DMTA and FTIR Investigation of the Phase Behavior of Poly(methyl methacrylate)−Poly(4-vinylphenol) Blends

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Received June 27, 1995; Revised Manuscript Received September 22, 1995[⊗]

ABSTRACT: The phase behavior of poly(methyl methacrylate) (PMMA)/poly(4-vinylphenol) (PVPh) blends was investigated using differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), small-angle X-ray scattering (SAXS), and Fourier transform infrared (FTIR) spectroscopy. Only one glass transition was observed by DSC in both pure states and blends. However, two loss tangent maxima observed in DMTA relaxation spectra indicate the existence of two phases in the blends. Thermal treatments were found to influence both the number of hydrogen bonds and the proportion of both phases in the blends: quick quenching leads to a lower concentration of hydrogen bonds and to an increase in the quantity of the minor phase. This minor phase gives rise to a tan δ peak appearing at low temperature. It has been assigned to domains composed of isotactic-like PMMA segments and PVPh (phase-i). The T_g determined by the major loss tangent maximum exhibits positive deviation from linearity in the T_g−composition curve and is likely due to the domain of syndiotactic-like PMMA sequence with PVPh (phase-s). Using DMTA and X-ray scattering measurements, it is estimated that less than 2% phase-i with average domain size 30 Å is dispersed in a phase-s matrix. This type of approach could be used to characterize subtle differences in the behavior of optically active hydrogen-bond-forming polymer blends related to tacticity.

Introduction

Miscibility in polymer blends results from the Gibbs free energy of mixing ΔG_m being negative. This term combines the effects of both entropy and enthalpy. It has been well established that the former generally has a weak contribution in the case of polymers because of their high molecular weight. The latter is related to interactions occurring at the segmental level between polymers and mainly dominates the miscibility of the blends. Experimentally, it is very difficult to assess the value of ΔG_m directly. Various techniques can however be used to determine the phases present in a blend, such as DSC, FTIR, optical transparency, electron microscopy, NMR, dielectric relaxation, and dynamic mechanical measurements.[1,2] Each technique bears intrinsic limitations in terms of sensitivity of detectable phase domain size. Therefore, the phase composition observed by various techniques is not a perfect reflection of the thermodynamical definition. Traditionally, it is DSC that has mostly been used to determine the phase diagram of polymer blends, a single transition temperature denoting a one-phase blend. However, DSC is not sensitive enough to investigate the phase behavior at the segmental level. It has been suggested that DSC is limited to the determination of domain size approximately larger than 100 Å.[1] Therefore, in some cases, blends previously having been found miscible using DSC were later shown to exhibit phase separation when using NMR,[3] dielectric relaxation, or dynamic mechanical measurements.[4−6]

In the case of studies on the orientation of hydrogen-bond-forming polymer blends, PMMA−PVPh has been found to be of particular interest. It has been reported, on the basis of experimental data as well as theoretical predictions, that PMMA forms a single amorphous phase with PVPh over the entire composition range and at all accessible temperatures[7−12] (from below ambient to the onset of significant degradation). Some contradicting data on the miscibility of PMMA and PVPh have however been reported.[3,13] These are believed to be related to the blend preparation method, which directly influences phase behavior.[9] In this article, miscibility of PMMA−PVPh blends prepared by a melting process will be reinvestigated using FTIR and DMTA measurements. The aim of the present work is twofold: First, a verification of the phase behavior of the blends for the specific polymers used in orientation studies was sought. Second, the relationship between the observed phase behavior, as determined by DMTA, and the formation of hydrogen bonds, for which FTIR is an experimental method of choice, was investigated.

Experimental Section

Poly(4-vinylphenol) (M_w = 30 000) and poly(methyl methacrylate) (M_w = 100 000) used in this study were purchased from Polysciences. The tacticity was determined from solution NMR spectra, which were obtained in dichlorobenzene at 110 °C with a Bruker 300 MHz spectrometer. The PMMA used for this study was found to contain 16% isotactic, 45% heterotactic, and 39% syndiotactic triads. A preliminary series of 30% w/w PMMA−PVPh blends were prepared using a Minimax mixer at temperatures of 180, 200, and 220 °C with blending times varying from 10 to 30 min. DMTA showed that samples blended for less than 10 min were incompletely mixed, resulting in important phase separation. When the blend time was longer than 10 min, however, the phase behavior was constant. For the three temperatures studied, likewise, the resulting phase composition was the same. Some thermal degradation could however be detected visually on samples prepared at 220 °C, and in order to limit thermal degradation-related problems, the final temperature chosen for the samples was 180 °C. Blends reported in this paper were subsequently prepared in a Rheocord System 40 mixer at 180 °C for 30 min. Torque monitor showed no variation, confirming that no significant degradation took place during blending. All blends were powdered in a mini-mill for further use.

A Perkin-Elmer DSC-4 apparatus was used to measure T_gs (recorded at the midpoint of the corresponding heat capacity jump) at a heating rate of 20 K/min and for a sample weight of 15 mg. Calibration was performed using indium. T_gs of the pure polymers were determined to be 94 °C for PMMA and 156 °C for PVPh.

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

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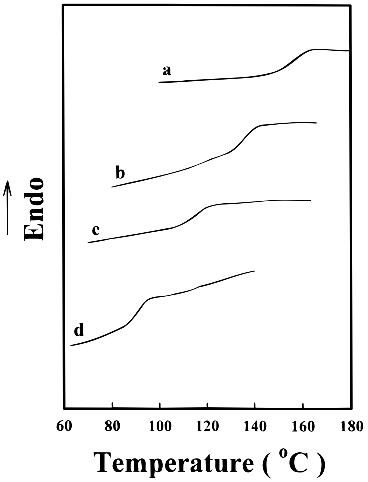

Figure 1. DSC endotherms for PVPh−PMMA blends: (a) pure PVPh; (b) 54.5 wt % PVPh; (c) 30 wt % PVPh; (d) pure PMMA.

Dynamic mechanical spectra were recorded on a Polymer Laboratories Mk II dynamic mechanical thermal analysis (DMTA) apparatus using the dual-cantilever bending mode with a free length of 5.0 mm on each side. Samples for dynamic mechanical measurements were prepared by compression of the powdered blends into a rectangular mold of 35 mm length, 10 mm width, and ca. 2 mm thickness at 180 °C. The resulting samples were placed in an oven at 180 °C for 1 h and then slowly cooled to room temperature during 5 h. This allowed relaxation of molecular chain orientation which could result from compression molding.

Films of the blends with a thickness suitable for FTIR measurements were prepared by directly compressing the powdered blends on potassium bromide windows at 180 °C. The maximum absorption of the resulting films was lower than one absorbance unit, which ensured that all spectra were within the linearity limits of the detector. A minimum of 100 scans at 2 cm^{-1} resolution was recorded on a Mattson Sirius 100 using a MCT detector. The Spectracalc software (Galactic Industries Corp.), was used to separate the two components of the carbonyl vibration band through a least-squares fitting method.

Small-angle X-ray scattering was performed on a 1 mm thick film using a Rigaku chamber equipped with vertical slits of 0.16 and 0.12 mm. X-rays were generated using a Rigaku RU200B rotating anode generator functioning at 55 kV and 190 mA. The Cu Kα radiation ($\lambda = 1.54178$ Å) was Ni-filtered and collected from 0.15 to 10° using a scintillation counter at a speed of 0.01°/min. The distance between the sample and the counter was fixed at 37.5 cm. A slightly faster scan was used for measurement of air scattering.

Results and Discussion

Miscibility Assessment Using DSC and DMTA. A simple and useful method to analyze the miscibility of polymer blends is the determination of their glass transition temperatures (T_gs) using DSC. As can be seen in Figure 1, for each composition, only one transition temperature is observed, and the T_gs increase linearly with global PVPh composition in the blends. From this observation, it can be concluded that PMMA−PVPh blends are composed of a miscible uniform phase at the DSC scale. This agrees well with previous studies on the phase behavior of PMMA−PVPh blends by DSC.[7,9−11,14,15] It is however in contradiction with NMR results.[3] It is therefore necessary to reevaluate the miscibility of this system in order to determine whether the observed discrepancies stem from intrinsic phase size limitations of DSC or from other factors.

A melting process was used to prepare the blends in this study instead of solvent casting, in order to eliminate the effect of solvent on miscibility.[9] Dynamic mechanical relaxation was used since it is sensitive to smaller domain sizes. Figure 2 shows the dynamic relaxation spectra of pure PMMA and PMMA−PVPh blends. It has been impossible to measure the relaxation spectra for pure PVPh and higher PVPh composition blends because of the brittleness of these samples.

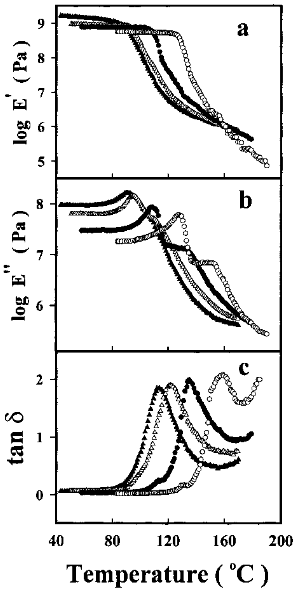

Figure 2. Storage modulus, loss modulus, and loss tangent as determined by DMTA for PVPh−PMMA blends at 10 Hz as a function of temperature: (▲) pure PMMA; (△) 10 wt % PVPh; (●) 30 wt % PVPh; (○) 54.5 wt % PVPh.

From Figure 2a, it can be seen that, for all systems, the logarithm of the storage modulus, log E', varies very little in the first section of the curve, called the plateau zone. A sharp decrease is then observed and is attributed to the change in segment mobility related to the glass transition. It was not possible to measure the behavior at higher temperatures because the sample is too softened to be gripped by the sample holder. It can be noted that the average log E' values of the plateau decrease gradually with the increase of global PVPh composition. The lower average plateau values for higher concentrations of PVPh could be related to a low storage modulus for pure PVPh. Within the plateau zone, differences in behavior could be noted between samples: the log E' value decreases slightly with temperature for pure PMMA, whereas it remains fairly constant for each PVPh−PMMA blend. The difference of storage modulus behavior between pure PMMA and the blends could be due to free volume changes related to hydrogen bond formation between PMMA and PVPh. PMMA alone has a relatively flexible side chain, which leads to a slight decrease of the modulus with temperature within the plateau zone. On the other hand, when blended with PVPh, the presence of a hydrogen bond network acts as a physical cross-link, and then the system exhibits only limited micro-Brownian segmental motions. Consequently, the log E' value remains constant within experimental error for the blends in the plateau zone.

Loss modulus changes as a function of temperature behave as expected for PMMA, as can be seen in Figure 2b. The α relaxation peak, which is seen on this graph, corresponds to the main glass transition. For the blends, this peak occurs at higher temperature with the increase of global PVPh composition. However, a second transition peak can be observed in DMTA spectra of the

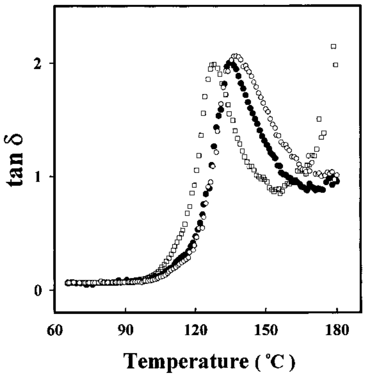

Figure 3. Dynamic mechanical spectra of a PVPh−PMMA blend containing 30 wt % PVPh: (□) 1 Hz; (●) 10 Hz; (○) 30 Hz.

blends. This second transition indicates that the blends do not exhibit a single uniform phase. The two peaks of tan δ therefore clearly indicate the presence of two PMMA−PVPh phases. Since, in order for the blending to be efficient, it must be performed at a temperature higher than the highest T_g of the two components (that of PVPh), it was important to ascertain that the chosen temperature was sufficiently high. This is particularly crucial for PVPh, since its T_g strongly depends on the molecular weight. The fact that, for the 30% w/w blend, blending temperatures up to 220 °C did not alter this behavior indicates that this phase separation is not related to a higher molecular weight chain fraction. In the following discussion, phase-s is used to denote for the major peak transition, and phase-i for the minor peak.

These separated domains were observed even more clearly when higher frequencies were used during DMTA measurements, as can be seen in Figure 3. At the lowest frequency used (1 Hz), the blend tends to behave as a uniform phase. A second transition clearly appears at higher frequencies. These observations can be explained through the diffuse boundary model.[8] Phase-i is presumably dispersed in the phase-s matrix without formation of clear boundaries. Polymer chains of each phase penetrate into the region in which the other polymer is the main component, forming diffuse boundaries. At low frequency, molecular chains in both phases have almost the same relaxation time and show a uniform behavior indicative of miscibility. When the frequency increases, differences in relaxation time related to local environment are emphasized and a minor peak appears. Therefore higher frequencies favor the observation of phase separation. However, higher frequencies cause a severe resonance after the major transition peak, which end the experiment prematurely. Therefore, a frequency of 10 Hz was chosen for the remaining relaxation spectra. From the intensity of the minor tan δ peak, it can be estimated that the amount of phase-i is less than 2% in the blends.

In order to better understand the behavior of the blends, the T_g−composition variations are often studied. In principle, the loss tangent maximum can be taken as the glass transition temperature.[21] However, the position of this peak is a function of the frequency used during the measurements. Likewise, T_g values obtained from DSC depend on the heating rate. When the T_gs of pure PMMA as determined by DMTA and DSC were compared, a notable difference was observed, the DMTA value being higher by 16 °C. In order to better compare the glass transition behavior of the two phases observed by DMTA to that of the single DSC phase, 16 °C was therefore subtracted from the values obtained through the loss tangent maxima, and the resulting modified values are compiled along with the DSC results in Figure 4. In this figure, it must be noted that the overall composition was used, since no known technique allowed measurement of the local composition of each phase in the blend. However, this approximation is totally justified for the major phase where, given the small amount of minor phase detected (approximately 2%), changes in composition should be approximately 1% at most. Under these circumstances, even a minor phase composed of pure PMMA would not explain the observed increase in T_g of the major phase. For instance, a pure PMMA minor phase would cause a change of composition of the major phase of 30% to 30.6%. If the T_g−composition linear relationship is to be obeyed as in DSC measurements, than the T_g of the major phase would be 112.9 °C as compared to the experimentally observed value of 120 °C. This discrepancy is even greater for the 54.5% blend, where the local phase composition of the major phase would be 55.6% and the T_g calculated using a linear relationship 128.5 °C, as compared to an experimental value of 141 °C. In the case of the minor phase-i, however, using the overall composition instead of the local composition may be an incorrect approximation and must therefore be regarded only as a working hypothesis.

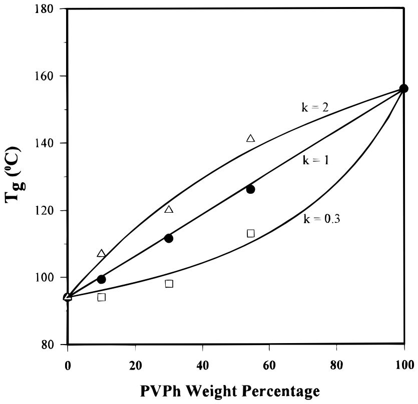

Figure 4. T_g−composition behavior of the blends: (●) T_g measured from DSC; (△) T_g measured from the tangent maximum of the major peak on DMTA minus 16 °C; (□) T_g measured from the tangent maximum of the minor peak on DMTA minus 16 °C. Solid lines represent predictions based on the Gordon−Taylor equation at different k values.

As can be seen, the two phases observed by DMTA display opposite behaviors. Phase-s exhibits a positive deviation from linearity, whereas phase-i shows a negative deviation. Neither of the two phases behaves according to a linear relationship, as was found for the larger domains investigated by DSC. This enlightens the difference in behavior of the two observed phases. It is noteworthy that the two observed phases show an increase in T_g with global PVPh composition, indicating that these two phases behave as two miscible PMMA−PVPh phases, but with a different T_g−composition behavior.

The Gordon−Taylor expression[23] is the most commonly employed equation to predict the glass transition temperature of binary polymer blends,

$$T_g = \frac{\omega_1 T_{g_1} + k\omega_2 T_{g_2}}{\omega_1 + k\omega_2}$$

where T_g is the glass transition temperature of the blend and ω_i the weight fraction of component i. The k parameter has been proposed to be related to the strength of intermolecular interactions between the blend components.[23,24] Positive deviations, leading to high k values, are related to blends with restricted chain mobility.

The k values obtained by curve fitting are 2 and 0.3 for phase-s and phase-i, respectively. The high k value of 2 indicates that the chain mobility is more restricted in phase-s. The formation of a higher number of hydrogen bonds is the most probable cause for the decrease in chain mobility. This could be related to differences in chain organizations or conformations, one favoring a large number of hydrogen bonds as compared to the other.

It could equally be due to differences in phase compositions, indicative of a LCST. If the observed behavior was related to the presence of a LCST, for a given temperature, the composition of the observed phases, and therefore their T_g's, would not vary with the global composition of the blend. The relative quantity of each phase would however vary with total phase composition. The observed phase behavior of this system does not follow this pattern: the T_g of phase-i increases substantially with increasing global PVPh composition of the blend, while the percentage of this phase varies very little. Such an observation could stem from variations in thermal history of the samples. However, for each composition, the experiment was repeated several times and yielded values of 2.0 ± 0.5% for the intensity of the minor peak. Therefore, the observed phase separation is not believed to stem from the presence of a LCST.

The second possibility implies differences in chain organizations or conformation. It is interesting to note that poly(vinylphenol) differs from polystyrene (PS) only by the presence of a para hydroxyl group on the aromatic cycle. PS−PMMA blends are completely immiscible at all concentrations. It is widely accepted that the miscibility of the PVPh−PMMA blends stems from the formation of favorable intermolecular interactions, and more specifically of hydrogen bonds between the hydroxyl groups of PVPh and the carbonyl groups of PMMA. Therefore, factors affecting the formation of hydrogen bonds will also influence the phase behavior in the blends. Recent studies show that the steric regularity of PMMA chains influences the miscibility of PMMA and poly(styrene-*co*-vinylphenol) containing 5 mol % of vinylphenol units (MPS-5).[17] Syndiotactic PMMA exhibits a better miscibility with PVPh than isotactic PMMA. The former is completely miscible with MPS-5 in all compositions, whereas the latter only shows miscibility at higher MPS-5 fractions (up to 70 wt %). The tacticity of the chain influences the adopted conformations and interchain interchain formation. In this respect, it is interesting to recall that the crystal structures of these two PMMAs are very different: syndiotactic PMMA crystallizes as single helices complexed with solvent molecules, whereas isotactic PMMA crystallizes as a double helix.[18] The two crystal structures have different backbone conformations as well as packing arrangements. Preferred conformations have been shown to be influenced by local tacticity[19] and are therefore likely to differ in the amorphous phase. The crystal structure conformation, although likely to be present in the amorphous phase, is only one of the low-energy conformations which are expected. According to the RIS (rotational isomeric state) model,[20] the probability of a conformation occurring is inversely proportional to its relative energy. Hydrogen bond formation is likely to be affected by the conformations adopted by the polymer segments. It is interesting to note that the syndiotactic conformer, which crystallizes as a single helix, is also the more miscible conformer when blended with PVPh. The better accessibility that this conformation provides is believed to favor the formation of hydrogen bonds.

Comparing with the 138 °C T_g of syndiotactic PMMA and the 60 °C T_g of isotactic PMMA,[17] the T_g of 94 °C measured for the PMMA used in this study indicates that the PMMA used is neither isotactic nor syndiotactic. While NMR results show that the PMMA used is composed of 16% isotactic triads and 39% syndiotactic triads, the proportion of longer syndiotactic or isotactic segments should be much smaller. However, a chain section for which the conformation is syndiotactic-like or isotactic-like could very well be present. The occurrence of two phases in the present study could be related to the existence of syndiotactic-like and isotactic-like portions along some PMMA chains. Each would interact differently with PVPh, leading to the observed phase separation. The fact that DMTA results are in agreement with a diffuse boundary model could also be explained by phase segregation of segments within a single polymer chain. The low T_g of phase-i could be related to the lower accessibility of carbonyl groups in the helical conformation of restricting isotactic-like PMMA segments, which would result in a lower number of hydrogen bonds formed with PVPh and therefore a higher chain flexibility. The fact that the more abundant triads, as measured by NMR, are the syndiotactic ones and the less abundant, the isotactic ones, is also in agreement with a major phase composed of syndiotactic-like segments and a minor phase of isotactic-like segments. It is however not possible to rule out the possibility that the tacticity of PVPh could play a role in the phase behavior. It is also much more difficult to investigate this factor, since the effect of tacticity on chain flexibility of PVPh is not known.

If, as implied by the proposed model, chain segments of a same chain can be found in the two different phases, the phase size should be fairly small. Indeed, the fact that the phase separation is not observed by DSC is indicative of a small domain size. Taking into consideration the DSC limitations, it can be surmised that the domain size of phase-i should not exceed 100 Å and could be considerably smaller. SAXS experiments have been performed on the 30% PVPh sample. A representative spectrum after subtraction of the air scattering appears in Figure 5. A broad, low-intensity peak is observed centered around 3°. The low intensity clearly indicates a very small electron density difference between the two phases which contribute to the peak. This is in agreement with the proposed syndiotactic- and isotactic-like segment segregation, since the slightly different segment conformation should induce small differences in density. The proportion of PVPh and PMMA in both phases could also be different from the bulk composition, which would also contribute to the density difference.

The width and low intensity of the interference peak are such that determination of the exact phase sizes was not attempted. However, an approximation can be made using the Bragg law ($2d \sin \theta = \lambda$), which assumes a regular alternance of the two phases. This yields an

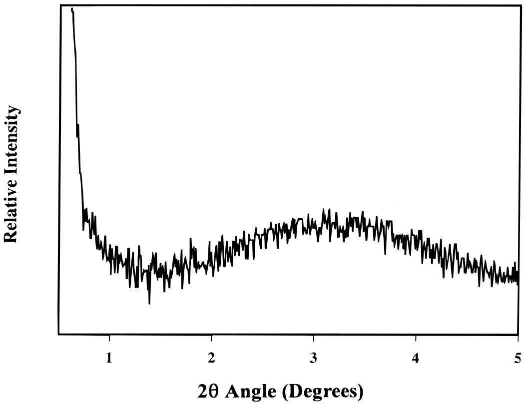

Figure 5. Small-angle X-ray scattering spectrum (after subtraction of the air scattering) of a PVPh−PMMA blend containing 30 wt % PVPh.

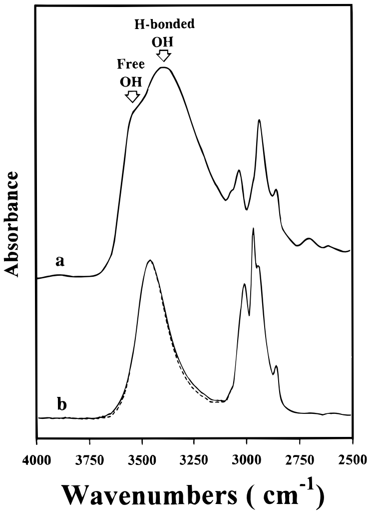

Figure 6. FTIR spectra recorded at room temperature of the hydroxyl valence vibration region of (a) pure PVPh and (b) PVPh−PMMA blend containing 30 wt % PVPh: dashed line, sample cooled slowly from 180 °C to room temperature in 5 h; solid line, rapidly quenched sample.

approximative value of 30 Å for the phase size. The maximum end-to-end distance of a chain in phase-i domains, therefore, cannot exceed this domain diameter of 30 Å. Using the conformation theory of Flory,[20] which states that $\langle r\rangle^2 = C_\infty n l^2$ ($\langle r\rangle^2$ is the average square of the end-to-end distance of the freely rotating chain, C_∞ is the characteristic ratio (taken as 6.9 for atactic PMMA),[20] l is the length of the C−C bond taken as 1.54 Å, and n is the number of C−C bonds in the chain backbone), it can be estimated that the average segmental length in phase-i domains should not exceed ca. 56 repeat chain units, or 5.66×10^3 g in terms of molecular weight of the chain. This value is less than the order of magnitude of the average molecular weight of the PMMA chain used in the studies. On the other hand, the T_g of phase-i increases with total PVPh composition in the blends, indicating that phase-i domains cannot consist of pure PMMA chains. Therefore, it is most likely that isotactic-like PMMA segments combine with PVPh to form the observed phase-i domains.

Influence of Hydrogen Bonds on Phase Behavior. In order to determine the effect of temperature on the observed phase behavior of the system in relation to hydrogen bond formation, FTIR spectroscopy was used. It is well known that thermal treatments influence the phase behavior of polymer blends. In the present case, the situation becomes more complicated since thermal treatments also influence hydrogen bond formation, which is the major favorable intermolecular interaction in the blends. It has been reported by Serman, Painter, and Coleman that temperature has a significant influence on hydrogen bonds:[7] the intensity ratio of free to hydrogen-bonded carbonyl group vibration increases with temperature, and this effect is reversible when the temperature is lowered again.

A 30 wt % PVPh−PMMA blend was chosen for the investigation of the influence of hydrogen bonds on phase behavior. At this composition, there is a sufficient proportion of carbonyl groups belonging to PMMA to allow formation of a measurable amount of interassociated hydrogen bonds with the hydroxyl groups of PVPh. This PMMA fraction also decreases the T_g to the extent that sample preparation and handling are easier. Ten samples were first heated to 180 °C. Half of the samples were rapidly quenched to room temperature within seconds, while the second half was kept in an oven and slowly cooled to room temperature during 5 h. Both types of sample were measured by FTIR and DMTA, respectively. For some of the samples, quenching and slow cooling were performed successively. After each thermal treatment, the FTIR spectrum was registered. Thermal treatments were performed while maintaining the sample fixed on a sample holder, which insured that the exact same portion of the sample was measured. In this way, the repeatability of the phenomenon was investigated. It was possible to verify, in this way, that the spectral changes reported were reversible and that they were therefore not related to poor blending of the original sample or to thermal degradation.

Figure 6 shows typical FTIR spectra of these samples in the area of the OH valence vibration. For pure PVPh, as can be seen in Figure 6a, the OH vibration is separated into two distinct bands. The first, corresponding to intraassociated hydroxyl groups, is centered at 3370 cm^{-1}. The second contribution, assigned to free hydroxyl groups, is centered at 3534 cm^{-1}. In the blend, only one band can be detected, indicating that within experimental error, all hydroxyl groups of PVPh form hydrogen bonds (intra- or interassociated). Meanwhile, the peak is shifted to a longer wavenumber of 3460 cm^{-1}, forming a stronger hydrogen bonding between PMMA and PVPh in the blend than in pure PVPh. Using the symmetrical and asymmetrical valence vibrations of CH_2 groups occurring from 3100 to 2800 cm^{-1} as an internal reference, the various spectra of thermally treated blends have been reported on a common scale. When slowly cooled and quenched samples are compared, a slight difference can be observed, as can be seen in Figure 6b. Slowly cooled samples systematically exhibit a slightly narrower hydroxyl group vibration. This implies that the geometry of the hydroxyl groups becomes more ordered after slow cooling. However, because of the overlap of inter- and intraassociated hydrogen-bonded hydroxyl vibrations, it is impossible to determine whether this is related to a change in the ratio of inter- or intraassociation or to an increase in the hydrogen bond geometry cohesion.

A second region worthy of attention in relation to hydrogen bonds is that of the carbonyl valence vibration PMMA, which is shown in Figure 7. Since PVPh is the minor constituent, it was expected that there would not be a sufficient quantity of OH groups to allow formation of hydrogen bonds with all carbonyl groups. Therefore,

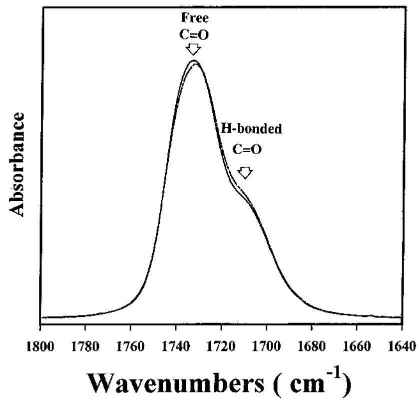

Figure 7. FTIR spectra of the carbonyl valence vibration region of a PVPh−PMMA blend containing 30 wt % PVPh recorded at room temperature: dashed line, slowly cooled sample; solid line, rapidly quenched sample.

Table 1. Semiquantitative Evaluation of the Carbonyl Fraction Using FTIR Spectroscopy

sample	vibration assignment	vibration position (cm^{-1})	area A	$A_f/(A_f + A_{HD})$ (%)[a]
quick quenching	free	1733.16	26.77	61.9
	hydrogen bonded	1706.80	16.50	
slow cooling	free	1732.95	24.47	59.7
	hydrogen bonded	1706.34	16.49	

[a] A_f = area of the free carbonyl vibration; A_{HD} = area of the hydrogen-bonded carbonyl vibration.

unlike OH groups for which only one vibration band appears, the C=O vibration is separated into two peaks centered at 1733 and 1706 cm^{-1}, which are assigned to the vibrations of free and hydrogen-bonded carbonyl groups, respectively. The influence of thermal treatment on the proportion of hydrogen bonds can be estimated using these two vibrations: the increase of the free carbonyl group vibration intensity is directly related to a decrease in the number of hydrogen-bonded carbonyl groups.

As mentioned previously, the number and strength of hydrogen bonds between the hydroxyl group of PVPh and the carbonyl groups of PMMA are significantly changed by temperature. At 180 °C, it has been reported that many hydrogen bonds are broken,[7] and this increases the proportion of the free hydroxyl and carbonyl groups. When the samples are slowly cooled to room temperature, molecular chains have time to relax, and the carbonyl groups of PMMA are able to completely recombine with the hydroxyl groups of PVPh. In contrast, when the sample is rapidly quenched, not all the broken hydrogen bonds recombine, and this is reflected in the spectrum obtained, as can be seen in Figure 7. The FTIR spectrum of the quenched sample, represented by a solid line, shows an increase of the intensity of the free C=O vibration, whereas that of the H-bonded C=O vibration decreases. These differences were reproduced several times using different samples in order to verify the reproducibility. This result clearly indicates that the quenching procedure results in a higher concentration of free carbonyl group in the blend due to hydrogen bonds being broken. A curve-fitting procedure was used to evaluate semiquantitatively the population of these vibration groups, and results are listed in Table 1 in terms of the ratio of the area of the free carbonyl band to that of the sum of the two bands. The intensity of the free carbonyl group vibration is approximately 2% higher in the quenched blend than in the slowly cooled blend. Since the absorption coefficients are not known, it is not possible to transform this value in terms of concentration change. If one supposes that the absorption coefficient is the same for the two vibrations, a difference of 2% in terms of the number of hydrogen-bonded groups is evaluated. This difference is of the order of magnitude of the error encompassed in the curve-fitting procedure, which explains why the term semiquantitative is used here. Nevertheless, since the change is readily observable in the spectrum itself, it is therefore not an artifact related to curve fitting. The change observed indicates that the concentration of hydrogen bonds in the PMMA−PVPh blends is directly dependent on the thermal treatment history of the samples. Again, the fact that this is a reversible point clearly indicates that the phase separation cannot be due to incomplete blending of a fraction of the polymers (such as less tractable, higher molecular weight chains).

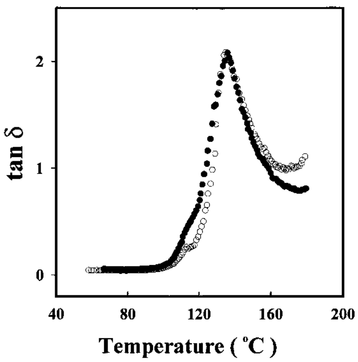

Figure 8. Influence of thermal treatment on dynamic mechanical spectra for a 30 wt % PVPh blend at 10 Hz: (○) slowly cooled sample; (●) rapidly quenched sample.

Hydrogen bond formation is known to contribute to miscibility of blends. The influence of thermal treatment on hydrogen bond formation is therefore likely to have an effect on the phase behavior. Figure 8 shows dynamical mechanical spectra recorded for both thermally treated blends. As expected, the change in cooling rates did not vary the position of the tan δ peak. Again, it must be recalled that, in the presence of a LCST, changing the thermal history would undoubtedly have resulted in a change of both T_gs and phase proportions. Quenching usually favors the observation of phase separation. The fact that the T_g does not change with thermal treatment is taken as a clear indication that the observed minor phase does not stem from a thermodynamical phase separation process. The relative ratio of the two observed phases is modified by thermal treatment, as reflected in the tan δ peak intensity changes: the minor phase, or phase-i, is increased by approximately 5% when the samples are quenched instead of slowly cooled. It is noteworthy that this change is accompanied by an increase of the number of hydrogen bonds of the same order of magnitude, namely 2%, as observed by FTIR. This confirms that phase-i contains fewer hydrogen bonds, presumably for steric reasons. The effect of thermal treatment can be understood in terms of segmental conformations: high temperatures favor the existence of higher energy conformations. In this particular case, it is surmised that these high-energy conformations are less able, for steric reasons, to accommodate the formation of PMMA-PVPh hydrogen bonds. Segregation in two phases with similar composition results in a high-energy conformation phase, called phase-i because of its similarity with isostactic PMMA-PVPh blends, and a low-energy conformation phase, called phase-s by analogy with syndiotactic PMMA−PVPh blends. When quenching, high-energy conformations are trapped and retained, whereas when slowly cooling, the proportion of high-energy conformations is lowered to that allowed by the thermal energy of the system.

Conclusion

Both DSC and DMTA were used to investigate the phase behavior of PMMA−PVPh blends. There appear to exist two phases when viewed by dynamic mechanical analysis, although only one transition moment was measured by DSC. The two phases are both blends of PMMA and PVPh but are believed to differ in terms of local organizations, such as chain conformation and hydrogen bond formation, as suggested by their T_g−composition behavior.

The major tangent maximum shows a positive T_g−composition deviation from linearity, indicating stronger interactions between PMMA and PVPh chains. These are attributed to blends of syndiotactic-like PMMA sequences and PVPh (phase-s). On the other hand, the minor tan δ peaks, appearing at low temperatures, show a negative T_g−composition deviation and are attributed to isotactic-like PMMA sequences and PVPh blends (phase-i). Segments belonging to the same PMMA chains are likely to be separated, and therefore diffuse boundaries are expected. This is in agreement with DMTA results. SAXS was used to determine domain size, which was found to be approximately 30 Å for the 30% PVPh blend.

Thermal treatments influence not only the formation of hydrogen bonds but also the proportion of both phases in the blends. Quick quenching leads to a lower concentration of hydrogen bonds and to an increase of phase-i in the blends. This would not be the case if a LCST was present.

Acknowledgment. The authors wish to thank Dr. C. G. Bazuin for valuable discussion. This work was made possible through financial support from NSERC (Natural Sciences and Engineering Research Council of Canada) and from FCAR (Fonds pour la Formation de Chercheurs et l'Aide à la Recherche). D.L. also acknowledges the support of a scholarship from the Ministère de l'Enseignement Supérieur et de la Science and of the Chinese Government.

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MA950909F