Macromolecules **1997,** *30,* 8425−8432

Orientation Behavior in Uniaxially Stretched Poly(methyl methacrylate)−Poly(4-vinylphenol) Blends

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Received April 11, 1997; Revised Manuscript Received October 1, 1997[⊗]

ABSTRACT: Infrared spectroscopy has been used to investigate the orientation behavior of poly(methyl methacrylate) (PMMA)−poly(4-vinylphenol) (PVPh) blends in uniaxially stretched films, for 0−54.5 wt % PVPh blend content. The orientation of PVPh chains increases upon addition of the lower T_g PMMA component, whereas the orientation of PMMA chains decreases upon addition of the more rigid PVPh. This behavior is proposed to be related to changes in hydrogen bonds and/or chain entanglements. As the number of hydrogen bonds formed between PMMA and PVPh increases, the system is rigidified, and the resulting number of chain entanglement decreases, resulting in a lower orientation function P_2 of the PMMA chains. At the same time, the number of hydrogen bonds between PVPh chains decreases, decreasing the number of intractable loops formed by some of these interactions. The result is a higher orientation of PVPh chains in the blends. A method is used to verify that changes in conformation, and therefore in α angles, are not responsible for this observation, through the use of the slope of ln $(\Delta P_2/\Delta\lambda)$ vs $1/T$. This slope, which corresponds to the apparent activation energy, ΔE_a, of the orientation−relaxation process, is proposed as a useful tool for comparing the behavior of a polymer in a pure state and in various blends.

Introduction

Orientation can be defined as the preferential alignment (either uniaxial or biaxial) of polymer chains or segments when submitted to an external force. Significant changes in properties result from the chain reorganization,[1] which can be either detrimental (such as weaknesses introduced by orientation in molded parts) or beneficial (such as an increase in tensile modulus and strength in the fiber direction during fiber extrusion), depending on the process used and on the properties sought.

Many factors influence the orientation behavior of polymer chains, including crystallinity, phase separation, free volume, chain rigidity, molecular friction, interchain interactions, and chain entanglements. These factors are often interdependent, interchain interactions leading to an increase in chain rigidity and molecular friction coefficient.

Entanglements and interchain interactions are probably the factors most often used to explain the orientation behavior of amorphous miscible blends, on which we will focus in the present article. The behavior of known systems has been reviewed by Jasse, Tassin, and Monnerie.[2] Behavior of blends varies greatly, but, in most cases, orientation achieved by both partners in a blend is either similar or greater than that of the pure polymers. When greater, the variation is usually monotonous with composition, such as in the case of the polystyrene (PS)−polyphenylene oxide (PPO) blend,[3−6] of the polystyrene−poly(*o*-chlorostyrene) (PoCS),[7] or of polymethyl methacrylate (PMMA)−polytrifluoroethylene (PF_3E).[8] In some instances, the orientation of one of the components of the blend does not vary with composition (for example, in the case of polyethylene oxide (PEO) when blended with PMMA[9]) or varies with tacticity of the chain (as shown for polyvinyl chloride (PVC) when blended with poly (α-methyl-α-(*n*-propyl)-*β*-propiolactone) (PMPPL)[10]). Cases which are more difficult to explain include the presence of a maximum in the orientation function for a given composition (as in the case of poly(vinyl methyl ether) (PVME)−PS[11,12]) or systems in which one partner exhibits a lower orientation in the blend as compared to the pure polymer (as in the case of PMMA−styrene-*co*-acrylonitrile blend (SAN)[2,13]).

Stronger interactions have been found to affect profoundly the orientation behavior. Intermolecular ionic interactions have been shown to result in very high segmental orientation in ionomer-based blends.[5,14] In this case, it is believed that ionic aggregations act as effective cross-links.

Since the energy of hydrogen bonds most often lies in the range 1−10 kcal/mol, the strength of hydrogen bonded interactions is much larger than that of van der Waals interactions (which are of the order of 0.2 kcal/mol) and weaker than that of ionic interactions. Contrary to ionic interactions, however, hydrogen bonds are directional. Therefore, the effect of hydrogen bonds on orientation behavior of polymer chains in miscible blends is expected to be different from that of ionic and/or van der Waals interactions. For this study, therefore, a blend for which miscibility had been established and for which quantitative evaluation of changes in hydrogen bonding was possible was selected, namely, the poly(vinylphenol) (PVPh)−PMMA blend. Previous work on this system has clarified its phase behavior,[15] the association mechanism of hydrogen bonds, and the effects of temperature on hydrogen bonds.[16] It is hoped that the present study will help gain a better understanding of the influence of specific interactions on orientation.

Experimental Section

Sample Preparation. Poly(methyl methacrylate) and poly(4-vinylphenol) (PVPh) used in this study were purchased from Polysciences Co. The weight-average molecular weights of PMMA and PVPh are 100 000 and 30 000 g/mol, respectively. PMMA−PVPh blends with various compositions were prepared in a Rheocord System 40 mixer at 180 °C for 30 min. Torque monitor showed no variation, indicating that no

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.

S0024-9297(97)00498-1 CCC: $14.00

Table 1. Properties of Polymers and Blends Used in This Study

sample	PVPh/PMMA in wt	molecular weight		T_g, °C
		mol	g/mol	
PMMA	0/100	0/100	100 000	94
PM19	10/90	8.5/91.5		99
PM37	30/70	26.3/93.7		114
PM54	54.5/45.5	50/50		129
PVPh	100/0	100/0	30 000	156

significant degradation took place during blending. The properties of the blends are listed in Table 1, in which PM19 represents the blend containing 10 wt % PVPh, 90 wt % PMMA, and so forth. X-ray diffraction was used to verify that the pure polymers and their blends were amorphous. Polymer films were compressed at 180 °C between two half-dies exhibiting a mirrorlike polished surface. After releasing the pressure, they were slowly cooled 2 or 3 h while maintained between the dies to eliminate the internal stress due to the compression. Birefringence was used to check that no compression-induced orientation remained after this time.

***T_g* Measurements.** The glass transition temperature (T_g) of samples was determined on a Perkin-Elmer differential scanning calorimeter Model DSC-4, calibrated with indium, at a heating rate of 20 °C/min and a sample weight of 10−15 mg. The T_g value was taken as the midpoint of the heat capacity jump. The T_g values of pure PMMA and PVPh were 94 and 156 °C, and an almost linear relationship was found between T_g and blend composition.

Film Stretching. Polymer film stretching was performed between two fixed clamps in a temperature controlled (±1 °C) chamber. Rectangular strips were cut from the compression molded film and each extremity was covered with Pyrotape (Aremco) to prevent slippage during stretching and inserted between the clamp jaws. The selected draw ratio was attained by raising the upper clamp at an exponential velocity, giving a constant strain rate, chosen as 0.1 s^{-1}. The drawing temperature was set at $T_g + 10$ °C for each sample. Before drawing, the sample was left at the draw temperature at least 15 min in order to reach the thermal equilibrium. After stretching, the sample was immediately quenched to room temperature by using a circulating fan. A maximum of 2−3 s passed between the end of stretching and the cooling of oriented samples below their T_g. For pure PVPh, a two-stage stretching procedure was used, as described in a previous paper.[17]

Orientation Measurements. A wire-grid polarizer was used to record spectra of films stretched at various draw ratios after in a Mattson SIRIUS 100 FTIR spectrometer equipped with a MCT detector. For each spectrum, 100 scans were taken at a resolution of 2 cm^{-1}. Oriented films were rotated by 90° in order to obtain spectra parallel and perpendicular to the polarization plane of the infrared beam. Dichroic ratio measurements were used to calculate the second moment of the orientation distribution function $\langle P_2(\cos\theta)\rangle$ (abbreviated P_2 in the text) by using the following equation:

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

in which $R_0 = 2\cot^2\alpha$, α being the angle between the dipole moment vector of the vibration under consideration and the chain axis and θ the angle between the chain axis and the stretching direction. R, the infrared dichroic ratio, is defined as $A_{\|}/A_{\perp}$, where $A_{\|}$ and $A_{\perp}$ are the integrated intensities of the vibration band in the parallel and perpendicular direction, respectively, to the film stretching direction.

The band located at 759 cm^{-1}, which is assigned to a CH_2 rocking vibration, was used for the measurement of dichroic ratio of the PMMA chains by using the α angle previously determined by Zhao, Jasse, and Monnerie[8] of 17°.

For PVPh, the CH in-plane bending vibration of aromatic ring at 1014 cm^{-1} was chosen for the measurement of the orientation function. For this vibration, in the pure polymer, an α angle of 90° was previously proposed.[17]

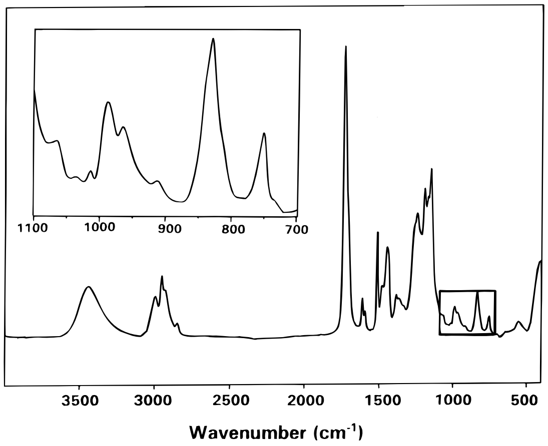

Figure 1. FTIR spectra of pure PMMA, pure PVPh, and a 30 wt % PVPh−PMMA blend recorded at room temperature.

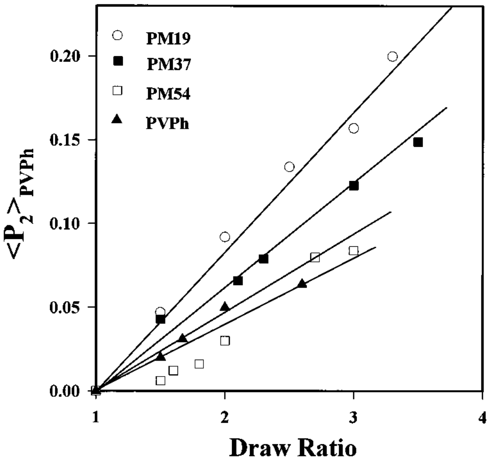

Figure 2. Orientation function P_2 versus draw ratio for the PVPh chain in its pure state and in blends with PMMA at draw temperature $T_D = T_g + 10$ °C.

In the blends, it was observed that those two vibration bands are at the same position as in the pure polymers, within experimental error, and are not superimposed with other vibrations, as shown in Figure 1. By use of the hypothesis that the α angles are the same in blends and in pure polymers, the orientation functions of both PMMA and PVPh chains were calculated from the areas of those two peaks determined after fixing a linear baseline.

Results and Discussions

Description of the Orientation Behavior of Polymer Chains in the Blends. The orientation function P_2 of PVPh in blends as well as in the pure polymer is reported in Figure 2. These were measured at room temperature after quenching the samples deformed at $T_g + 10$ °C with an exponential deformation rate of $s = 0.1$ s^{-1}. Blends containing more than 54.5 wt % PVPh are extremely brittle and have therefore not been studied due to the difficulty encountered in making sufficiently thin films and in stretching these films. In the composition range studied, PVPh chains reach a higher orientation function in blends than in the pure state. At the same draw ratio, within experimental error, the blend with the lowest percentage of PVPh content, PM19 with 10 wt % PVPh, exhibits a P_2 which is almost twice that of pure PVPh.

The orientation function P_2 of PMMA chains in the blends was measured from the CH_2 rocking vibration

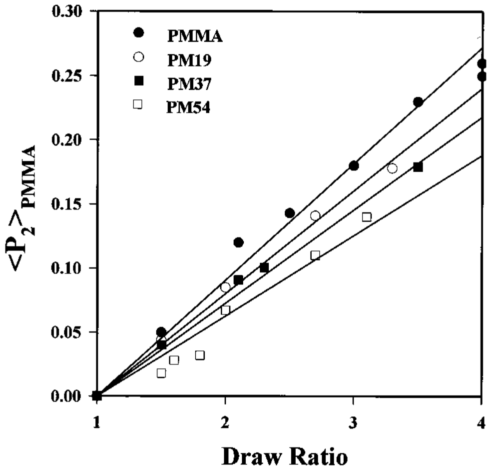

Figure 3. Orientation function P_2 versus draw ratio for the PMMA chain in its pure state and in blends with various PVPh composition at draw temperature $T_D = T_g + 10$ °C.

mode and is shown in Figure 3. For this polymer, at the same draw ratio, the orientation function P_2 of PMMA reaches a higher value in the pure state than in the blends. With a slight increase in PVPh content, the orientation of PMMA chains decreases, although some fluctuations are evident. As mentioned in the introduction, this behavior is highly unusual. Two main factors can be invoked to rationalize this behavior: interchain interactions and chain entanglements.

Intermolecular interactions, as defines by the χ interaction parameter, are often used to rationalize the behavior of miscible blends. Although the value of the χ parameter has not been determined for the PVPh−PMMA blend to our knowledge, a model compound study strongly suggests that it should be negative,[19] which would also correspond to the fact that interchain hydrogen bonds are known to occur.[16,20] However, strong interchain interactions should lead to a decrease in relaxation because of the increase in chain friction, and should therefore lead to an increase in P_2, which is definitely not the case in this system.

Entanglements have been found to be an alternative rationalizing concept for orientation of miscible blends. Indeed, in the case of the PMMA−SAN blend,[2,13] the lower orientation for PMMA in the blend was proposed to be attributed to the increase in molecular weight between entanglement, M_e, upon addition of SAN, although the authors stressed that friction coefficient also played a role in relaxation. The increase in orientation of SAN upon blending, likewise, was attributed to a decrease in chain entanglements upon blending. A similar phenomenon could also explain the observed behavior of the PMMA−PVPh blend. Unfortunately, in the present case, due to the brittleness of PVPh, it was not possible to measure the value of M_e for this polymer, neither does it appear in the literature to our knowledge. Therefore, at the moment, no formal experimental evidence can confirm this proposed explanation.

To quantitatively evaluate the magnitude of orientation behavior differences of both chains in the blends, the slopes of the graphs of P_2 against draw ratio λ, shown in Figures 2 and 3, have been plotted with respect to the PVPh mole fraction in Figure 4. It can be seen that, in the range studied, a linear relationship is observed for the orientation behavior of PMMA. This shows that, in a PMMA-rich blend, for a given set of draw conditions, the orientation of PMMA chains linearly decreases with the increase of PVPh content in the blends. The PVPh chains, which always exhibit higher orientation in blends than in the pure state, also experience a decrease in orientation when more PVPh is blended in. Eventually, at a 1:1 mole ratio of PVPh to PMMA, which corresponds to 54.5 wt % PVPh or blend PM54, PVPh chains have an orientation behavior more similar in the blends than in pure PVPh.

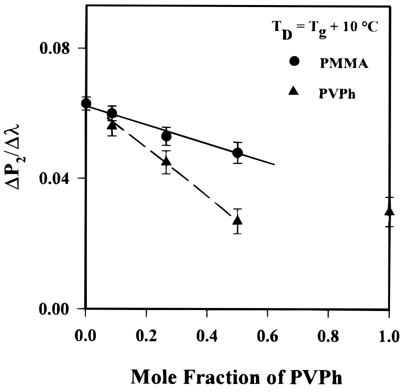

Figure 4. Relationship between the slope of P_2 vs λ and PVPh composition of the blends.

It must be noted that, in this respect, PMMA−PVPh differs from PMMA−SAN; PMMA was the higher T_g component of the blend in PMMA−SAN, and its orientation varied very little from 0 to 40% SAN, while it decreased much more markedly from 40 to 80% SAN. A second system which showed a decrease in orientation is PMPPL-PVC,[10] where, on the other hand, the orientation of the higher T_g component of the blend did not vary. Therefore, the present blend behavior appears to be rather unique. Three factors which could explain this uniqueness will be discussed in more details in the present article: Phase behavior, the presence of hydrogen bonds, and the effect of changes in conformation.

Effect of Phase Behavior on Orientation. The phase behavior of the PVPh−PMMA system studied here has been investigated previously using DSC and DMTA measurements.[15] It was shown that the blend is miscible, but not totally homogeneous, since there exists small amounts of lower T_g phases with domain sizes of the approximately 30 Å in the blend.[15] The existence of these domains was linked to difference in behavior of segments with tacticity. The effect of these domains on the overall orientation function must first be discussed.

It is well established that the orientation of blends is markedly affected by phase behavior. The most striking effect is observed for immiscible blends, where the minor phase often exhibits a low or no orientation, whether its T_g is higher or not than that of the major phase.[21,22] This stems from the fact that orientation strongly depends on the drawing temperature, which is generally chosen slightly above the glass transition temperature of the major phase. The orientation behavior of a chain is governed not only by chain alignment along the stretching direction under extensional forces but also by chain relaxation that inevitably occurs during stretching and causes a loss of orientation. When the T_g of the minor phase is higher than that of the major phase, at a stretching temperature slightly above the T_g of the major phase, the external force only changes the shape of the minor phase[21] or breaks it up into smaller subdomains.[22] Therefore, no chain orientation is developed in the minor phase. In the opposite case, where the T_g of the major phase, which fixes the stretching

Table 2. Percentages of Intra- and Inter-Hydrogen Bonds in the Blends

sample	inter-hydrogen bonds, mol %	intra-hydrogen bonds, mol %	free O−H, mol %
PM19	95[a]	5[b]	0[b]
PM37	75[a]	25[b]	0[b]
PM54	45	60[b]	4[b]
PVPh	0	70[b]	40[b]

[a] Estimated via interpolation. [b] Semi-quantitative evaluation.

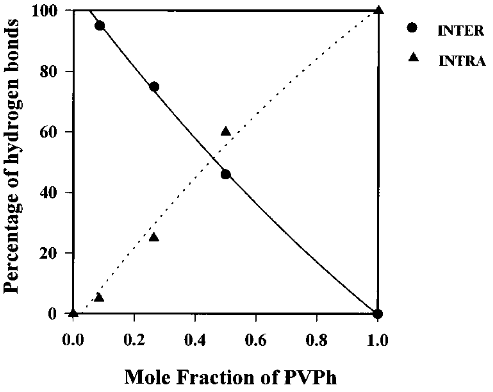

Figure 5. Changes in hydrogen bonds with PVPh composition.

temperature, is higher than that of the minor phase, it is the chain relaxation during stretching that explains the absence of orientation. Since chain relaxation is proportional to the temperature in the viscoelastic state, the higher the temperature, the faster the speed of relaxation, which leads to a lower or no orientation.

The latter case is the situation of the PVPh/PMMA blend system studied here. The small phase-separated domains have a low T_g as compared to the matrix phase. Therefore, it is expected that the PMMA chains in these domains will have a low or no orientation.

It was estimated that approximately 2 wt % of the lower T_g phases exists in the blends. The 25% decrease in overall orientation of PMMA observed for the PM54 blend therefore cannot be attributed solely to the presence of this minor phase. Other factors must be responsible for the decrease of PMMA chain orientation with the increase of PVPh content in the blends.

Effect of Hydrogen Bonds on Orientation. PVPh forms not only interassociated hydrogen bonds between hydroxyl groups of PVPh and carbonyl groups of PMMA but also intraassociated hydrogen bonds between two hydroxyl groups of PVPh.[16] Table 2 lists the percentage of free O−H groups and of intra- and interassociated hydrogen bonds in the blends studied here, whereas Figure 5 reports the relative evolution of inter- and intrachain hydrogen bonds with composition. It must be noted that, although these measurements were performed at room temperature, determination of the number of hydrogen bonds at temperatures close to T_g were also performed, and it was shown that, at $T_g + 30$ deg, only 3.5% of the initial hydrogen bonds were broken, which is small compared to variations in the number of hydrogen bonds with composition. Therefore, the use of the percentages determined at room temperature is justified, even though the orientation is performed near T_g.[18] With the increase of PVPh content in the blends, the percentage of interassociated hydrogen bonds decreases, while the percentage of intraassociated hydrogen bonds increases. At a 1:1 mole ratio of chain repeat units between PMMA and PVPh (which corresponds to the PM54 blend), there are approximately the same number of inter- and intrachain hydrogen bonds (45% vs 60%), considering the semiquantitative nature of the measurements performed to determine the hydrogen bond percentage.[17]

The only quantitative investigation, to our knowledge, of the orientation function of an amorphous system presenting variations in the number of hydrogen bonds was performed on a copolymer. Zhao, Bazuin, and Prud'homme[23] observed the orientation behavior of poly(styrene-*co*-methacrylic acid) (S−MAA) copolymer with different acid content up to 12.3 mol%. As compared to polystyrene, they found that the presence of hydrogen bonds in the copolymers does not lead to any increase in chain orientation when taking T_g as a reference temperature. A study on blends of S−MMA copolymers with poly(styrene-*co*-4-vinylpyridine) copolymers yielded the same conclusion.[24] These studies showed without ambiguity the superiority of ionic interactions over hydrogen bonds in improving the orientation of polymer blends. However, only 6% of MMA groups were present. FTIR spectra showed that the percentage of these groups which form a hydrogen bond is small (approximately 10−20% as estimated from the area of hydrogen-bonded C=O vs free C=O valence vibrations). Under these conditions, the hydrogen bond network may not exist, and only isolated chains would be affected by interaction formation during the orientation process. Therefore, this system did not allow full understanding of the effect of hydrogen bonds on orientation.

Wang and Cooper [25,26] studied the separation of polymer blends forming hydrogen bonds without, however, comparing the observed orientation behavior to that of the pure polymers or without quantifying the hydrogen bonds in the systems they studied.

In the PMMA−PVPh system studied here, it was observed that, for pure PVPh and for all blends studied here, the orientation of PVPh chains is lower than that of PMMA chains. The orientation of PVPh was also much lower than that of PS[17] which has a similar chain repeat, except for the absence of the para-substituted hydroxyl group in PVPh.

The fact that orientation is lowest for the compositions where intrachain hydrogen bonds dominate (PM54 and pure PVPh) indicates that intraassociation is not favorable to orientation. This could possibly be related to the association geometry, which may hinder chain orientation through the formation of intrachain loops along a given polymer chain. These would orient much less than a chain which is only submitted to "regular" chain entanglements, since the density of chain entanglement is generally much smaller than the density of hydrogen bonds. As a result, the size of the loops created by hydrogen bonding, and therefore the number of units between these interactions, is possibly much smaller than that of entanglements. Furthermore, successive units can be linked in this fashion, creating a region of high rigidity, contrarily to the occurrence of entanglements. The same type of behavior could explain the lower P_2 values observed for S−MAA as compared to the polystyrene homopolymers which do not contain hydrogen bonds,[23,24] since intraassociated dimers are present in S−MAA.[27,28]

Of course, hydrogen bonds are also expected, as any other interchain interaction would, to increase the friction coefficient, therefore decreasing the relaxation time and leading to a higher value of the P_2 orientation function. However, the magnitude of this effect is clearly small in this case, since the overall orientation is seen to decrease.

In blends of lower PVPh content, interassociated hydrogen bonds between hydroxyl groups of PVPh and carbonyl groups of PMMA become more abundant than intrachain hydrogen bonds. These are proposed to play a different role in the orientation behavior of PVPh chains. For example, in PM19, more than 95% hydroxyl groups are interassociated with carbonyl groups of PMMA. These inter-hydrogen bonds cannot lead to intrachain loops, which are believed to be detrimental to orientation, as mentioned above. They can, however, act as rigidifiers, changing the local organization and entanglement mode of the chains. Upon stretching, the orientation behavior at low PVPh content is probably governed by the PMMA network. The external force deforms the PMMA matrix, leading to orientation of PMMA chains. The density of entanglements is presumably decreased, which leads to a lower orientation of PMMA as compared to the pure polymer.

At the same time, PMMA chains drag PVPh along because of the presence of inter-hydrogen bonds. As a result, the orientation function of PVPh segments forming hydrogen bonds with PMMA tends to be similar to the orientation of PMMA chains. With the increase in PVPh content from PM19 to PM37, the percentage of interassociated hydroxyl groups can be estimated via intrapolation to be reduced from 95% to 75% in the blends. Therefore, the efficiency of interhydrogen bonds to transfer the force between the two types of chains decreases. Eventually, for PM54, which has a 1:1 mole fraction of chain repeat units, the intraassociated PVPh mers become dominant in the blend, and the contribution of interassociated hydrogen bonds to the orientation of PVPh chains becomes secondary. As a result, the orientation behavior of PVPh chains becomes similar to that of the pure state.

Effect of Conformational Changes on P_2. One of the major approximations that is made in most polymer blend studies involving FTIR is that the α angle of the vibration studied is the same in the pure polymer and in the blend. Rarely can one verify this hypothesis, since vibration band overlap severely limit the number of vibrations for which the dichroic ratio can be measured. The α angle is the angle between the vibration vector and the chain axis, which is defined for an average conformation in the blend. The definition of this chain axis is far from being straightforward, and the existence of an average conformation which resembles an actual minimum energy conformation should be an interesting element for understanding what actually is the amorphous phase, along with data from other techniques such as X-ray scattering or molecular simulations. More directly of interest for orientation studies is the fact that this angle changes with the average chain. When the approximation is made that the α angles does not change in the blend, one is actually making the approximation that the overall distribution of conformations does not change. This approximation is acceptable when studying a blend showing only weak interactions, since these would probably be insufficient to disrupt appreciably the conformation distribution of the chains, which is energy-dependent.

When dealing with polymers forming stronger interactions, the energetics involved in these interactions are sufficiently large to disrupt appreciably the conformation distribution. Therefore, this issue becomes much more important in blends containing stronger interactions such as hydrogen bonds. Unfortunately, as is often the case, band overlap is too important to allow a verification of the α angles of both polymers of the blends. The possible effects of changes in P_2 with variations in α are nevertheless important to ascertain in order to understand better the behavior of the present polymer system.

In order to discuss this issue, it is interesting to recall how the determination of α angles for pure PVPh was performed, since it is by no means an absolute determination. In the first article published on this subject,[17] an average value of α of 90° for the CH_2 vibrations was proposed on the basis of the observation that the CH_2 asymmetrical and symmetrical valence vibrations, the CH_2 scissoring vibration vectors and an in-plane bending vibration of the aromatic ring all yielded, within experimental error, the same P_2 value.[17] This definition, although fitting well the experimental data, was not unambiguous, since other conformations could have lead to such an observation. However, the 1611-cm^{-1} vibration, which can be attributed to a quadrant stretching mode of the aromatic ring, has since been measured. Its resultant dipole is perpendicular to the C−O vibration of the hydroxyl group, and it is sensitive to the rotation of the aromatic ring with respect to the aliphatic chain backbone. Determination of its α angle using the P_2 determined for a trans conformation of the backbone yields a value of 42°, with an estimated error of 4%, which corresponds remarkably well with the minimum energy conformation, as determined by molecular modeling, for which this angle would be 40°. This therefore supports the validity of the proposed conformation and α angles. It must be stressed, however, that this represents an average over all possible conformations and not the only existing conformation in the amorphous state.

Unfortunately, due to vibration overlaps, no verification of the conformation is possible for the blends. However, it is interesting to note that the minimum P_2 value is obtained when the $(R_o + 2)/(R_o - 1)$ value reaches its maximum in terms of absolute value, which happens when α is equal to 0° or 90°. This is precisely the value used in this study for the vibrations quantifying the orientation of PVPh in both the pure polymer and the blends. Therefore, conformational changes in the blend could lead to lower P_2 values than reported.

In the case of PMMA, however, changes in the conformation could lead either to lower or higher P_2 values and could in effect change dramatically the interpretation that one makes of the orientation behavior of this system. For this reason, an orientation-related parameter which would be independent on the actual α angle value used was sought.

Conformation-Independent Comparison of Orientation Behavior. Taking T_g as the reference temperature, the orientation function measured as a function of drawing temperature for PMMA and PVPh chains in the PM37 blend, which contains 30 wt % or 26.3 mol % PVPh, is shown in Figure 6. This composition has been selected since it was the highest PVPh concentration at which detailed information could be obtained at a relatively high ΔT with respect to T_g. The fraction of interassociated hydroxyl groups is approximately 0.75. It can be observed that, with the increase in drawing temperature, both PMMA and PVPh chain orientation decreases in a similar way. Small differences can be found in the higher temperature range,

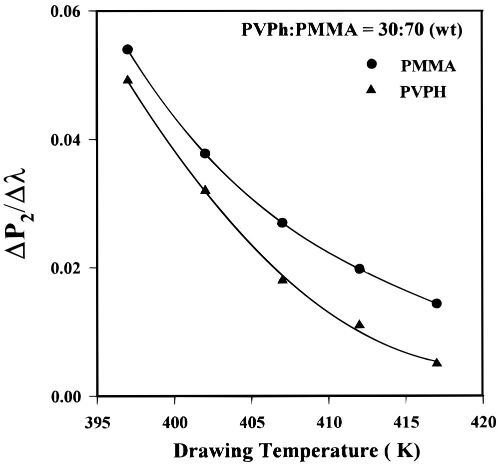

Figure 6. Relationship between the slope of P_2 vs λ and the draw temperature in 30 wt % PVPh−PMMA blend.

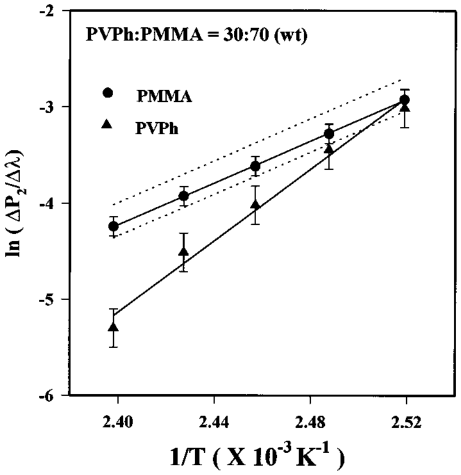

Figure 7. ln($\Delta P_2/\Delta\lambda$) versus $1/T$ for PMMA and PVPh chains in 30 wt % PVPh−PMMA blend. Upper dotted line represents values obtained by using an α angle of 27°, lower dotted line using 7°, and full line using the α angle of 17° proposed in the literature.

where the orientation of PVPh chains is slightly lower than that of PMMA chains.

The observed orientation change of PMMA chains in the blend can be replotted through ln($\Delta\langle P_2\rangle/\Delta\lambda$) versus $1/T$, as can be seen in Figure 7. A linear relationship is observed for PMMA chains. This is indicative of an Arrhenius behavior in the temperature range investigated, yielding

$$\Delta\langle P_2\rangle/\Delta\lambda = K_a \exp(\Delta E_a/RT) \qquad (2)$$

where K_a is a constant related to properties of the polymer chain and T is the stretching temperature. ΔE_a is the overall Arrhenius activation energy of the various processes involved, which include the initial orientation deformation and the subsequent, and often simultaneous, relaxation. From the slope of the graph reported in Figure 7, ΔE_a was calculated as 22 ± 1 kcal/mol for the PMMA chains in the blend.

Using eq 1 for P_2 and taking into account the fact that R_0 is constant for a vibration of a given polymer, while R represents the experimental data, one can write for ΔP_2

$$\Delta P_2\left(\frac{R_0+2}{R_0-1}\right) \times \Delta\left(\frac{R-2}{R+1}\right) \qquad (3)$$

If one replaces ΔP_2 in Eq. 2, one can write,

$$\ln \frac{\left(\dfrac{R_0+2}{R_0-1}\right) \times \Delta\left(\dfrac{R-1}{R+2}\right)}{\Delta\lambda} = \frac{\Delta E_a}{RT} + \ln K_A \qquad (4)$$

which, after rearrangement, yields

$$\ln \frac{\Delta\left(\dfrac{R-1}{R+2}\right)}{\Delta\lambda} = \frac{\Delta E_a}{RT} + \ln K_A - \ln\left(\frac{R_0+2}{R_0-1}\right) \qquad (5)$$

Therefore, as can be seen, a change in α, which only affects the value of R_0, will not affect the slope of the ln $\Delta P_2/\Delta\lambda$ vs $1/T$ graph, but will merely shift the line along the y axis. The ΔE_a calculated from the slope is independent of the value of the α-angle used to calculate P_2. Changes in conformation, which would affect α in unpredictable ways, will simply shift the curve along the y axis without changing its slope. These may, however, be translated in energy variations related to the ease in orienting and relaxing the new conformers as compared to those of the pure polymers. The use of ΔE_a in comparative studies could therefore lift any doubt pertaining to the effect of changes in orientation on α angle values, and therefore on calculated P_2 variations, in particular for blends presenting strong interactions, for which the possibility of conformational changes is more important.

In order to illustrate the relative magnitude of the shift, two dotted lines representing the changes occurring on the graph when using an α angle 10 deg higher or lower than the value proposed for pure PMMA have been plotted in Figure 7. As can be seen, the shift is not of the same order of magnitude in both directions, which is due to the cotangent function relating α to P_2.

It is also interesting to observe the temperature behavior of PVPh chains in blends in this figure. Unfortunately, errors are greater in this case, which is related to the lower intensity of the band used to measure the dichroic ratio. It is therefore difficult to ascertain whether, in this case, a linear relationship really holds. However, within experimental error, a linear regression can be drawn through the data and yields a value of ΔE_a of 37 ± 3 kcal/mol, a value quite different from that of PMMA. This strongly suggests that the deformation−relaxation modes of PVPh are different from those of PMMA in the blend.

Since ΔE_a is proposed as an α-insensitive comparison factor, other systems to which these values could be compared were sought. For PVPh, no reported data appeared in the literature, and evaluations for the pure polymer were too imprecise to be used. For PMMA, on the other hand, two sets of data from the literature were amenable to this type of calculations.

The first set is that of pure PMMA, as reported by Zhao, Jasse, and Monnerie,[8,30] PMMA chain orientation decreases with the increase of drawing temperature above T_g. If taking the experimental data of ref 29 and replotting it as ln($\Delta\langle P_2\rangle/\Delta\lambda$) vs $1/T$, it can be seen in Figure 8 that the PMMA chains in their pure state also follow, to a good approximation, a linear relationship. From the slope, it can be estimated that ΔE_a is 28 ± 1 kcal/mol for pure PMMA. Compared to the value of ΔE_a =22 kcal/mol for PMMA chains in the PM37 blend studied here, it can be proposed that the lower orientation behavior of PMMA chains in blend versus pure state is not due to the use of improper α angles for the

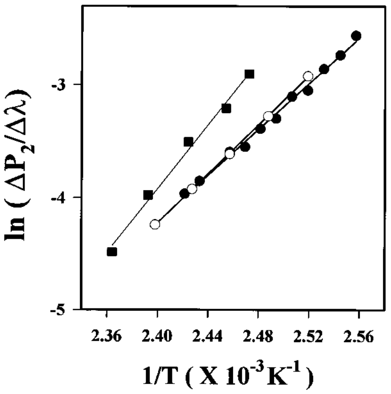

Figure 8. ln($\Delta P_2/\Delta\lambda$) versus $1/T$ relationship for PMMA: ■ pure PMMA, as plotted by using data taken from Figure 1 of ref 31, ○ PMMA in PMMA−SAN blend containing 25 wt % SAN, as plotted by using data taken from Figure 6d of ref 13, and ● PMMA in 30w% PVPh−PMMA blend.

blends, following a change of conformation, but to change in the activation energy of the processes involved in orientation and/or relaxation.

The second system was that the PMMA−SAN blend, for a 25wt % SAN composition.[13,30] A value of ΔE_a = 20 ± 1 kcal/mol was obtained from the slope of ln($\Delta\langle P_2\rangle/\Delta\lambda$) versus $1/T$ in Figure 8 for PMMA chains in this system, a value equal, within experimental error, to that of the PVPh-PMMA system studied here, which had an activation energy of 22 ± 1 kcal/mol. In both systems, PMMA orientation is lower than in the blend. Therefore, the PMMA behaves in a similar way in terms of orientation, notwithstanding the absence of hydrogen bonds in the PMMA−SAN blend. This indicates that the effect of hydrogen bonds may be taken into account in ΔE_a.

Possible Relationship between ΔE_a and Existing Theories on Deformation and Relaxation. In order to better understand the relationship between the Arrhenius activation energy of orientation−relaxation, ΔE_a, and the orientation behavior, it is interesting to recall the theories pertaining to these two overlapping processes.

Deformation theories have been the subject of numerous articles, although a definite, universal theory has still to be found. This is partly due to the inherent difficulty in isolating deformation from relaxation, whereas it is possible to follow relaxation alone by measuring the evolution of orientation with time after deformation.

Most existing models for deformation do not take directly into account the effect of temperature. The random chain or affine model of Kuhn and Grün,[32] as modified using Treloar's expansion,[33] is often used to describe deformation. It takes the following mathematic form:

$$\langle P_2 \cos \alpha\rangle = \frac{1}{5N}(\lambda^2 + 1/\lambda) + \frac{1}{25N}(\lambda/3 - 4/3\lambda^2) + \frac{1}{35N^3}(\lambda^2 + 3\lambda^2/5 - 8/(5\lambda)^3) \quad (6)$$

where N is the number of statistical segments between entanglement points. The first part of the equation represents the elastic contribution to deformation, whereas additional terms account for deviations from perfect elasticity. Ward[1] reports that it does not work very well for most polymers. Raha and Bowden[34] have proposed that N should be replaced by N_{eff}, the effective value of chain entanglements, which increases with increasing deformation. This increase in N_{eff} has been proposed to be related to interchain interactions, which behave as weak cross-links, and may therefore become weaker as deformation proceeds.[34] If this is the case, part of ΔE_a may be related to this decrease in N. An alternate mathematical expression also derived within the framework of the random chain model has been proposed more recently by Erman et al.,[35] which takes directly into account the end-to-end vectors of the chain both in the deformed and in the undeformed state. In this case, ΔE_a could be related to the value of the end-to-end vectors in the deformed states, since this value will be a function of interchain interactions. Other models have also been proposed or used, such as the pseudo-affine model. Again, the lack of consensus clearly reflects the experimental difficulty in isolating deformation from relaxation.

In the case of relaxation, the most widely used theory stems from the concept of chain reptation proposed by de Gennes,[36] coupled with the Doi and Edwards,[37,38] tube model, which describes the motion of polymer chains. In this theory, chain relaxation following a sudden deformation is described in three steps. First, Rouse chain relaxation between entanglements occurs with a relaxation time τ_A (step A). The second, longer process (step B), associated with relaxation time t_B, is the retraction of the primitive chain along the tube formed by the neighboring chains to recover its equilibrium contour length. Finally, in step C, the primitive chain leaves the deformed tube in order to reach an equilibrium isotropic conformation. The characteristic relaxation times τ_A, τ_B, and τ_C for the three steps have been given by[39,40]

$$\tau_A = (\xi b^2 N_s^2/6\pi^2 k_b T)^2 \quad (7)$$

$$\tau_B = 2(N_c/N_e)^2\tau_A \quad (8)$$

$$\tau_C = 6(N_c/N_e)^3\tau_A = 3(N_c/N_e)\tau_B \quad (9)$$

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

The orientation behavior of chains has been related to the relaxation times and draw ratio λ.[41,42] The PMMA used in the study has an average molecular weight of 100 000 g/mol, which is much higher than the molecular weight between chain entanglements, M_e, which is 9130 as reported in the literature.[43] It can therefore be deduced that, for PMMA, $N_c/N_e \simeq 11$, and that $\tau_A << \tau_B << \tau_C$. Under the present experimental conditions, only τ_A is believed to affect P_2 significantly, and the relationship between P_2 and t can be simplified as

$$P_2(\lambda,t) \propto \exp\left(-\frac{t}{\tau_A}\right) \quad (10)$$

where t is the time in the experimental scale. Under these conditions, it can clearly be seen that the relaxation, and therefore the observed orientation of polymer chains is largely dominated by τ_A, which is proportional to ξ^2/T^2 through eq 7.

Combining the Debye–Rouse theory[44,45] and Eyring's activation theory,[46] Wu[43] deduced a simple expression for the friction coefficient, given by:

$$\xi = K \exp(E^*/RT) \qquad (11)$$

where K is a constant related to chemical properties of the polymer chain, and E^* is the activation energy for flow. According to this theory, the relaxation time τ_A, and therefore the orientation function P_2, must be a function of T and E^*. Since the activation energy for flow E^* does not depend on the temperature, it can be used to compare the orientation behavior of a given polymer in different systems.

A similarity between eq 2 abd eq 11 suggests that E^* could be related to the Arrhenius activation energy of orientation–relaxation, as measured by the slope of ln($\Delta\langle P_2\rangle/\Delta\lambda$) vs $1/T$. This implies that under conditions in which τ_A dominates, the relaxation process leads to a linear relationship, which remains to be verified. Temperature plays an important role in the control of the orientation behavior of polymer chains through the phenomena of chain relaxation, which is well described by Doi and Edwards' tube model.[37,38] However, part of the ΔE_a value may also be related to the deformation process, and it is impossible at this time to evaluate how the two factors are combined.

Conclusion

The orientation behavior of the PMMA–PVPh from 0 to 54.5 wt % PVPh was studied by using FTIR spectroscopy. The observed behavior is quite surprising: the minor component, PVPh, exhibits a higher orientation than in the pure form, whereas for PMMA, the opposite is observed.

For PVPh chains, the orientation behavior parallels that of the decrease in intraassociated hydrogen bonds. The highest orientation was achieved for PVPh when diluted in the PMMA network and therefore when intrachain interactions were minimal. Upon increase in PVPh concentration, orientation decrease until, eventually, at a 1:1 mole fraction of PMMA and PVPh chains in PM54 blend, a similar orientation was observed for PVPh chains in the blend and in the pure polymer. This is proposed to be due to the combination of the disappearance of intrabonded loops, which are detrimental to the development of orientation, and to the chain-dragging effect of PMMA chains through the effect of hydrogen bond association.

The presence of interchain association was accompanied by a decrease in orientation of PMMA chains, which could be due either to a decrease in density of chain entanglements related to the incorporation of PVPh or to the rigidifying effect of interchain hydrogen bonds, which may also contribute to a decrease in chain entanglement of PMMA in the blends.

It was verified that the orientation behavior could not be attributed to a change in average conformation (and therefore α angles) in the blends as compared to the pure polymer. For this purpose, and as a useful quantity to compare various systems, a calculation of apparent ΔE_a was derived from the slope of ln($\Delta\langle P_2\rangle/\Delta\lambda$) vs $1/T$. This value, contrarily to P_2, is insensitive to the α angle used for the calculation and therefore to possible conformation changes which could occur in blends, most particularly when strong interactions are present.

Acknowledgment. We acknowledge the financial support of the National Sciences and Engineering Research Council of Canada (NSERCC) and the Fonds par la Formation des Chercheurs et l'Aide à la Recherche (FCAR).

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MA970498Y