PEO component was observed for 30 wt % PEO, whereas the orientation of the PVPh component began to increase significantly at this composition. The composition for this maximum, 30 wt %, is close to a 1:1 mole ratio of interacting units, and data from the literature indicate that it is in this range that the number of hydrogen bond interactions reaches a maximum. The observed orientation behavior is attributed to the formation of these strong hydrogen bonds which can influence entanglement density, chain friction coefficient, and local organization of the chains. The curves of $\ln(\Delta P_2/\Delta\lambda)$ vs $1/T$ yield similar apparent activation energies for the processes, suggesting that local organization, and therefore α angles used to calculate $\langle P_2 \rangle$, are affected by these interactions.

Introduction

Orientation characterization of polymer blends offers a particular challenge, since few techniques allow measurement of orientation of the individual components. FTIR spectroscopy has been intensively used for characterization of blends because it allows measurement of the chemical components of the blend, of given chemical groups, and, in some instances, of specific conformation populations of these chemical groups. However, vibration overlap is often severe, which limits the available information.

Blend orientation studies involve a further challenge, that of rationalizing the resulting data. Our understanding of the mechanisms involved in orientation and its subsequent relaxation is based on the reptation theory of de Gennes[1] and on the chain relaxation model developed by Doi and Edwards.[2,3] In this model, the environment of a given chain is expressed as a tube of neighboring chain constraints in which the chain relaxes locally, retracts, and finally reptates. Molecular weight of an average chain, molecular weight between entanglements, and chain friction coefficients determine the relaxation behavior in this model. These variables have therefore been used to explain both qualitatively and quantitatively the observed orientation of pure polymers and of blends.[4] In the latter case, prediction is almost often impossible, which illustrates the limits in our understanding, for blends, of the relationship between molecular weight between entanglement and chain friction coefficient, the type, number, and strength of the interactions present, and the orientation of each component of the blend.

To better understand how intermolecular interactions influence orientation in a polymer blend, our research group has been focusing in the past years on hydrogen bond forming polymers and blends.[5−7] This strong interaction is directional and amenable to FTIR characterization, which prompted its choice over stronger but nondirectional ionic interactions or weaker, nondirectional van der Waals interactions. Very few orientation studies on hydrogen bond forming blends have been reported in the literature. A first study by Wang and Cooper showed cooperativity in the case of poly(vinyl chloride) blends with cellulose, polyurethane, and polyether urethane−urea.[8] In the work of Zhao, Bazuin, and Prud'homme, hydrogen bonds between carboxylic groups were shown not to influence orientation of poly(styrene-*co*-methacrylic acid) copolymers for up to 12% MAA co-units[9] and of blends of polystyrene-*co*-4-vinylpyridine with polystyrene-*co*-methacrylic acid.[10] On the other hand, hydrogen bonds between sulfonic groups of poly(styrene-*co*-styrenesulfonic acid) copolymers seem to be responsible for a substantial orientation increase as compared to the case of polystyrene.[10]

In our research group, Li characterized the orientation of pure PVPh[5] and of the PMMA/PVPh system from 0 to 54.5 wt % PVPh.[6] PMMA orientation is larger than that of PVPh in the blends but decreases with increasing PVPh composition. PVPh orientation, on the other hand, increased upon addition of PMMA. It was proposed that hydrogen bonds forming between PMMA and PVPh allowed PVPh to be dragged along, increasing its final orientation.

In the present work, we have focused on the PVPh/PEO system. The miscibility of this system is well established.[11,12] More important, contrary to PMMA/PVPh, infrared spectroscopy reveals that interassociation hydrogen bonds formed between PVPh and PEO are stronger than so-called intraassociation PVPh−PVPh hydrogen bonds.[11−15] It was hoped, and was indeed found true, that this would lead to differences

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* To whom correspondence should be addressed.

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in the orientation behavior in relation with hydrogen bond formation.

Experimental Section

Polymers Used in This Study. Poly(ethylene oxide) (PEO) from Aldrich was used for this study. Molecular weight was determined by steric exclusion chromatography in tetrahydrofuran with polystyrene reference using a Waters 590 programmable HPLC pump and a Waters 410 differential interferometer. Measured molecular weight was 82 500 g mol^{-1} weight-average and 45 500 g mol^{-1} number-average, with a polydispersity of 1.81. Poly(vinylphenol) (PVPh) was purchased through Polysciences, Inc., and molecular weight determination using the same technique yielded values of 5200 g mol^{-1} weight-average, 2200 g mol^{-1} number-average, and polydispersity of 2.3.

Blend Preparation. Four blends of PVPh/PEO were prepared, with 20 wt % of PEO (PEO20%), 25 wt % (PEO25%), 30 wt % (PEO30%), and 35 wt % (PEO35%), which correspond respectively to 40, 48, 54, and 59 mol %. Temperature and residence time were carefully controlled in order to limit thermal degradation.

The dried powders of the two polymers were hand-mixed in appropriate weight ratios and blended by melt extrusion with a MiniMax blender model CS-183 at a temperature between 165 and 175 °C.

Thermal Analysis. Glass transition temperature of blends was measured by differential scanning calorimetry (DSC) with a Perkin-Elmer microcalorimeter DSC-7 equipped with a thermal analysis controller TAC7 and a controlled cooling accessory CCA7. Capsules of 15−25 mg of sample were prepared. The DSC apparatus was calibrated with indium (melting temperature = 156.6 °C), and scans were performed between −100 and 200 °C with at a heating rate of 10 °C/min. For each blend, the reported T_g corresponds to the midpoint of the transition and is the average value after the second scan for three different samples. Glass transition temperatures of 58, 73, 88, and 105 °C were obtained respectively for the PEO35%, PEO30%, PEO25%, and PEO20% blends.

Oriented Films Preparation. Extruded pellets were pressed between two Teflon films in a SPECAC P/N 15620 constant thickness molder with a model C Carver press at 0.5−1 metric ton and at a $T_g + 55$ °C temperature for 5−10 min. The films hence made, 25−40 μm thick, were placed in a vacuum oven between two light aluminum sheets at $T_g + 30$ °C for 1 h in order to relax compression-induced orientation. The films were cut with a razor blade to obtain 15 mm × 10 mm strips. Resulting polymer strips were marked every millimeter on one side with a thin point marker to verify stretching uniformity. The two strip ends were placed between pieces of temperature-resistant tape (Pyro-Tape Aremco 682). The strip was then inserted in the temperature-controlled enclosure of a stretching apparatus by placing each tape extremity that was extending beyond the polymer strip between one of the two clamps of the stretcher. The bottom clamp was fixed while the top clip was motor-driven to perform the stretching. An exponential stretching rate of 0.1 s^{-1} was chosen. Draw ratios l/l_0 (l being the final length of the strip and l_0 its initial length) or λ from 1.5 to 4.0 and draw temperatures of $T_g + 10$ °C, $T_g + 12$ °C, $T_g + 15$ °C, $T_g + 18$ °C, and $T_g + 20$ °C were used when possible. Before stretching, the sample was maintained 20 min at drawn temperature to allow thermal equilibration. It was verified, in all cases, that no significant change in the FTIR spectra occurred following such thermal treatments and concluded that no detectable thermal degradation occurred under these conditions. After stretching, the sample was quenched at room temperature with an air fan.

Spectroscopic Measurements. FTIR spectra were recorded by using a Mattson Sirius 100 spectrometer. For each spectrum, 100 scans were taken at a resolution of 2 cm^{-1} using a MCT detector. In each case, a polarizer was inserted before the sample, and spectra were recorded with polarizer parallel and perpendicular to draw direction of the sample. The absorbance of given vibrations $A_{\parallel}$ (for the spectrum with polarizer parallel to the stretching direction) and $A_{\perp}$ (polarizer perpendicular to stretching direction) were measured by determining the absorbance of the maximum of the peak after having defined a linear baseline with respect to predetermined positions on each side of the peak for each vibration used. The absorbance thus measured is then used to calculate the dichroïc ratio $R = A_{\parallel}/A_{\perp}$. In all cases, only the vibrations for which the absolute absorbance was inferior to 0.8 were used in the calculations, to remain within the linearity limits of the technique.

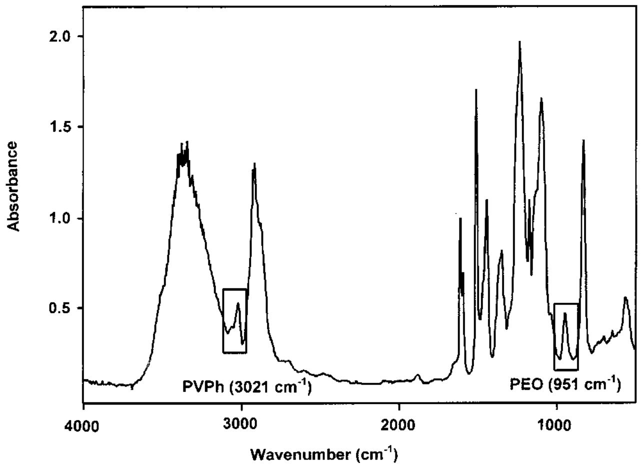

Figure 1. FTIR spectra of a 30 wt % PEO/PVPh blend. Vibrations used for orientation are framed.

The second-order moment of the orientation function $\langle P_2(\cos\theta)\rangle$, abbreviated $\langle P_2\rangle$ throughout the text, can be evaluated from R using the following relationship:

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

where

$$R_0 = 2\cot^2\alpha \qquad (2)$$

α being the angle between the polymer chain axis and the dipole transition moment vector of the vibration being considered and θ the angle between the chain axis and the stretching direction.

Vibration absorptions are very strong in the PVPh/PEO system. For the experimentally achievable thicknesses, considering the brittleness of the samples, most vibrations were above the linearity limit of 0.8. The only reasonably well-isolated peaks of acceptable intensity were located at 951 cm^{-1} for PEO and 3021 cm^{-1} for PVPh, as shown in Figure 1. These were therefore used for orientation characterization.

PEO chains adopt, in the crystalline phase, a helical conformation with a trans, gauche, trans (TGT) conformation of the COCC, OCCO, and CCOC sequences.[16−21] In the melt state, analogous to the amorphous state in terms of conformations adopted by the chain, infrared spectroscopy reveals conformational irregularity and the presence of trans segments, although most segments adopt a gauche conformation.[20−25] Many authors have studied the conformations of PEO and of model compounds, and it is not the aim in the present article to review these. However, it is of interest to estimate what is the approximate percentage of gauche conformers in order to gain an insight into the validity of using a vibration sensitive only to gauche conformers to evaluate the orientation of PEO. Calculations using the rotational isomeric state model predict a PEO conformer distribution of 61% gauche units and 39% trans units at 25 °C,[26,27] while ab initio calculations predict a slightly larger number of 79% gauche units.[28,29] In short, gauche units form the major conformation but nevertheless cannot account for the overall orientation of PEO, as trans segments are liable to orient differently from gauche segments.

The coupled CO stretching (ν(CO)) and gauche CH_2 rocking ($\delta_r(CH_2)$) vibrations have been assigned to the dichroic perpendicular infrared band at 960 cm^{-1} and to the dichroic parallel one at 947 cm^{-1}.[16−19] For the molten PEO, the only band observed around 945 cm^{-1} as well as an ill-defined shoulder at 915 cm^{-1} are associated mainly to the gauche CH_2 rocking vibration, but more precisely to a combination of CH_2 rocking, CO and/or CC stretching vibrations.[20] Since preliminary measurements of the 951 cm^{-1} absorption band dichroic ratio R seemed to be consistent with a increasing draw ratio λ, and since the 915 cm^{-1} shoulder and any other possible contributions have been checked not to induce a significant error, this 951 cm^{-1} absorption band was chosen to evaluate the orientation of the gauche PEO segments.

It must be stressed that only the orientation of the gauche segments could be measured in this case. No information will thus be gained with respect to changes in the conformation population changes of PEO as orientation proceeds. A second problem lies in the estimation of the α angle for this vibration. Overall conformation of the chain can vary while orientation occurs in amorphous polymers;[30] three approaches were possible for PEO. In the first, the chain axis could be defined locally as the axes passing through two successive oxygen atoms. This definition depends solely on the local conformation, which is gauche for this vibration, and therefore the α angle should not vary. However, it yielded negative values of the orientation function and was thus rejected. A second possibility would have been to simulate the amorphous phase and determine the α angle using this simulated amorphous phase, but if defining the chain axis in the same fashion, the problem remained. Instead, it was decided to use as a most probable "ideal" conformation, one toward which the amorphous phase tends as orientation proceeds. For the gauche segments, it is proposed that it will be that of the crystalline phase, since, at least for pure polymers, stress-induced crystallization can occur at high draw ratios. From the helical conformation adopted in the crystal phase, the Quanta software running on a Silicon Graphics workstation was used to measure a value of 48° for the α angle between the chain axis and the dipole transition moment vector of the gauche $r(CH_2)$ rocking vibration, in agreement with the value proposed by Davison.[23] This value of α angle yielded positive orientation factors of reasonable magnitudes. The use of this α angle is based on the following assumptions: (1) The average conformation of PEO is the same in the pure polymer and in the blend. (2) The average local chain axis of PEO does not change with draw ratio. (3) The conformation toward which the gauche segments tends is that of the crystalline phase.

For PVPh, several aromatic CH stretching vibration modes are responsible for the 3021 cm^{-1} absorption band. This vibration occurs in a spectral region in which no PEO vibrations appear. Therefore, to verify whether it could be used to assess orientation, a preliminary calculation using data for pure PVPh was performed: The dichroic ratio of this vibration, as determined after correction with a linear baseline defined from 3088 to 2992 cm^{-1}, was plotted against the dichroic ratio of the 1015 cm^{-1} vibration. This yielded a linear relationship, and the slope was used to deduce an α angle of 90° when using a previously estimated values for the α angle of pure PVPh.[5] As a first approximation, this α angle was used for PVPh in the PVPh−PEO blends.

Error calculations for $\langle P_2\rangle$ values were calculated using Student's t statistical treatment with a confidence level of 95%. For each sample, three measurements were performed on slightly different positions of the sample. Each $\langle P_2\rangle$ value reported represent the average for 2−10 different samples. Only when it was extremely difficult to get oriented samples were only two values taken, resulting in much larger calculate errors (typically combinations of high PVPh composition and draw temperatures). For PVPh, while error percentages are similar, reported error values are usually larger than those of PEO because the of lower observed values of dichroic ratios and of $\langle P_2\rangle$. For $\Delta P_2/\Delta\lambda$ values, which are the values of the slopes of $\langle P_2\rangle$ vs λ graphs, the least-squares approach was used to determine the error, as was the case for the activation energies.

Results and Discussion

Choice of Polymer Blend. The PVPh−PEO blend is the first system, to our knowledge, for which orientation is investigated and which forms stronger hydrogen bonds between the two components of the blends than between chains of the pure polymers.

The low molecular weight of PVPh is partly responsible for the observed brittleness of the films, which limits experimental conditions under which orientation can be induced in the samples. To minimize this effect, a relatively high molecular weight was chosen for PEO (M_w = 82 500 g mol^{-1}). Despite this, for a weight composition below 20 wt % PEO, the films are too brittle to be subjected to deformation without failure. Above 35 wt % PEO, the T_g of the blend is too close to room temperature to allow quenching before substantial orientation is lost. Furthermore, when the concentration of PEO is high, PEO crystallizes, as was verified by X-ray diffraction. The system becomes biphasic, which was not desired in the present study. This therefore limited the experimentally accessible concentration range. It was nevertheless sufficiently large, as will be seen, for variations in behavior to be observed.

Orientation with Respect to Temperature. Orientation of the PVPh component of blends with 30 and 35 wt % PEO is reported in Figure 2a. Results for PEO20% and PEO25% blends are not considered here because of a large data dispersion, attributed partly to experimental handling difficulties, which severely limited the number of oriented samples that were obtained. A second important source of error was the low orientation of the samples, which resulted in dichroic ratios very close to 1 for the 3021 cm^{-1} vibration, increasing the relative error of the second moment of the orientation function $\langle P_2\rangle$.

As expected, $\langle P_2\rangle$ increases linearly with increasing draw ratio λ for PVPh and also increases with decreasing draw temperature. This behavior is usual for amorphous polymers and is ascribed to a faster chain relaxation in the experimental space-time at higher temperatures.[31] It is probable that an additional relaxation step becomes predominant at high draw ratios.

Orientation of gauche segments of PEO is reported in Figure 2b. In the studied concentration range, PEO orientation is easily measurable. This is in itself significant, since for the PMMA/PEO system, at a glass transition temperature very close to that of our system (78° for 15% PEO−PMMA vs 75° for 30% PEO−PVPh), Zhao, Jasse, and Monnerie[31] reported no detectable orientation. They proposed that the PEO relaxation time was shorter than the experimental range time, which meant that, although PEO chains probably oriented during deformation, fast relaxation eliminated completely this orientation prior to measurements.

As expected, the measured orientation of gauche conformers of PEO also increases with an increasing draw ratio λ and with decreasing draw temperature. PEO is not only oriented but is even more so than PVPh. In this respect, the behavior is similar to that of the PVPh−PMMA blend. However, contrary to the PVPh−PMMA blend and to most blends when stretched under a constant strain rate and at constant temperature $T_g + \Delta T$,[5] the relationship between orientation and defor-

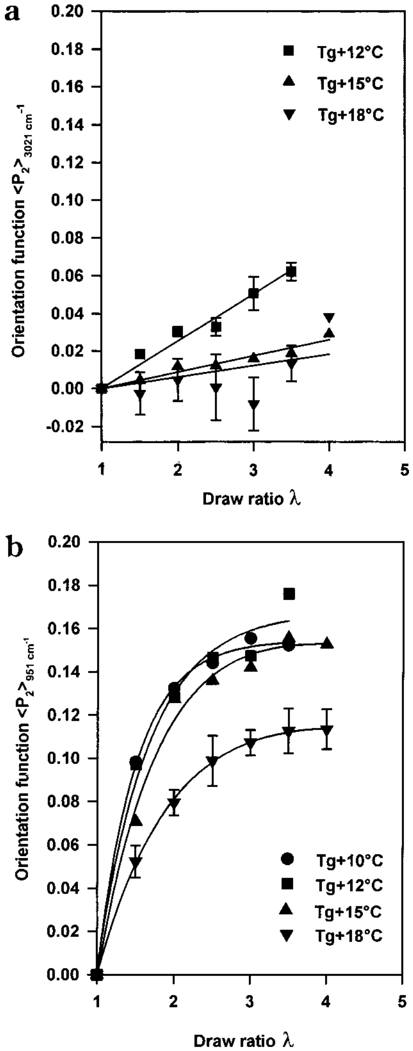

Figure 2. Orientation of the 30 wt % PEO/PVPh blend as a function of draw ratio λ at various temperatures: (a) PVPh and (b) gauche conformers of PEO.

mation ratio is not linear. PEO seems to orient itself easily and quickly at low draw ratios but reaches a plateau near $\lambda = 3.0$. The nonlinearity of $\langle P_2 \rangle$ vs λ curve in Figure 2b suggests that, when stretching lasts longer (at higher λ), PEO chain relaxation competes significantly more with the orientation process, indicating that a longer relaxation step must have started. It is proposed that PEO relaxation is considerably slower than in the PEO/PMMA system[6] but still much faster than for most polymers studied. Hydrogen bonds therefore partially slow relaxation, which is still much faster for PEO than for PVPh, although a single T_g is observed for the blend.

Since pure PEO is semicrystalline and since its glass transition temperature T_g is around −60 °C, its orientation behavior has not been characterized and cannot be compared to that observed in the blend.

Evolution of Orientation with Blend Composition. When reorganizing data in order to present one given drawing temperature (T_g + 15 °C), as reported in Figure 3, it is possible to compare the orientation factor $\langle P_2 \rangle$ as a function of draw ratio λ for different compositions. For PVPh, again, measurements are limited to two compositions. It can clearly be seen that, as the composition in PVPh increases, measurement error becomes more important. Nevertheless, orientation of PVPh is clearly increasing with increasing PEO content.

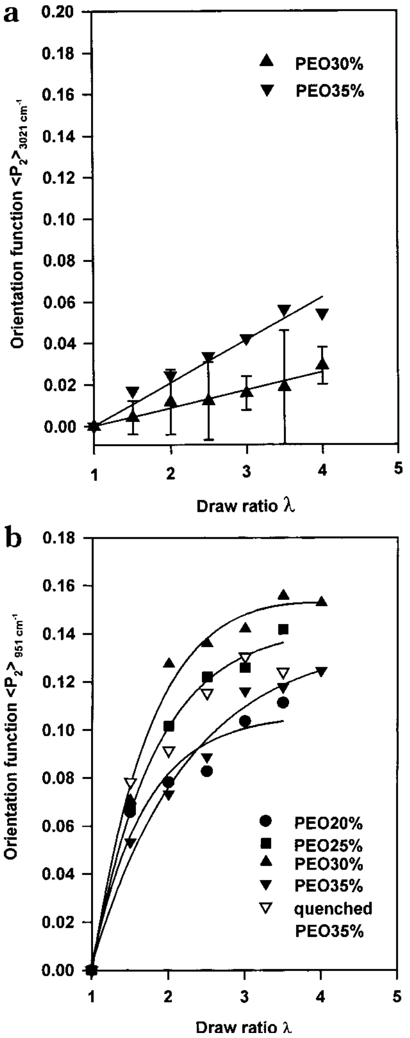

Figure 3. Orientation of the various blends as a function of draw ratio λ at T_g + 15: (a) PVPh and (b) gauche conformers of PEO.

As the PEO percentage increases, the orientation of the gauche conformers of PEO, as expressed by $\langle P_2 \rangle$, increases at first to reach a maximum at 30% PEO. At 35% PEO, the PEO orientation decreases to return to values similar to those at 20% or 25% PEO. Since the T_g of the 35% PEO blend is closer to room temperature, the time required to bring the sample under T_g after stretching is longer, which could have explained the observed decrease in PEO orientation at 35 wt %. Additional measurements were made at a drawing temperature of T_g + 15 °C, but by quenching stretched strips with liquid nitrogen instead of the air fan, which ensured rapid quenching even for this low-T_g composition. This technique was used only for this composition and one draw temperature, since sample breakage was much higher. The measured orientation was, as expected, higher than when samples were air-cooled. However, as was seen in Figure 2b, orientation stayed significantly lower than that obtained with air-cooled PEO30%, which confirms that this maximum is not an artifact due to measurement conditions.

Figure 4a sums up the orientation behavior of the blends with respect to composition. The maximum in orientation of PEO in the PEO30% blend stands out, both at low draw ratio ($\lambda = 1.5$) and, to a lesser extent, at a higher one ($\lambda = 3$). It must be noted that the error is very large in the latter case, which is due to the

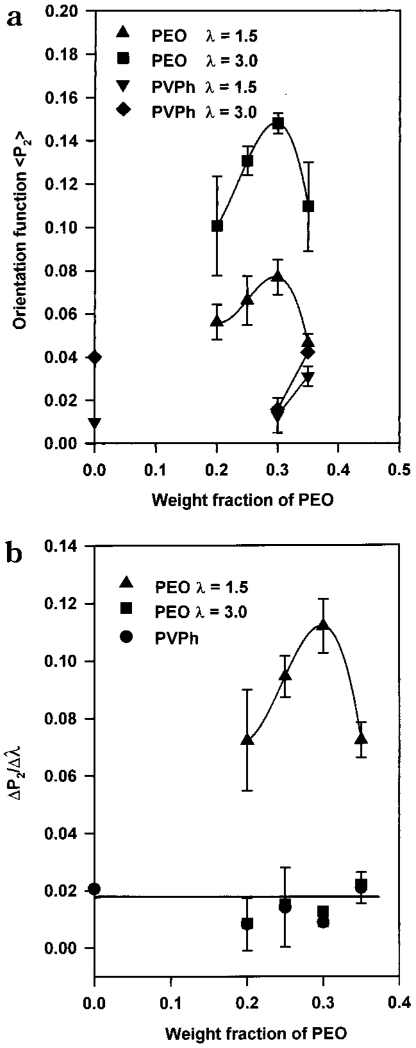

Figure 4. Orientation behavior as a function of composition: (a) variation of P_2; (b) variation of $\Delta P_2/\Delta\lambda$.

limited number of samples that we were able to orient to a high λ Nevertheless, for $\lambda = 1.5$, the observed errors are less severe, and the maximum is clearly observed. PVPh orientation in PEO30% is similar to that of pure PVPh and increases for PEO35%, unlike that of PEO which decreases at this composition.

Visualizing data by plotting the derivative relative to the λ variation, $(\Delta P_2/\Delta\lambda)$, against blend composition[4] is often useful when analyzing polymer orientation. Since a high draw ratio corresponds to a longer experimental lapse of time, $(\Delta P_2/\Delta\lambda)$ is a measure of how easily or how fast polymer chains will orient. Nevertheless, the observed orientation is always the sum of two competing processes: orientation induced by deformation and relaxation that occurs before the stretched sample is quenched below its T_g. A low value of $(\Delta P_2/\Delta\lambda)$ can thus point out to a difficulty for the polymer to orient, possibly because of chain stiffness. On the other hand, it can also indicate that the polymer relaxes rapidly, even if it is oriented easily or significantly when stretched.

The $(\Delta P_2/\Delta\lambda)$ curves reported in Figure 4b have been obtained differently for PVPh and for PEO. Curves of $\langle P_2\rangle$ versus λ are usually linear, and $(\Delta P_2/\Delta\lambda)$ values are then calculated by evaluating the slope. This procedure was used for PVPh. Since linearity is not observed for PEO, the $\langle P_2\rangle_{PEO}$ versus λ curves have been treated with the Jandel Peakfit software to obtain, at predetermined values of λ, the derivative $(\Delta P_2/\Delta\lambda)$ of simulated curves. λ values of 1.5 and 3.0 have been chosen because the PEO orientation behaviors are different at low λ and at higher λ.

At low draw ratio λ, for all experimental draw temperature studied, $(\Delta P_2/\Delta\lambda)$ values for PEO are relatively high and reach a maximum at 30% PEO. The position of this maximum, not surprisingly, is the same as that already observed for the curves of PEO orientation function versus blend composition. Relatively high $(\Delta P_2/\Delta\lambda)$ values for $\lambda = 1.5$ indicate that PEO orients easily at the beginning of the deformation process. At this draw ratio, only 6−7 s has elapsed between the stretching onset and the time when the sample is quenched (4 s for stretching and 2−3 s for quenching). Chain relaxation is therefore more limited. It is proposed that the $(\Delta P_2/\Delta\lambda)$ variation for PEO at $\lambda = 1.5$ gives information mostly on the deformation or proper orientation process of PEO and/or the early stages of the relaxation process.

In contrast, at $\lambda = 3.0$, the $(\Delta P_2/\Delta\lambda)$ ratio is much smaller and remains constant over the range of studied compositions. Since PEO was oriented significantly at the beginning of the stretching process, it is proposed that the lower value of $(\Delta P_2/\Delta\lambda)$ is due to relaxation and more specifically to relaxation steps that involve intermediate or long relaxation times. In this case, the experimental time lapse between stretching onset and completion of quenching is close to 16 s.

For PVPh, the speed at which molecular chains orient is low and remains the same, within experimental error, at both compositions where it was measured. It is concluded that PEO gauche conformers orient faster than PVPh but that, at higher λ values, where relaxation influences more the observed orientation, the behavior of the two polymers becomes similar. This would agree with a cooperativity of relaxation at the molecular or segmental level, as was observed by Saito, Takahashi, and Inoue[32] for other miscible blends.

Effect of Chain Entanglement on Orientation. In an amorphous rubber network, molecular orientation is inversely proportional to the average number of segments between cross-links.[33] Entanglements play a similar role in amorphous polymers: A higher number of chain entanglements, or a smaller average mass M_e between two entanglements, results in a higher chain orientation.[34] Zhao, Prud'homme, and Bazuin[9] suggested that polymer orientation depends on blend composition only when the entanglement spacing is influenced simultaneously by entanglements formed between similar and dissimilar chains. If a polymer is very diluted, its orientation remains constant since chain entanglement density depends only on its entanglement with the matrix chains. PEO has an average weight between entanglements of approximately 2200 g mol^{-1}.[35] Although the M_e of PVPh is not known, a low propensity of chain entanglement is expected from the presence of aromatic cycle, as in the case of polystyrene. Since the molecular weight of PVPh used in this study is low, PVPh should have a very low entanglement, in agreement with its observed low orientation in the pure state. This would also explain why PMMA and PEO orient significantly more than PVPh in their respective blends. PEO diluted in PVPh is susceptible to entangle more with PVPh than PVPh with itself. As for PMMA, since it formed the major fraction in the blends previously studied, the orientation of PMMA should depend on entanglement of PMMA with PVPh, which is expected to be higher than that of PVPh with itself.

Hydrogen bonding between polymer chains can modify the local organization of the chains and the density of chain entanglements. Athermal case blending rules proposed by Wu[35] and by Tsenoglou[36] allow prediction of molecular weight between entanglements M_e for blends for which interactions do not modify M_e. Negative deviations indicate a repulsive effect of thermodynamic interactions on entanglement probability, and inversely, positive deviations caused by attractive effects increase entanglement probability. Therefore, the blend composition for which a maximum in interaction (in either number of strength) occurs should also exhibit a higher molecular weight between chain entanglement and a higher orientation than expected for a weakly interacting blend. However, the sharpness of the observed orientation maximum far exceeds that expected from a possible chain entanglement increase due to deviations from the athermal blending model.

Therefore, it is proposed that chain entanglement can explain the relative orientation of each component in the blend but is less apt to explain the magnitude of the observed maximum in PEO orientation at 30 wt %.

Influence of Hydrogen Bonds on Orientation. A second important factor used to explain orientation is chain interactions, which affect the chain friction coefficient. The polystyrene (PS)/poly(vinyl methyl ether) (PVME) system, characterized over the whole composition range by Abtal and Prud'homme,[37] shows some similarities to PVPh−PEO blends. The PS and PVME orientations are also going through a maximum, which was related to a maximum in interaction strength.[37] In the present case, hydrogen bonds clearly form the dominant interaction in the blend. This system was selected specifically because PEO−PVPh hydrogen bonds were found to be stronger than PVPh−PVPh or PVPh−PMMA hydrogen bonds.[12] The fact that the orientation maximum occurs at a composition close to 1:1 mole ratio points to the possibility that this maximum be related to a maximum in interactions in the blend. If one considers the hydrogen bonds contribution to enthalpy of the system to be the driving force in miscibility, this enthalpy should be maximum at a 1:1 mole ratio, since at this composition the same numbers of hydroxyl and ether groups are present and are therefore apt to form an optimal hydrogen bond network. However, it may not be justified to neglect entropic contributions to miscibility in this specific case, considering the low molecular weight of PVPh. It is therefore necessary to rely on FTIR and NMR spectroscopy results, which can both be used to assess the composition at which the maximum in either strength or number of hydrogen bond interaction does occur.

A FTIR study by Moskala, Varnell, and Coleman[11] shows that hydrogen bonds occur both at low (20 wt %) and high (80 wt %) PEO composition, which was confirmed by a study by Qin, Pirez, and Belfiore.[12] No quantification is reported, and since the absorptivity ratio can vary, the composition at which the maximum in hydrogen bond interaction between PVPh and PMMA occurs cannot be assessed directly from the reported spectra.

Zhang, Takegoshi, and Hikichi[38] measured via high-resolution solid-state ^{13}C NMR spectroscopy the relaxation times ^{1}H T_1, $T_{1\rho}$, and T_2 for the PVPh−PEO blends. Values of T_2 show that mobility is restricted, as compared to pure PEO, in 27 wt % PEO blends. For 42 and 69 wt % PEO, a second T_2 appears, indicating that some PEO molecules acquire a larger mobility in the blend. This more mobile fraction has a T_2 value close to that of amorphous PEO and is therefore proposed to consist of chains not interacting with PVPh. The maximum impingement on mobility due to hydrogen bond interactions with PVPh occurs near 27 wt %. Although no intermediate concentrations were measured using NMR, this composition is in agreement with the observed position where the maximum in orientation occurs. Beyond the optimal concentration (close to the 1:1 ratio of interaction units), part of the PEO chains are more mobile and therefore either are less deformed or relax more readily after deformation. The mobility should be related to lower values in chain friction coefficients, to lower entanglement densities and M_e, and to faster relaxation times, which all affect the final observed orientation.

The occurrence of a concentration where hydrogen bonds are optimized near 30 wt % can also be related to the fact that PVPh chains start to orient themselves only from this concentration up, dragged along by the PEO chains via hydrogen bond coupling. This same phenomenon is observed for PVPh in a PMMA major phase.[6]

Conformation-Independent Comparison of Orientation. When using infrared spectroscopy, measurements are always a function of both the orientation of the segment and of the angle α formed between the segment and the vibrating dipole. The latter depends on the local average conformation of the segment and is usually determined, for the pure polymer, either via comparison with results from another technique or via simulations. When studying blends, it is normally assumed that the α angle value is the same for blends than for the pure polymer. One rarely has a choice to use this approximation, since many orientation measurement techniques (such as birefringence) give an overall value of the orientation, not allowing for quantification of components separately. Furthermore, this approximation is quite justified for blends showing weak interactions, where the overall conformations are not believed to be affected by blending. As the interaction strength increases, however, the possibility that conformations rearrangements occur within the blend also increases. Before concluding on the effect of hydrogen bonds, it must be first determined whether the observed variations in orientation factor stem from real changes in the orientation of the gauche segments or whether they are related to a conformational change with composition, which in turn would change the value of the α angle that should be used to calculate $\langle P_2 \rangle$.

Our research group has proposed the use of $\ln(\Delta P_2/\Delta\lambda)$ values as a function of the inverse of temperature as a conformation-independent means of comparing orientation.[6] It was shown that, for the PVPh−PMMA blend, an Arrhenius-type relationship was obtained:

$$\frac{\Delta P_2}{\Delta \lambda} = K_a \exp(\Delta E_a/RT) \tag{3}$$

where K_a is a system-related constant, R is the gas constant, T is the draw temperature, and ΔE_a is the apparent Arrhenius activation energy of combined deformation and relaxation processes. More important,

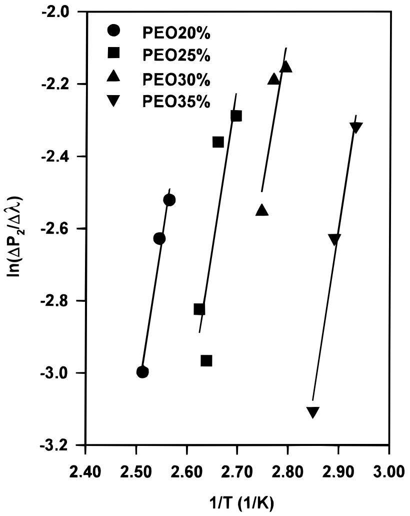

Figure 5. $\ln(\Delta P_2/\Delta\lambda)$ variations as a function of temperature for PEO in the PEO−PVPh blend.

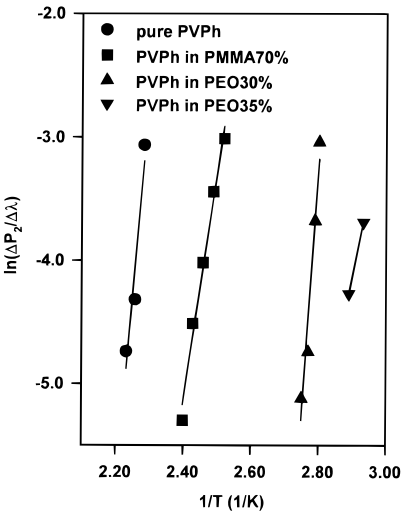

Figure 6. $\ln(\Delta P_2/\Delta\lambda)$ variations as a function of temperature for PVPh in various blends.

Table 1. Activation Energies and Maximum Orientation Factor of Various PEO−PVPh Blend Compositions

composition	$\Delta E_a/R \pm 1$, 10^{-3} K^{-1}	$\Delta E_a \pm 10$, kJ mol^{-1}	$\langle P_2\rangle_{max} \pm 0.02$
20 wt % PEO	9.5	79	0.10
25 wt % PEO	9.4	78	0.14
30 wt % PEO	8.6	72	0.15
35 wt % PEO	9.4	78	0.11

Table 2. Activation Energies and Maximum Orientation Factor for PVPh in Different Systems

polymer	$\Delta E_a/R$, 10^{-3} K^{-1}	ΔE_a, kJ mol^{-1}	$\langle P_2\rangle_{max}$
pure PVPh	33 ± 2	275 ± 15	0.05
30 wt % PEO−PVPh blend	37 ± 2	310 ± 15	0.06
70 wt % PMMA−PVPh blend	19 ± 1	160 ± 10	0.15

the slope of $\ln(\Delta P_2/\Delta\lambda)$ versus $1/T$ does not depend on the α angle of the vibration moment used in infrared spectroscopy to calculate $\langle P_2\rangle$. Comparing slopes of these graphs allows to compare orientation behavior of a specific polymer in different systems whether the local conformation changes or not. This is however more difficult in the case of PEO, since the relationship is not linear and the errors associated with the measurements large. As mentioned previously, tangents to the curves were drawn at $\lambda = 1.5$ and 3.0. The slopes of the first tangent are used in the data analysis. For the second tangent, for which an additional relaxation process is believed to be present, a negative activation energy is obtained, indicating that this empirical approach is not applicable in condition where a change in main relaxation mode is occurring.

As can be seen in Figure 5 and in Table 1, ΔE_a derived from the slopes of $\ln(\Delta P_2/\Delta\lambda)$ versus $1/T$ for the gauche conformers of PEO at the beginning of the stretching process (for $\lambda = 1.5$) are comparable, within experimental error, for PEO20%, PEO25%, PEO30%, and PEO35% blends. The maximum in orientation observed for the PEO30% at $\lambda = 1.5$ could not, therefore, be explained by changes in the deformation−relaxation process, as expressed by ΔE_a, unless these changes cancel out or unless the changes are within experimental error, which is improbable if one considers that the change in orientation is almost 2-fold. These results strongly suggest that a change in local conformation occurs with composition, but are not totally conclusive, and further work will be necessary to verify this point.

Paucity of data on PVPh precludes the use of this approach for this component of the blend. However, in this case, it is possible to compare PVPh in different systems. Results for pure PVPh, PMMA/PVPh blend with 70 wt % PMMA, and PVPh/PEO with 30 wt % appear in Figure 6. ΔE_a derived from slopes are reported in Table 2. Values reported for PVPh in the 35 wt % PEO blend will not be considered in this discussion, since it was obtained with only two data points, which is insufficient even for a rough approximation of the error. For the remaining three values, it is interesting to note that pure PVPh and PVPh in the 30 wt % PEO blend have similar ΔE_a values, within experimental error. These exhibit comparable orientation. For the PVPh in PMMA blends, where ΔE_a was approximately half of that for the previously studied systems, the orientation factor reached considerably higher values. The observed tendency for a high orientation corresponding to a low activation energy therefore holds true, within experimental error, for the PVPh/PEO system.

Conclusions

In the PVPh/PEO blends, the presence of a nonnegligible PEO orientation is significant and is attributed to the hindering effect of hydrogen bonds on relaxation. Curves of the orientation function $\langle P_2\rangle$ versus draw ratio λ are not linear, which indicates that relaxation is nevertheless relatively rapid. At the beginning of the stretching process, PEO and PVPh do not have the same propensity to orient, as can be seen from the values of $(\Delta P_2/\Delta\lambda)$ values at small draw ratios. Nevertheless, after a sufficient laps of time, their behavior seem to become cooperative, and $(\Delta P_2/\Delta\lambda)$ values become comparable.

The most salient observation of the present work is that PEO goes through a maximum orientation at 30 wt % PEO. PVPh seems to be just beginning to orient at this composition. It is proposed that this maximum is related to a maximum in the number of hydrogen bond interactions near this composition. These interactions are liable to affect chain friction coefficient, chain entanglement density, or the local conformation, as reflected by the α angle.

Comparing the approximately linear curves of $\ln(\Delta P_2/\Delta\lambda)$ as a function of the inverse of the draw temperature for PEO at different compositions indicates that the deformation occurs in a similar fashion energywise. For this reason, it is proposed that the orientation maximum mainly reflect changes in the local average conformation of gauche segments which result in changes in the α angle. Hydrogen bonds would therefore be responsible for a decrease in relaxation times of PEO and for important changes in average conformation. However, the maximum orientation could also result from changes in chain friction coefficient or chain entanglement density, which can be related to, or be independent of, the average conformation. Further work in molecular modeling and rheology of this system is needed to clarify these points.

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