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Miscibility and Specific Interactions in Blends of Poly(hydroxy methacrylates) with Poly(vinylpyridines)

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ABSTRACT: Poly(4-vinylpyridine) and poly(2-vinylpyridine) were found to be miscible with poly(2-hydroxyethyl methacrylate) and poly(3-hydroxypropyl methacrylate). This miscibility is proved by calorimetric studies in conjunction with infrared analysis of the blends. All blends show a single glass transition which is of a higher value than the glass transitions of the blends calculated on the basis of additive behavior. Furthermore, the variation of the glass transitions of the blends follows the Jenckel–Heusch equation. Infrared studies show that carbonyl, hydroxyl, and pyridine ring peaks undergo important changes which were attributed to hydrogen bonding between the hydroxyl groups in both methacrylates and the basic nitrogen atom present within the pyridine ring. These interactions were observed to be of greater relevance for poly(4-vinylpyridine) than for poly(2-vinylpyridine). Finally, phase transitions were also studied. No phase separation was found for blends having poly(4-vinylpyridine), whereas blends including poly(2-vinylpyridine) show a low critical solution temperature at 140–175 °C.

Introduction

Poly(vinylpyridines) show a marked basic Lewis character: the nitrogen atom incorporated within the side-chain aromatic ring is amenable to share a free electron pair with Lewis acids. Thus, this polymer has been extensively studied as a component of polymer blends where strong acid–base interactions are predominant.[1–5] In this connection the following studies are noteworthy: (i) blends of poly(vinylpyridines) with poly(carboxylic acids) such as poly(methacrylic acid)[2] and poly(ethylene-*co*-methacrylic acid);[3] (ii) insoluble polyelectrolyte complexes of poly(vinylpyridines) and poly(AMPS);[4] (iii) blends with alcohols such as poly(vinylphenol).[5] All of these blends are miscible. This miscibility was attributed to the formation of strong interactions between acidic and basic units of the blend precursors. Thermodynamically, these interactions provide two opposite contributions to the Gibbs free energy of mixing: (i) a favorable one driven by the enthalpy of mixing and (ii) an unfavorable one due to the entropy of mixing which decreases as a consequence of the strong interactions which force the molecules to take constrained conformations.

Hydrogen bonding provides in these blends the necessary negative enthalpic contribution to the free energy, avoiding the unfavorable entropic contribution. Infrared spectroscopy has been a powerful tool to prove the decisive importance of such specific interactions in these kinds of blends.

This work presents a study of polymer blends formed by poly(vinylpyridines) in their 2- and 4-isomeric forms and hydroxyl derivatives of ethyl and propyl polymethacrylates. Taking into account the proton acceptor character of poly(vinylpyridines) and the presence of hydroxyl groups in the second component, specific interactions through hydrogen bonding leading to miscible systems are readily expected. The aim of the present work is to establish the conditions of miscibility for these systems and to evaluate the type and extension of specific interactions playing a role in these cases.

Experimental Section

Preparation of Samples and Blends. Methanol solutions of poly(4-vinylpyridine) (P4VP) and poly(2-vinylpyridine) (P2VP) were kindly provided by Reilly Chemicals. Samples were purified by successive precipitations from methanol into ethyl ether. The molar masses of both poly(vinylpyridines) were reported to be 200 000 g/mol by the supplier.

Poly(2-hydroxyethyl methacrylate) (PHEMA) and poly(3-hydroxypropyl methacrylate) (PHPMA) were purchased from Aldrich and used as received. In all cases, blends were prepared by solvent casting. Methanol and a methanol–water mixture (88:12 v:v) were used as solvent for systems containing PHPMA and PHEMA polymers, respectively. The initial concentration of the blend solutions was 3 g/dL. Films of the blends were obtained by rapidly evaporating the solutions on Petri dishes at 135 °C. The films obtained were dried under vacuum for 12 h at room temperature to ensure total elimination of solvent. Samples were stored in desiccators until analysis to prevent moisture sorption.

Thermal Analysis. Thermal analysis was performed in a Mettler Model TA4000 DSC. Temperature and energy calibration was carried out with indium. Sample weights between 10 and 15 mg were used in all cases. The scan rate was 20 K/min. The glass transition temperature (T_g) was calculated as the inflection point of the jump of heat capacity. All samples were subjected to a rapid heating (100 $°C \cdot min^{-1}$) from room temperature to 175 °C followed by a quick quenching to room temperature to preclude misleading results derived from the sample thermal history.

FTIR. Infrared spectra were recorded on a Nicolet 520 FTIR spectrometer. A total of 200 scans were averaged in all cases. Spectral resolution was 1 cm^{-1} in order to perform proper quantitative analysis. Samples were prepared by solvent casting directly onto KBr pellets. Films were thin enough to meet Lambert–Beer law requirements. The influence of temperature on the spectral features of the blends was studied by using a Specac P/N 21.5000 variable-temperature cell. Temperature was controlled with a Eurotherm 847 controller. Least-squares curve fitting of the spectra was performed using Nicolet FOCAS curve analysis software installed in a Nicolet 620 station. This software enables one to obtain a preliminary determination of the number of peaks to be analyzed and their position by a Fourier self-deconvolution method. After selection of the number of peaks and their tentative location, curve analysis simulates the location, peak width, and peak shape of each individual peak which forms the pattern of overlapping bands found in the sample spectrum.

Results and Discussion

Although the most accepted experimental criterion to establish miscibility of a pair of polymers is the presence of a single T_g intermediate between that of the pure

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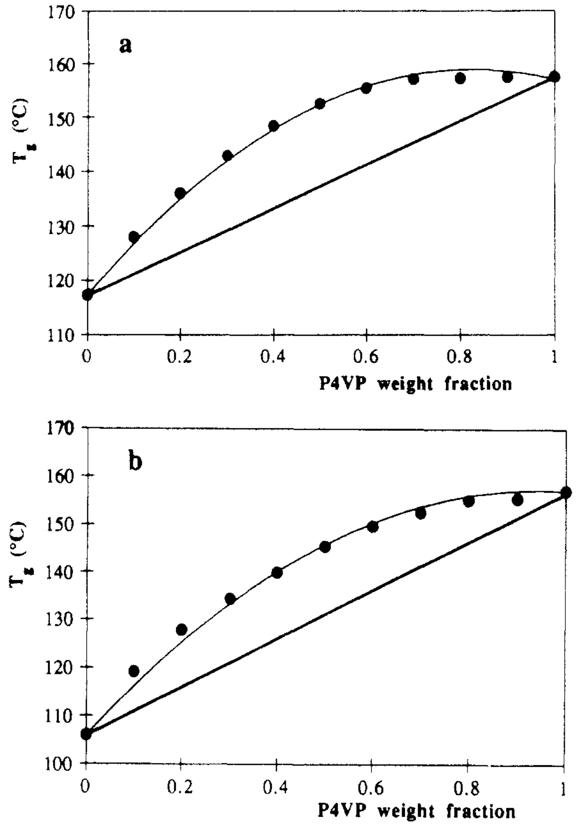

Figure 1. Glass transition temperature dependence with blend composition: (a) P4VP/PHEMA; (b) P4VP/PHPMA. Weight average of the T_g's of the pure compounds and experimental data fitting to eq 2 are also shown.

components, serious limitations appear in cases in which the pure components have very close T_g values. Usually it is difficult to discriminate if the mixture presents one or two glass transitions when the T_g's of the pure components differ by less than 15 K. This is the case in two of the systems studied here. Thus, the T_g's associated with P2VP and P4VP are 382 and 430 K; with the second blend components PHEMA and PHPMA present, the T_g's are 390 and 379 K, respectively. Accordingly, simple calorimetric analysis will enable us to establish miscibility in blends having P4VP as one precursor but will not be a suitable technique for characterizing blends having P2VP. Consequently, the latter blends will be studied by using a new calorimetric method which will be described in detail later in the text.

P4VP Blends. P4VP/PHEMA and P4VP/PHPMA blends form transparent films at all compositions, and DSC results show a single T_g; consequently, both systems are taken as miscible. On the other hand, solutions of these systems in methanol show no immediate formation of any kind of precipitate, from which it is deduced that interactions between components are not strong enough to form a polymer–polymer complex. In this sense, it is worthy to remark that interpolymer complex formation is strongly influenced by the solvent used.[6] However, according to Wang et al.,[7] methanol is one of the solvents more favorable to the formation of polymer–polymer hydrogen bonding. Thus, as can be observed from Figure 1, the T_g's obtained for the blends are higher than those calculated as a weight average of the T_g's of the pure compounds. This behavior is observed in the entire composition range. Calorimetric results show that strong polymer–polymer interactions are taking place between the blend components.

Similar results were reported elsewhere for polymer blends in which the components establish strong interactions through hydrogen bonding[5,8,9] and in interpolymer complexes.[7,10] This behavior is usually attributed to a decrease of chain mobility as a consequence of the strong interactions, i.e., hydrogen bonding. This inhibition of chain mobility produces an increase in the glass transition temperature.

The strength of interpolymer interactions can be quantified by using the Kwei equation,[8] which is a modified version of the Gordon–Taylor equation:

$$T_g = \frac{W_1 T_{g1} + k W_{21} T_{g2}}{W_1 + k W_2} + q W_1 W_2 \qquad (1)$$

In eq 1 W_1 and W_2 are the weight fractions of each of the blend components, T_g, T_{g1}, and T_{g2} are the glass transition temperatures of the blend and pure components 1 and 2, respectively, and k and q are adjustable parameters. Equation 1 is applicable to most polymer blends which present strong interactions between the constituent polymers. For systems such as those considered here, k can be taken as unity and eq 1 can be written as

$$T_g = W_1 T_{g1} + W_2 T_{g2} + q W_1 W_2 \qquad (2)$$

Equation 2 is similar to the one proposed by Jenckel and Heusch.[11] The adjustable quantity q could be considered as a measure of the strength of the specific interactions acting in the blend. Equation 2 has been applied to the experimental data corresponding to P4VP/PHEMA and P4VP/PHPMA blends. The best fittings between data and equation occurred for values of q equal to 61 and 57 for P4VP/PHEMA and P4VP/PHPMA, respectively. Figure 1 shows both experimental data and the data obtained by means of eq 2 for the values of q mentioned above. As can be seen from this figure, experimental data and calculated values of T_g are very similar for both systems. Similar values of q have been obtained for polymer blends in which strong interpolymer interactions take place.[8,9]

P2VP Blends. As indicated above, the usual calorimetric analysis of P2VP/PHEMA and P2VP/PHPMA blends becomes difficult due to the small difference between the T_g's of the components, 8 and 3 K, respectively, which is not large enough to observe two distinct heat jumps in a DSC scan of a blend of immiscible polymers. Recently, calorimetric methods have been demonstrated to be a valid experimental technique even when the T_g's of the blend components are very close to each other.[12] The procedure relies on the phenomenon of enthalpy recovery in physically aged glassy blends.

The relevant quantity in the enthalpy recovery method is the effective aging time which is characteristic for each component of the blend. According to Grooten and ten Brinke,[13] in the case of blends having T_g differences on the order corresponding to the system P2VP/PHEMA (8 K), the most adequate method is to choose the aging temperature relatively close to the T_g of the pure component with the lowest glass transition temperature in such a way that the enthalpy recovery peak of this component approaches equilibrium after a short aging time, whereas the position of the enthalpy recovery peak of the component with the highest T_g increases. The overall result is an increase of the difference in the positions of the maxima (T_{max}) of the enthalpy recovery peaks corresponding to each component of the blend as a function of aging time. To know the equilibrium position of T_{max} for P2VP and PHEMA, samples of each one of the pure components were heated to 413 K for 5 min, cooled by quenching in liquid nitrogen, and aged at 372.5 K for different times. Figure 2 shows the results; after a short

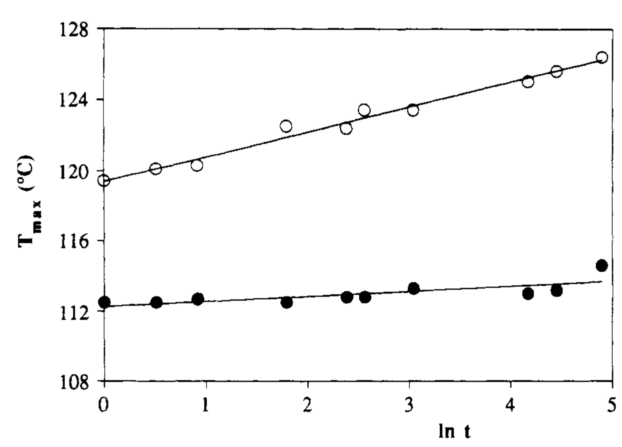

Figure 2. Variation of T_{max} with aging time at 99.5 °C: (●) P2VP; (○) PHEMA.

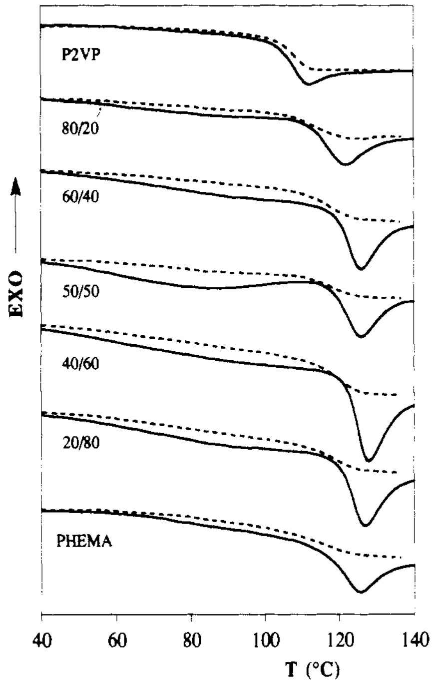

Figure 3. Thermograms of pure components and blends of different compositions after thermal aging at 99.5 °C: (—) first scan; (- - -) second scan.

period of time, P2VP reaches an equilibrium position, whereas the position of the enthalpy recovery peak of PHEMA shifts continuously to higher temperatures as the aging time increases. The difference of T_{max} is 7 K after 1 h and 13 K after 86 h. This difference is large enough to discern both T_g's.

Once the equilibrium position of T_{max} was established for each of the components, samples of the blend were subjected to aging and analyzed by DSC. Figure 3 shows thermograms corresponding to pure polymers and to blends of different compositions for an aging time of 134 h. The existence of a single maximum in the enthalpy recovery peaks for these blends proves the miscibility of the P2VP/PHEMA system. The values of T_g determined are given in Figure 4a. These results will be discussed below.

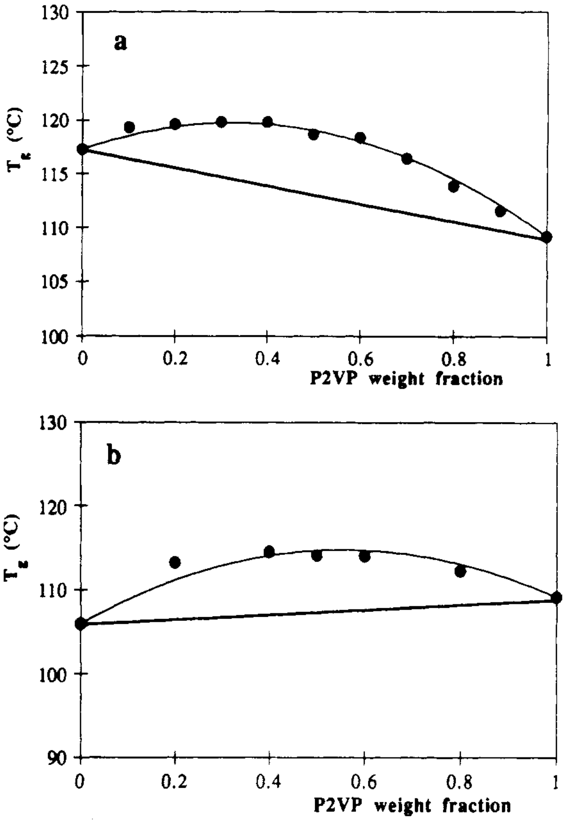

Figure 4. Glass transition temperature dependence with blend composition: (a) P2VP/PHEMA; (b) P2VP/PHPMA. Weight average of the T_g's of the pure compounds and experimental data fitting to eq 2 are also shown.

With regard to P2VP/PHPMA blends both polymers have a T_g at similar temperatures. Consequently, assessment of miscibility in this case is more complex than for P2VP/PHEMA blends. This problem was circumvented by taking into consideration the work by Grooten and ten Brinke,[13] who established that, for a given aging time, the peak height passes through a maximum when the sample is annealed at a temperature 20 K below the T_g. However, the small difference found between T_{max} for both polymers (1 K) did not enable us to evaluate adequately whether the blends are miscible or immiscible. Despite this fact, experimental T_g's have been calculated. The results are given in Figure 4b. It is apparent from Figure 4 that P2VP/PHEMA and P2VP/PHPMA blends show a behavior similar to that found for P4VP-based blends; viz., the values of T_g corresponding to the blends are higher than those calculated as the weight average of the homopolymer T_g's. Equation 2 has also been applied to these systems. The best fittings were found for values of q equal to 24 and 28 for P2VP/PHEMA and P2VP/PHPMA, respectively. These values are significantly lower than those obtained for P4VP-based blends, which indicates that the strength of interpolymer interactions is larger for the latter systems.

A greater number of polymer blends exhibit phase demixing when subjected to high temperature. The phase temperature behavior of the blends studied here has also been characterized. P4VP/PHEMA and P4VP/PHPMA blends were annealed at 180 °C for 5 min. This temperature is close to thermal degradation. After this thermal treatment, the blend T_g's were measured again. A single T_g was obtained in all cases, which indicates that no phase demixing takes place in these systems at temperatures below those at which thermal degradation occurs. Consequently, it can be established that these blends do not exhibit an LCST.

With regard to P2VP blends, phase behavior has only been studied for the P2VP/PHEMA system, taking into account that P2VP/PHPMA blend shows no reliable results in the enthalpy recovery method. After annealing at 175 °C, samples were subjected to the enthalpy recovery method protocol. Figure 5 shows the thermograms obtained after annealing in comparison with a nonannealed

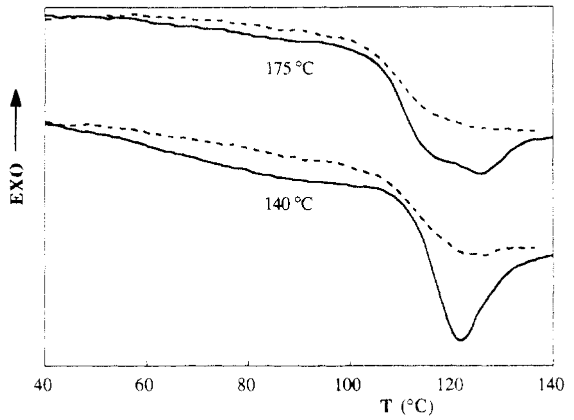

Figure 5. Enthalpy recovery peaks for P2VP/PHEMA (80/20%) and subsequent scan (dashed lines) after two different temperature annealings (140 and 175 °C).

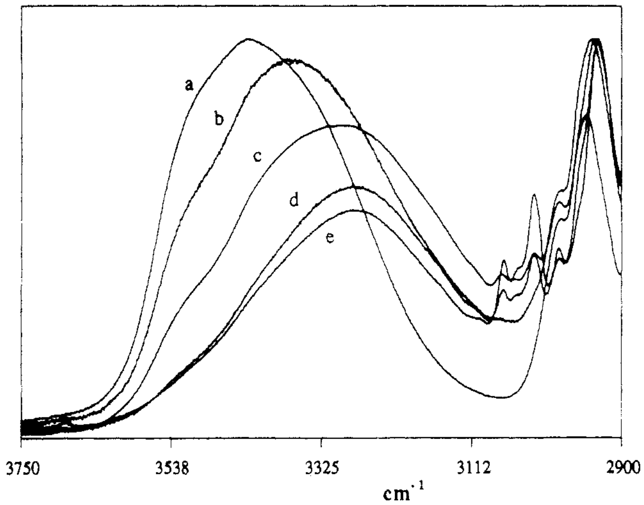

Figure 6. Scale-expanded infrared spectra in the range 2900–3750 cm^{-1} for (a) pure PHEMA and (b–e) P4VP/PHEMA blends of different compositions: (b) 20/80; (c) 40/60; (d) 60/40; (e) 80/20.

sample at the same blend composition. Clearly, the enthalpy recovery peaks are broader and correspond to two overlapped peaks. Furthermore, the higher the compositions of P2VP, the more prominent this behavior becomes. These results suggest an LCST phase behavior for P2VP/PHEMA blend.

FTIR Analysis. Infrared spectroscopy has been proved to be a powerful tool for the study of specific interactions between polymers. Considering the chemical structure of the polymers used here, the existence of hydrogen bonding between the binary mixtures studied is expected as a result of the interaction between the hydroxyl groups of PHEMA and PHPMA and the nitrogen atoms of the pyridine rings of P2VP and P4VP. The mechanism of interpolymer miscibility through the formation of hydrogen bonds can be studied by infrared spectroscopy both qualitatively and quantitatively. This type of interaction was already found to occur in the case of low molecular weight alcohols and pyridines and was analyzed by infrared spectroscopy.[16] Figure 6 shows the spectra of PHEMA and some blends with P4VP in the hydroxyl stretching 3100–3600-cm^{-1} region. In the case of pure PHEMA a broad band centered at 3370 cm^{-1} and a slight shoulder at 3524 cm^{-1} can be observed. This is typical of self-associated polymers containing hydroxyl groups as in the case of poly(vinylphenol)[15] or poly(vinyl alcohol).[16] The shoulder at higher wavenumbers corresponds to the contribution of free hydroxyl groups in the polymer, whereas the maximum at lower wavenumbers is attributed to inter- or intramolecular associated hydroxyl groups. Taking into account the chemical structure of PHEMA, self-association may occur especially by hydroxyl–carbonyl or hydroxyl–hydroxyl hydrogen bonding. Figure 7 shows the carbonyl stretching region for PHEMA. For pure PHEMA a maximum is observed at 1727 cm^{-1}, and close to it, at lower wavenumbers, a clear shoulder is observed which indicates the presence of carbonyl groups hydrogen bonded to hydroxyl ones. The characteristics of both the hydroxyl and the carbonyl stretching regions are notably affected by the presence of the second component in the blend. As the P4VP content increases, the shoulder at 3524 cm^{-1} decreases and the maximum of absorbance is shifted to lower wavenumbers up to 3278 cm^{-1} for blends containing 80% P4VP content (see Figure 6). Accordingly, as the P4VP content increases in the blend, the contribution corresponding to associated hydroxyl groups becomes more important at the expense of free hydroxyl ones. These facts suggest that hydrogen bonding between PHEMA and P4VP is stronger than PHEMA self-association. In the same spectral region (3100–3600 cm^{-1}), blends of P2VP/PHEMA, P2VP/PHPMA, and P4VP/PHPMA show similar results, and, consequently, the conclusions drawn before are also applicable to these systems.

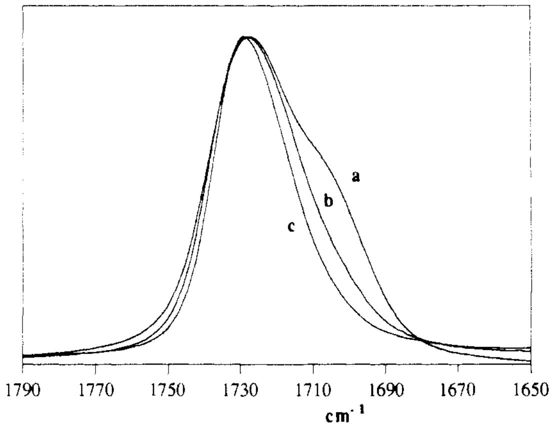

Figure 7. Scale-expanded infrared spectra in the range 1650–1790 cm^{-1} for (a) pure PHEMA, (b) P4VP/PHEMA (40/60) blend, and (c) P4VP/PHEMA (60/40) blend.

The preference of hydroxyl groups of PHEMA for interacting with nitrogen atoms of the pyridine ring compared with carbonyls of the same polymer is clearly proved after analysis of the carbonyl stretching region of PHEMA and its P4VP blends (Figure 7). Spectra of the blends show clearly a diminution of the shoulder at low wavenumbers and a narrowing of the band as P4VP content increases. Similar effects are found in the rest of the systems under study confirming the stated preference.

At this point it is interesting to perform a quantitative study of the evolution of the fraction of free and associated carbonyl groups as the poly(vinylpyridine) content varies in the blend. For that purpose a least-squares curve-fitting method has been applied to the carbonyl stretching bands. The two bands corresponding to the contributions of free and associated carbonyls, respectively, fit well to a Gaussian function. Table I shows the calculated results for the systems under study. It must be pointed out that the free carbonyl fraction, f_F, has been determined from

$$f_F = \frac{A_F}{A_F + A_A/a}$$

where A_F and A_A are the areas (absorbances) under the peaks corresponding to free and associated carbonyl

Table I
Curve-Fitting Results of Carbonyl Stretching Bands

	free C═O band			bonded C═O band			
wt %	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	f_F
P4VP/PHEMA							
0/100	1728	22	57.1	1707	26	42.9	0.67
20/80	1728	22	69.2	1708	24	30.8	0.77
40/60	1728	24	74.3	1708	24	25.7	0.81
60/40	1728	22	80.5	1708	20	19.5	0.86
80/20	1728	21	80.3	1708	21	19.7	0.86
P4VP/PHPMA							
0/100	1729	22	55.9	1707	27	44.1	0.66
20/80	1728	23	63.5	1708	26	36.5	0.72
40/60	1728	22	71.6	1709	24	28.4	0.79
60/40	1727	22	77.6	1708	22	22.4	0.84
80/20	1727	22	78.4	1708	23	21.6	0.84
P2VP/PHEMA							
40/60	1729	23	66.5	1707	27	33.5	0.75
60/40	1729	23	75.7	1708	27	24.3	0.82
80/20	1729	21	80.7	1708	22	19.3	0.86
P2VP/PHPMA							
20/80	1729	23	58.2	1707	27	41.9	0.68
40/60	1729	22	65.2	1708	28	34.8	0.74
60/40	1728	22	73.5	1709	28	26.5	0.81
80/20	1728	22	77.0	1709	23	23.0	0.83

groups, respectively, and a is the ratio of the molar absorption coefficients: A_A/A_F. A value of 1.5 was taken for the a ratio, according to previous infrared studies in similar systems.[17-19] With the limitations indicated, some valuable conclusions can be drawn:

(i) The fraction of free carbonyl groups is higher in P4VP in comparison with P2VP ones. This suggests a greater ability of P4VP for hydrogen bonding than P2VP.

(ii) The break of self-association varies almost linearly as the poly(vinylpyridine) content increases up to 60% in the case of P4VP and up to 80% for P2VP. Beyond these limits a stabilization seems to occur in both cases.

The analysis of spectral bands of poly(vinylpyridines) also gives insight into the type of interpolymer interactions occurring in the systems. According to previous studies of the infrared spectrum of pyridine hydrogen bonded with alcohols[14] and of interpolymer P2VP/poly(ethylene-*co*-methacrylic acid) complexes,[3] the most affected bands are those concerned with stretching modes of the pyridine ring: 1590, 993, and 625 cm^{-1} for P2VP and 1597, 993, and 627 cm^{-1} for P4VP. Upon formation of hydrogen bonds, these bands shift to higher frequencies. This effect is attributed to changes in electronic distribution in the pyridine ring due to the formation of stronger bonds.

The bands at 1590 and 1597 cm^{-1} for P2VP and P4VP, respectively, are of particular interest, since in this region there is no significant absorbance of PHPMA and PHEMA. It can be observed that these peaks become broader and shift to lower wavenumbers as the PHEMA and PHPMA contents increase in the blend. For blends having 80% weight of PHPMA or PHEMA, the shift of the peak is about 5 cm^{-1} in blends with P4VP and 3 cm^{-1} in blends with P2VP. These features are shown in Figure 8. The observed changes would be the result of the contribution of free and associated pyridine rings and should be explained by considering that a higher content of the component with hydroxyl groups increases the probability of hydrogen bonding with pyridine rings. The band located at 993 cm^{-1} coincides in position in both isomeric forms of poly(vinylpyridines). At this location there is a partial overlap with bands of PHEMA and PHPMA, for which a subtraction of the spectrum of these components is necessary to analyze the band. Fortunately, there are also small bands in the 980–850-cm^{-1} region, corresponding to vibration modes of PHEMA and PHPMA and located in a region where P2VP and P4VP do not show any remarkable absorbance. Since these bands are not affected by interactions in the blend, they facilitate the digital

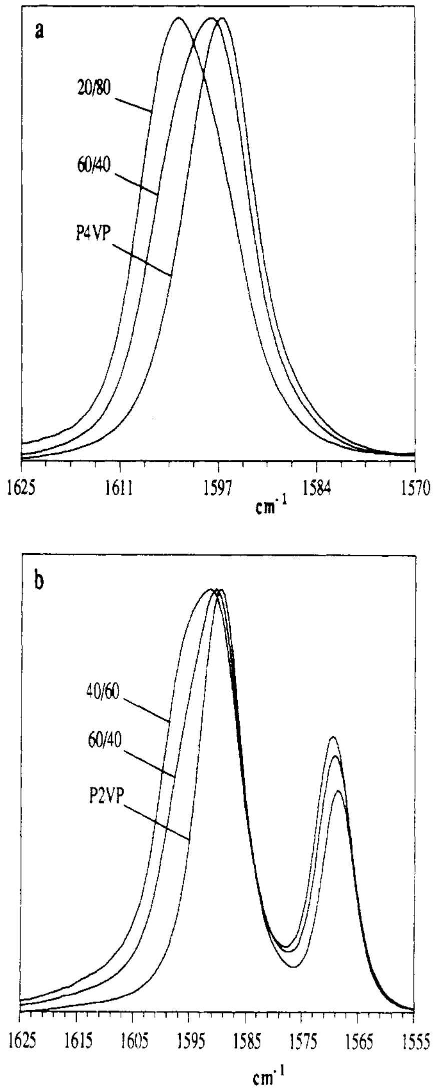

Figure 8. Scale-expanded infrared spectra corresponding to pyridine ring modes for (a) P4VP/PHEMA blends and (b) P2VP/PHEMA blends.

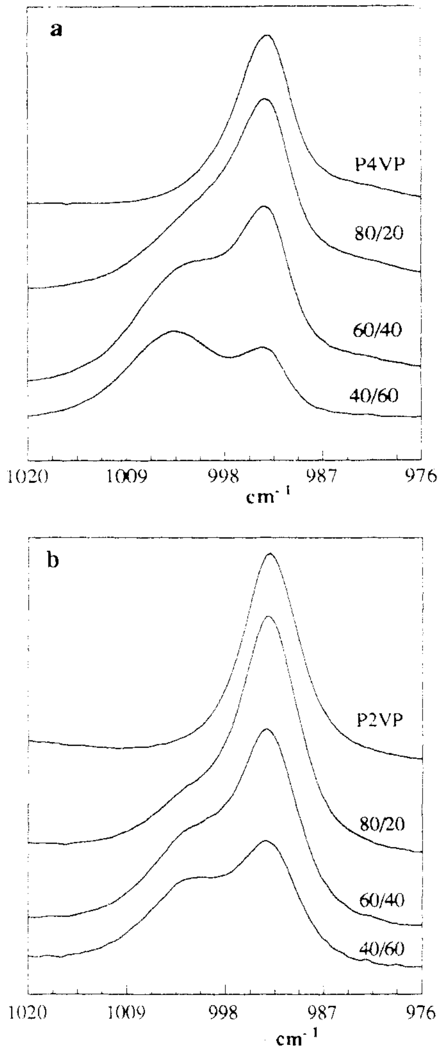

Figure 9. Scale-expanded infrared spectra in the range 976–1020 cm^{-1}: (a) P4VP/PHPMA blends; (b) P2VP/PHPMA blends. For both, the PHPMA spectrum has been digitally subtracted.

subtraction of the spectrum of each component. Figure 9 shows the subtracted spectra for two different blends with P2VP and P4VP. A new band corresponding to hydrogen-bonded pyridine rings can clearly be observed, whose contribution becomes more important as the content of the hydroxylated component increases. The new band is located at 1002 cm^{-1} for blends of P2VP and at 1004 cm^{-1} for P4VP blends. At 625 cm^{-1} all the components present absorbance bands. However, subtraction of spectra is not a useful technique in this case because the absorbance of poly(vinylpyridine) is very low in this region, so that the subtracted spectra are too noisy for a precise analysis.

In sum, FTIR analysis confirms the presence of specific interactions by hydrogen bonding in the systems under study. On the other hand, it is possible to perform a quantitative analysis of the fraction of pyridine rings associated in these interactions.

Again we use a curve-fitting procedure, now for the bands corresponding to pyridine ring modes located at 1597 cm^{-1} for P4VP blends and 1590 and 1569 cm^{-1} for those where P2VP is the second component. The choice of these bands is justified by the absence of any significant absorbance from PHEMA or PHPMA in this particular region. For the blends containing P2VP, the 1569-cm^{-1} band must be included in the curve-fitting analysis, because, despite the fact that this band remains unaffected by hydrogen bonding, it overlaps with the 1590-cm^{-1} band. All these bands fit to curves essentially Lorentzian in character. In Table II results are summarized for several blends. Some comments are necessary about the reported percentage of free pyridine groups in Table II. As stated previously, it is necessary to know the corresponding absorptivity ratio of the hydrogen bonded to free pyridine bands to perform this calculation. As has been pointed out by Lee et al.[3] in their study on P2VP/poly(ethylene-*co*-methacrylic acid) blends, the 1569-cm^{-1} band can be employed as an internal standard. As this pyridine mode remains unaffected by the presence of hydroxyl groups, differences in the absorption coefficients of the 1590- and 1596-cm^{-1} bands should yield a systematic change in the fractional area of the 1570-cm^{-1} band with blend composition. As can be seen in Table II, the fractional area of this band, employed as an internal standard, remains constant at 0.26 for both P2VP systems, in excellent accord with data reported by Lee et al.[3] In a similar way the 1557-cm^{-1} band can be employed as an internal standard in P4VP systems versus the 1597- and 1604-cm^{-1} bands; its fractional area remains constant, now at 0.13. Thus, an absorptivity ratio of unity has been assumed for all these blends in the data reported in Table II.

Table II
Curve-Fitting Results of Stretching Pyridine Ring Bands

	free pyridine ring band			bonded pyridine ring band			
wt %	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	wavenumber (cm^{-1})	width (cm^{-1})	rel area (%)	f_F
P4VP/PHEMA							
20/80	1597	12	34.3	1604	11	65.7	0.34
40/60	1597	12	47.5	1604	11	52.5	0.48
60/40	1597	11	61.5	1604	11	38.5	0.62
80/20	1597	11	75.7	1604	11	24.3	0.76
P4VP/PHPMA							
20/80	1597	11	42.2	1604	11	57.8	0.42
40/60	1597	11	53.6	1604	11	46.4	0.54
60/40	1597	10	67.7	1604	10	32.3	0.68
80/20	1597	11	77.4	1604	10	22.6	0.77
P2VP/PHEMA							
40/60	1590	10	55.5	1596	11	44.5	0.56
60/40	1590	10	67.7	1596	10	32.3	0.68
80/20	1590	9	90.6	1596	9	9.4	0.91
P2VP/PHPMA							
20/80	1590	9	50.0	1596	10	50.0	0.50
40/60	1590	9	59.0	1596	9	41.0	0.59
60/40	1590	9	73.3	1596	9	26.7	0.73
80/20	1590	9	85.9	1596	9	14.1	0.86

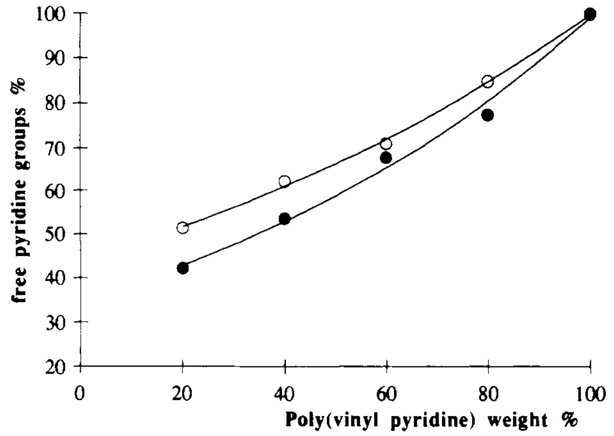

Figure 10. Percentage of free pyridine groups as a function of poly(vinylpyridine) content in the blends: (○) P2VP/PHPMA; (●) P4VP/PHPMA.

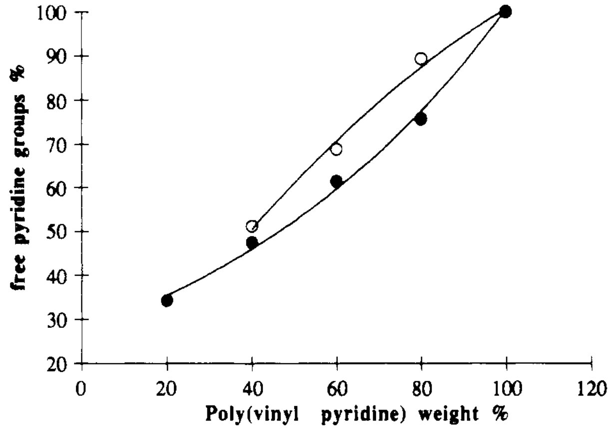

Figure 11. Percentage of free pyridine groups as a function of poly(vinylpyridine) content in the blends: (○) P2VP/PHEMA; (●) P4VP/PHEMA.

The obtained results agree with our previous qualitative digression. As displayed in Figures 10 and 11, the percentage of free pyridine groups in the blend remarkably diminishes as the amount of hydroxylated component increases, according to the fact that a higher number of hydroxyl groups are available for hydrogen bonding. A second point of interest is that for the entire composition range the percentage of hydrogen-bonded pyridine groups is higher in P4VP blends than in P2VP blends. This last result corroborates our previous conclusions in the carbonyl band analysis.

Finally, a study of the evolution of the specific interactions in the blend as a function of temperature was carried out. In this study the pyridine ring mode at 993 cm^{-1} was chosen as the most accurate band for the detection of hydrogen-bonded pyridine groups. The necessary digital subtraction of the PHEMA and PHPMA spectra was performed according to the protocol reported above and using the PHEMA and PHPMA spectra at the same temperatures of the blends. The obtained results show an important decrease in the number of pyridine rings associated by hydrogen bonding as the temperature increases (see Figure 12). Nevertheless, there are important differences in comparing the spectra of P4VP blends to those of P2VP blends. In the first systems, even at high temperatures (170 °C), there are a certain number of hydrogen-bonded pyridine groups (shoulder at high wavenumbers), whereas in the second systems the shoulder disappears. In fact, at high temperatures this band is similar to that of the unblended P2VP. In addition, after the sample reaches room temperature (see Figure 12), spectra corresponding to P4VP blends show a recovery of the hydrogen bonding; on the contrary, any recovery in the hydrogen-bonded pyridine groups can be observed in the case of P2VP blends. These results agree with DSC results for P2VP/PHEMA and confirm that a phase separation occurs by an irreversible breaking of hydrogen bonds in the system. Providing that this behavior is similar in P2VP/PHPMA (Figure 12), we can conclude that LCST behavior occurs in both blends. In addition, hydrogen-bonding recovery in P4VP blends agrees with the fact that phase separation was not observed by DSC.

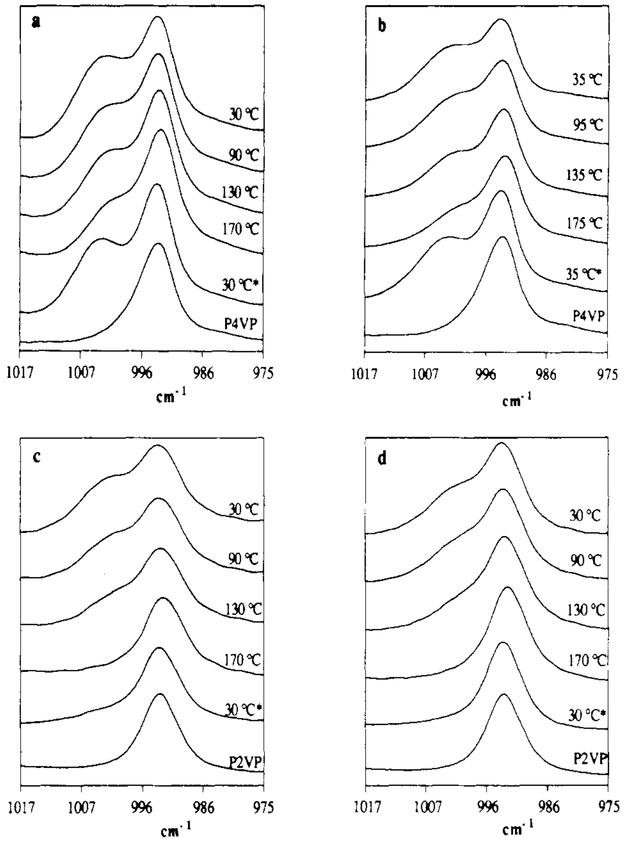

Figure 12. Scale-expanded infrared spectra in the range 975–1017 cm^{-1} at different temperatures for 60/40 blends: (a) P4VP/PHEMA; (b) P4VP/PHPMA; (c) P2VP/PHEMA; (d) P2VP/PHPMA.

Conclusions

The reported results clearly show that we are in the presence of polymer blends whose miscibility is hydrogen bonded controlled. These specific interactions become evident in the thermal behavior of the blends, where we have found T_g values that are higher than the weight average of their components, as a consequence of the mobility restrictions imposed by hydrogen bonds.

A second characteristic to be pointed out is the influence of the nitrogen atom position in the pyridine ring. Calorimetric results and infrared spectra indicate that P4VP has a greater ability to hydrogen bond with PHEMA or PHPMA than P2VP. This fact suggests that the nitrogen atoms in P2VP are sterically hindered, being closer to the main chain than those in P4VP. The importance of steric hindrance effects on specific interactions between polymers was pointed out by Garton[19] in the earliest works about infrared spectra of polymer blends; in the case of poly(vinylpyridines), steric hindrance seems to play a decisive role in hydrogen-bonding ability and thus in phase behavior. Recently, we found[20] that P4VP is miscible with poly(vinyl acetate-*co*-vinyl alcohol) co-polymers over a broad range of compositions, while P2VP is not. Moore et al.[21] reported a similar result in blends of poly(vinylpyridines) with poly(enamino nitrile). In our blends there is not such a dramatic influence, but we do in fact observe differences in the phase–temperature behavior: blends containing P4VP do not show an LCST behavior as occurs in P2VP blends.

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References and Notes

(1) Ulrich, H. *Introduction to Industrial Polymers*; Hanser: München, 1982.
(2) Smid, J.; Tan, Y. Y.; Challa, J. *Polym. Commun.* **1986**, *27*, 148.
(3) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 954.
(4) Huglin, M. B.; Rego, J. M. *Polymer* **1990**, *31*, 1269.
(5) Vivas de Meftahi, M.; Frechet, J. M. J. *Polymer* **1988**, *29*, 477.
(6) Bekturov, E. A.; Bimendina, L. A. *Adv. Polym. Sci.* **1981**, *41*, 99.
(7) Wang, L. F.; Pearce, E. M.; Kwei, T. K. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, *29*, 619.
(8) Kwei, T. K. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 307.
(9) Kwei, T. K.; Pearce, E. M.; Pennacchia, J. R.; Charton, M. *Macromolecules* **1987**, *20*, 1174.
(10) Yang, T. P.; Pearce, E. M.; Kwei, T. K.; Yang, N. L. *Macromolecules* **1989**, *22*, 1813.
(11) Jenckel, E.; Heusch, R. *Kolloid Z.* **1953**, *30*, 89.
(12) Bosma, M.; ten Brinke, G.; Ellis, T. S. *Macromolecules* **1988**, *21*, 1465.
(13) Grooten, R.; ten Brinke, G. *Macromolecules* **1989**, *22*, 1761.
(14) Takahashi, H.; Mamola, K.; Plyler, E. K. *J. Mol. Spectrosc.* **1966**, *21*, 217.
(15) Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* **1985**, *26*, 228.
(16) Ping, Z.; Nguyen, Q. T.; Neel, J. *Makromol. Chem.* **1988**, *189*, 437.
(17) Moskala, E. J.; Howee, S. E.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1984**, *17*, 1671.
(18) Coleman, M. M.; Lichkus, A. M.; Painter, P. C. *Macromolecules* **1989**, *22*, 586.
(19) Garton, A. *Polym. Eng. Sci.* **1984**, *24*, 112.
(20) Cesteros, L. C.; Isasi, J. R.; Katime, I. *J. Polym. Sci.*, submitted.
(21) Moore, J. A.; Kim, J. H. *Macromolecules* **1992**, *25*, 1427.