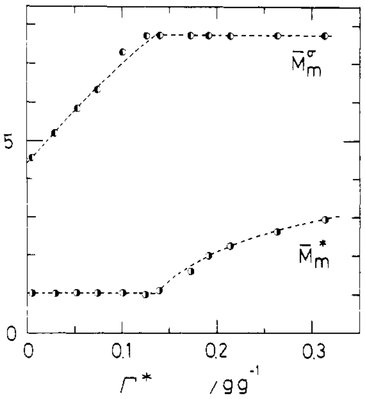

Figure 10. Plots of the average molecular weights $\bar{M}_m^\sigma$ (◐) on the surface and $\bar{M}_m^*$ (◑) in the bulk solution vs. nonadsorbed amount of Γ^* for a mixture of PS-77.5 and PS-10.2. Dashed lines are calculated from eq 7-10.

and the equilibrium concentration where the adsorption is attained to be the plateau excellently agree with the values calculated from the theory. This discrepancy may be due to the overwhelming preferential adsorption of large molecules over small molecules.

Another interesting aspect of the present work is the determination of the average molecular weights on the surface and in the bulk solution using polystyrene samples with a narrow molecular weight distribution and also the GPC technique. Therefore, we note that important conclusions are obtained since the validity of assumptions based on the theoretical prediction is confirmed experimentally.

Registry No. Polystyrene (homopolymer), 9003-53-6; silica, 7631-86-9.

References and Notes

(1) Roe, R.-J. *Polym. Sci. Technol. Ser.* **1980**, *12B*, 629.
(2) (a) Felter, R. E.; Moyer, E. S.; Ray, L. N. Jr. *J. Polym. Sci., Part B* **1969**, *7*, 529. (b) Felter, R. E.; Ray, L. N., Jr. *Colloid Interface Sci.* **1970**, *32*, 349. (c) Felter, R. E. *J. Polym. Sci., Part C* **1971**, *34*, 227.
(3) Howard, G. J.; Woods, S. J. *J. Polym. Sci., Part A-2* **1972**, *10*, 1023.
(4) Vander Linden, C.; Van Leemput, R. *J. Colloid Interface Sci.* **1978**, *67*, 63.
(5) Cohen-Stuart, M. A.; Scheutjens, J. M. H. M.; Fleer, G. J. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 559.
(6) Koopal, K. K. *J. Colloid Interface Sci.* **1981**, *83*, 116.
(7) Furusawa, K.; Yamashita, K.; Konno, K. *J. Colloid Interface Sci.* **1982**, *86*, 35.
(8) Hlady, V.; Lyklema, J.; Fleer, G. J. *J. Colloid Interface Sci.* **1982**, *87*, 395.
(9) Cohen-Stuart, M. A.; Fleer, G. J.; Bisterbosch, B. H. *J. Colloid Interface Sci.* **1982**, *90*, 310.
(10) Fontana, B. J.; Thomas, J. R. *J. Phys. Chem.* **1961**, *65*, 480.
(11) Robb, I. D.; Smith, R. *Eur. Polym. J.* **1974**, *61*, 413.
(12) Barnett, K. G.; Cosgrove, T.; Vincent, B.; Sissons, D. S.; Cohen-Stuart, M. A. *Macromolecules* **1981**, *14*, 1018.
(13) Killmann, E.; Eisenlauer, J.; Korn, M. *J. Polym. Sci., Part C* **1977**, *61*, 413.
(14) Kawaguchi, M.; Hayakawa, K.; Takahashi, A. *Polym. J.* **1980**, *12*, 265.
(15) Kawaguchi, M.; Sano, T.; Takahashi, A. *Polym. J.* **1981**, *13*, 1019.
(16) Kawaguchi, M.; Kamiya, K.; Takahashi, A. *Polym. J.* **1982**, *14*, 563.
(17) Kawaguchi, M.; Aoki, M.; Takahashi, A. *Macromolecules* **1983**, *16*, 635.
(18) Boehm, H. P.; Schneider, M. *Z. Anorg. Allg. Chem.* **1959**, *301*, 326.

On the Role of Intermolecular Hydrogen Bonding in Miscible Polymer Blends

Eric J. Moskala, Stephen E. Howe, Paul C. Painter, and Michael M. Coleman*

Department of Materials Science and Engineering, Polymer Science Program, The Pennsylvania State University, University Park, Pennsylvania 16802.
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ABSTRACT: The results of a Fourier transform infrared study of poly(vinylphenol) blends with poly(vinyl acetate) and ethylene-vinyl acetate copolymers are presented. Infrared bands attributed to intermolecular hydrogen-bonding interactions involving the phenolic hydroxyl group with the acetate carbonyl group are identified. A quantitative measure of the fraction of hydrogen-bonded carbonyl groups in the blends has been obtained as a function of temperature. The results are considered in terms of an effective equilibrium constant, and an estimation of the strength of the intermolecular interaction has been gained. Ramifications concerning polymer-polymer miscibility and the effect of temperature, solvent, and glass transition temperature on the structure of polymer blends are discussed.

Introduction

In a series of previous publications,[1-8] we have presented the results of Fourier transform infrared (FT-IR) studies of a number of binary compatible polymer blend systems. Perhaps the most significant conclusion of this work is that infrared spectroscopy can be employed to detect and identify the presence of intermolecular interactions occurring between different polymeric components in many compatible blends. An excellent example is the study of the compatible polymer blend system containing the poly(hydroxy ether of bisphenol A) (Phenoxy) and poly(ϵ-caprolactone) (PCL).[5] A hydrogen-bonding type of intermolecular interaction was unambiguously identified involving the PCL carbonyl group with the hydroxyl group of the Phenoxy polymer. Furthermore, it was demonstrated that the relative strength of this intermolecular interaction was weaker than that occurring in pure Phenoxy (self-association).

These intermolecular interactions are considered to play a key role in polymer compatibility. As discussed in the elegant paper of Patterson and Robard,[9] polymer-polymer compatibility may be viewed as a balance between a free volume term (which is always unfavorable to mixing) and an interactional term (potentially favorable). If the latter

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is negative and overrides the free volume contribution at any given temperature, a miscible polymer blend system is indicated. As temperature increases, the magnitude of the interactional term decreases while that of the free volume term increases. At the point where the free volume term cancels the interactional contribution, a lower critical solution temperature (LCST) is reached and the blend phase separates. Recent FT-IR studies performed in our laboratories of polymer blends containing an ethylene–vinyl acetate (EVA) copolymer with either poly(vinyl chloride) (PVC) or chlorinated polyethylene (CPE) appear to substantiate the above hypothesis.[8] It was concluded that the average strength of the intermolecular interactions occurring between EVA and CPE (or PVC) decreases in a nonlinear fashion as a function of increasing temperature and that the LCST of the system occurs at the point where these intermolecular interactions become very weak.

It is our overall objective to attempt to use infrared spectroscopy to obtain a quantitative (or at least a semiquantitative) measure of the strength and number of intermolecular interactions as a function of temperature occurring in the pure individual polymeric components (self-association) and in the miscible blend (association of unlike species). Information such as this should lead to a better understanding of miscible polymer blend systems and their phase behavior. However, in this and a subsequent paper, we will be primarily concerned with the results we have obtained from a number of polymer blends containing poly(vinylphenol) (PVPh). This represents a natural extension to our previous studies where we have been progressively increasing the strength of the potential intermolecular hydrogen-bonding interactions between the components in a blend. The aromatic hydroxyl group of PVPh is capable of forming stronger hydrogen bonds with esters, ethers, etc. than the aliphatic hydroxyl group of phenoxy. Thus, it occurred to us that if we increase the strength of the intermolecular interaction, it may be possible to compatibilize polymers with PVPh that have been previously shown to be incompatible with phenoxy and PVC. For example, poly(vinyl acetate) (PVAc)[10] and poly(β-propiolactone) (PPL)[11] have been shown to be incompatible with PVC at ambient temperature. However, as we will see later, they are compatible with PVPh.

We have performed extensive studies on the PVPh blends and there are several important results that warrant discussion. Accordingly, we will present the results obtained for the PVPh blends with PVAc and EVA copolymers in this paper and defer a discussion of the blends containing polyesters, poly(alkyl vinyl ethers), poly(vinylpyrrolidone), and poly(alkyl oxides) to the subsequent paper in this series.

Experimental Section

The poly(4-vinylphenol) and poly(vinyl acetate) polymers were obtained from Polysciences Inc. and have reported molecular weights of M_w = 1500–7000 and 60000 (undefined), respectively. The glass transition temperatures of these two polymers are approximately 130 and 28 °C, respectively, as determined by differential scanning calorimetry. Ethylene–vinyl acetate copolymers containing 70, 45, and 25 wt % vinyl acetate were obtained from Mobay Chemical Co. (the former two copolymers) and Polysciences Inc. (the latter).

Thin films of the blends prepared for the FT-IR and thermal analysis measurements were cast from 1% (w/v) tetrahydrofuran solutions onto potassium bromide windows at room temperature. After the majority of the solvent had evaporated, the films were transferred to a vacuum desiccator to remove residual solvent and stored under vacuum.

Infrared spectra were obtained on a Digital FTS/15E FT-IR spectrometer. A minimum of 32 scans at a resolution of 2 cm^{-1} was averaged and stored on a magnetic disk system. The frequency scale is internally calibrated with a reference helium–neon laser to an accuracy of 0.2 cm^{-1}. A SPECAC high-temperature cell mounted in the spectrometer was employed to obtain elevated-temperature spectra to an accuracy of ±2 °C. All of the films used for the infrared studies were sufficiently thin to be within the range where the Beer–Lambert law is obeyed.[12]

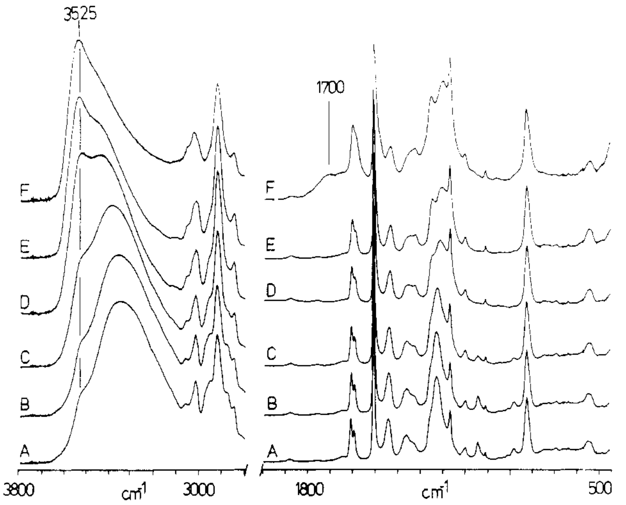
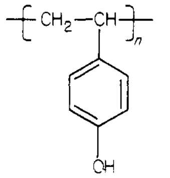


Figure 1. FT-IR spectra of PVPh recorded at (A) room temperature, (B) 50 °C, (C) 100 °C, (D) 150 °C, (E) 200 °C, and (F) 250 °C.

Thermal analysis was conducted on a Perkin-Elmer differential scanning calorimeter (DSC-2B) coupled to a computerized data station. A heating rate of 20 °C min^{-1} was used in all experiments and the glass transition temperature was taken as the midpoint of the heat capacity change.

Results and Discussion

Infrared Spectrum of Poly(vinylphenol). PVPh is an atactic polymer containing the chemical repeating unit



To our knowledge, no detailed vibrational analysis has been performed on PVPh. However, one might anticipate an infrared spectrum for the polymer that would be characterized at room temperature by relatively sharp bands associated with the predominantly conformationally insensitive modes of the aromatic ring and relatively broad bands attributable to conformationally sensitive backbone modes together with hydrogen-bonded hydroxyl modes. This is indeed what is observed, as illustrated in Figure 1. This figure is split into two frequency ranges, 3800–2800 and 2000–450 cm^{-1}. It is important to emphasize that for clarity of presentation the higher frequency region has been expanded on the absorbance scale by a factor of approximately 4 times over that of the lower frequency region. The spectra shown in Figure 1 were obtained over a range of temperatures from ambient to 250 °C. Using the group frequency approach,[13] one may reasonably assign the bands occurring at 825, 1100, 1170, 1445, and 1595/1610 cm^{-1}, which incidentally do not appear to change significantly upon increasing temperature, to the aromatic ring. In contrast, relatively broad bands in the 1200–1400-cm^{-1} region of the spectrum change markedly as a function of temperature. This is classically where phenols absorb in the solid state and the bands are attributed to OH deformation and C–O stretching vibrations which are mixed to some degree.[13]

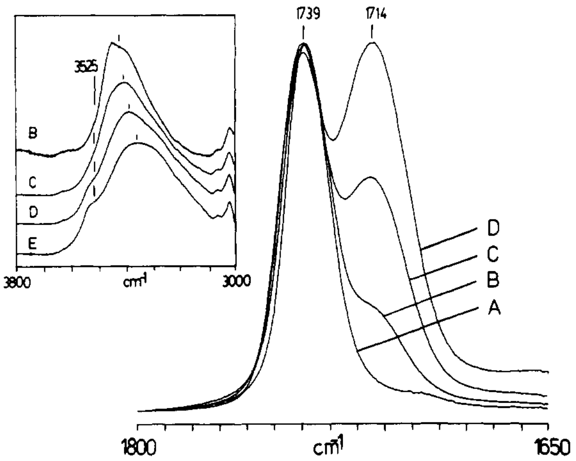


Figure 2. FT-IR spectra in the regions 3800–3000 and 1800–1650 cm^{-1} recorded at room temperature of PVPh–PVAc blends cast from THF containing (A) 100, (B) 80, (C) 50, (D) 20, and (E) 0 wt % PVAc.

Of particular significance to the current study is the high-frequency region from 3800 to 3000 cm^{-1}, where the hydroxyl stretching vibration is observed. At room temperature, the polymer cast from THF solution is characterized by a very broad band centered at 3360 cm^{-1}, attributed to wide distribution of hydrogen-bonded hydroxyl groups, and a much narrower band observed at 3525 cm^{-1}, which is associated with free (non hydrogen bonded) hydroxyl groups. With increasing temperature, the relative absorbance of the free hydroxyl band increases while that of the hydrogen-bonded hydroxyl groups decreases. In addition, the maximum peak position of the hydrogen-bonded hydroxyl mode *increases* in frequency, which is attributable to a decrease in the *average* strength of intermolecular hydrogen-bonded species. These results are similar and analogous to those previously described for the Phenoxy polymer.[5] There are, however, some subtle differences. The frequency of the free hydroxyl group occurs at 3570 and 3525 cm^{-1} for the Phenoxy and PVPh polymers, respectively, reflecting the increased electron attracting power of the aromatic ring. Nevertheless, the *difference* in frequency at room temperature between the free hydroxyl stretching vibration and the maximum in the band of the hydrogen-bonded hydroxyls is similar (~ 175 cm^{-1}) in both polymers. Presumably, this reflects a similar average strength of intermolecular hydrogen bonds (self-association).

Two other observations are worthy of mention. Between 200 and 250 °C there is evidence of some oxidative degradation as seen by the appearance of a band at 1700 cm^{-1}. Accordingly, the maximum temperature that can be used for our blend studies is about 200 °C. It should also be pointed out that there is only a very weak absorbance in the 1700–1800-cm^{-1} region of the spectrum of PVPh. (The very weak bands at approximately 1760 and 1880 cm^{-1} are overtones associated with a para-disubstituted aromatic ring.[13]) This is important because we require a "window" in this region if we are to study shifts in carbonyl bands in the blends without serious overlap from underlying bands.

PVPh Blends: Room-Temperature Films Cast from THF. In common with our previous experimental practice, we initially studied the room-temperature FT-IR spectra obtained from blend films of varying composition cast from a common solvent, in this case THF. Figure 2 shows FT-IR spectra in the hydroxyl stretching (3800–3000 cm^{-1}) and carbonyl stretching (1800–1650 cm^{-1}) regions of blends of PVPh and PVAc. The carbonyl stretching vibration of pure PVAc in the solid state (self-associated) occurs at 1739 cm^{-1}. Upon blending of PVAc with PVPh, an additional band at 1714 cm^{-1} is observed which increases in relative intensity as a function of increasing PVPh content and may be readily attributed to the stretching vibration of hydrogen-bonded carbonyl groups, i.e., $>C{=}O\cdots HOC_6H_4$. The shift in frequency of the hydrogen-bonded carbonyl group in relation to that of pure PVAc is significantly greater than those we have previously published for analogous polymer blend systems and reflects the increased strength of the intermolecular interaction. In fact, unlike the PCL blends with PVC,[1] vinylidene chloride copolymers,[4] and Phenoxy polymers,[5] the two carbonyl bands are well separated from one another and easily resolved. Curve fitting reveals that only two bands are necessary to satisfactorily match the spectra of the blends in the carbonyl region (after the weak absorbance due to the overtone occurring at 1760 cm^{-1} has been removed). As expected, the 1714-cm^{-1} band is significantly broader than that of the 1739-cm^{-1} band, which reflects a reasonably wide distribution of hydrogen bond distances and geometries in the blend. If we had information concerning the relative absorbance coefficients for the two carbonyl stretching vibrations, a measurement of the fraction of interacting species could be calculated from the fractional area of the 1714-cm^{-1} band. We will return to this subject later in the text, after we have described the temperature and annealing experiments.

We have previously mentioned that the pure PVPh polymer cast from THF exhibits two bands in the hydroxyl stretching region of the infrared spectrum: one at 3525 cm^{-1} attributable to free hydroxyl and the second, a very broad band centered at 3360 cm^{-1}, associated with hydrogen-bonded hydroxyls (self-association). As seen in Figure 2, as the concentration of PVAc is increased in the blends the free hydroxyl band is reduced and is not evident in the 80:20 PVAc–PVPh blend. Concurrently, the frequency maximum of the hydrogen-bonded hydroxyl band *increases* from about 3360 to 3430 cm^{-1}. (We must caution that the relatively sharp band at 3450 cm^{-1} superimposed upon the broad hydrogen-bonded hydroxyl band arises from an overtone present in the spectrum of PVAc. This band is only observed in PVAc-rich blends and may be readily eliminated by spectral subtraction.) Upon careful examination of the spectra of the blends it is evident that there are at least three major components. The first is due to free hydroxyls, the second to hydrogen-bonded hydroxyls (self-association of PVPh), and the third to hydroxyl groups associated with the carbonyl groups of PVAc. In any event, the average overall strength of the hydrogen bond between PVPh and PVAc, as measured by the difference in frequency from that of the free hydroxyl (~95 cm^{-1}), is *less than* that of the average strength of the self-associated pure PVPh (~165 cm^{-1}). Similar observations were reported previously for the Phenoxy–PCL system.[5]

The above infrared spectral observations of the PVAc–PVPh blends are entirely consistent with a miscible polymer blend system.[1-8] Differential scanning calorimetry studies reveal a single glass transition temperature (T_g) occurring between those of the pure polymers and which varies systematically with blend composition.

The results obtained for the PVPh blends with varying concentrations of the ethylene–vinyl acetate copolymer containing 70 wt % vinyl acetate (EVA (70)), are very similar to those of the analogous PVPh–PVAc blends. The carbonyl stretching frequency of pure amorphous EVA(70) in the solid state occurs at 1738 cm^{-1}. When EVA(70) is

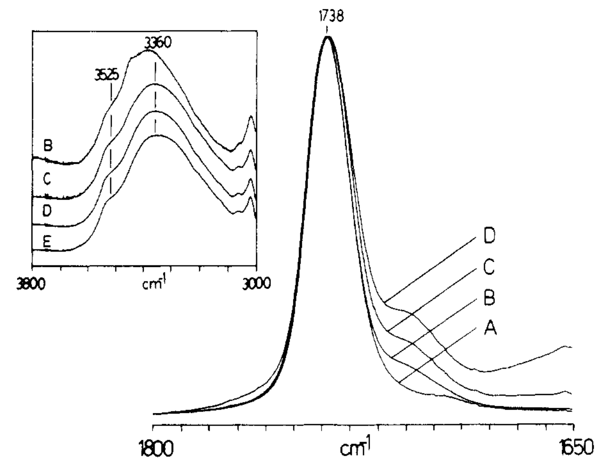


Figure 3. FT-IR spectra in the regions 3800–3000 and 1800–1650 cm^{-1} recorded at room temperature of PVPh–EVA(45) blends cast from THF containing (A) 100, (B) 80, (C) 50, (D) 20, and (E) 0 wt % EVA(45).

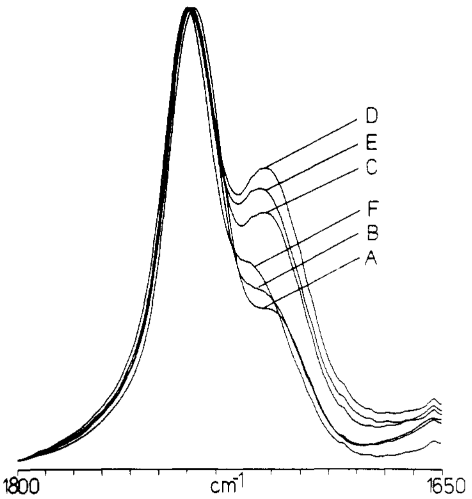


Figure 4. FT-IR spectra in the region 1800–1650 cm^{-1} of an 80:20 wt % PVPh–EVA(45) blend cast from THF and recorded as a function of increasing temperature: (A) room temperature, (B) 90 °C, (C) 110 °C, (D) 130 °C, (E) 150 °C, and (F) 190 °C.

mixed with PVPh, an obvious second band, attributed to carbonyl groups hydrogen bonded to the hydroxyl group of PVPh, is observed at 1708 cm^{-1}. This band increases in relative intensity as a function of PVPh concentration. In addition, the changes in the hydroxyl stretching region of the spectrum are almost identical with those described above for the PVPh–PVAc blends.

In contrast, we were surprised at the initial results obtained for the PVPh blends with the ethylene–vinyl acetate copolymer containing 45 wt % vinyl acetate (EVA(45)). PVC appears to be compatible with EVA(45) at ambient temperatures although the LCST occurs in a relatively low temperature range (about 100–130 °C).[8] Accordingly, with the increased strength of the intermolecular interaction in PVPh blends compared to PVC, we anticipated a miscible blend of PVPh with EVA(45). Figure 3 shows the infrared spectra obtained from films of blends containing PVPh and EVA(45) which were cast from THF solution. There is a striking difference between the spectra shown in Figures 2 and 3. In the carbonyl stretching region the spectra are dominated by the band at 1738 cm^{-1}, which is associated with the carbonyl stretching vibration of EVA(45) in the amorphous solid state. Only a very weak band is observed as a shoulder at about 1710 cm^{-1}, where we would anticipate the hydrogen-bonded carbonyl groups to absorb. Furthermore, the hydroxyl stretching region of the spectrum shows little, if any, significant differences. The band at 3525 cm^{-1} (free hydroxyl) is observed in all the blend spectra regardless of composition (a characteristic common to all the incompatible polymer blends containing hydroxyl groups that we have studied to date). Additionally, the broad hydrogen-bonded hydroxyl band does not shift or narrow to any measurable extent. This is in contrast to the spectral features observed in compatible phenoxy–poly(vinyl methyl ether) blends.[6]

In any event, the spectral results obtained for the PVPh–EVA(45) blend suggest that the system is at best only marginally compatible. To reiterate, this was a surprising result and as we will see later not entirely a correct conclusion. Complications arising from the way the sample is prepared have a major effect on the phase behavior of these blends.

Predictably, PVPh blends with ethylene–vinyl acetate copolymers containing 25 wt % vinyl acetate (EVA(25)) cast from THF solution show similar results to those obtained for the PVPh–EVA(45) blends. However, there is even less evidence for hydrogen-bonded carbonyl groups and the spectra are complicated somewhat by the occurrence of polyethylene-type crystallinity. In essence, the infrared spectral evidence suggests an incompatible system.

PVPh Blends: Elevated-Temperature Studies. Elevated-temperature FT-IR studies were performed on all the blends of PVPh with PVAc, EVA(70), EVA(45), and EVA(25). Our original intent was to obtain data concerning the relative strength of the intermolecular hydrogen-bonding interaction involved in the PVPh blends (i.e., $>C{=}O\cdots HOC_6H_4$) as a function of temperature. Similar studies on the CPE–EVA(45) polymer blend system[8] had been most informative. The average strength of the intermolecular interaction (in this case most probably a hydrogen-bonding type of interaction involving the EVA(45) carbonyl group and the methine protons of CPE (i.e., $>C{=}O\cdots HCCl$) was estimated from the relative shift of the hydrogen-bonded carbonyl band to that of pure EVA(45) in the amorphous state in a temperature range of approximately 20–160 °C. Between 90 and 110 °C, the strength of this intermolecular interaction was observed to be very weak and, significantly, this correlates with the independently measured LCST for this particular blend.[14] Comparable studies of the PVPh blends should be even more rewarding. Unlike the CPE–EVA(45) system, where the carbonyl stretching region of the blends represents a poorly resolved composite band with contributions from both the hydrogen-bonded and non-hydrogen-bonded carbonyls, in the PVPh blends the two contributions are well separated and resolved. In this case it should also be possible to obtain a measure of the fraction of the total number of hydrogen-bonded carbonyls. However, before we discuss this aspect of our work, it is necessary to consider a major problem that besets all polymer blend studies and appears to be particularly acute in the PVPh–EVA blends.

It might be recalled that we were particularly surprised that the infrared results on the films prepared at room temperature from THF solution indicated that the PVPh–EVA(45) blend was only marginally compatible. Spectra in the carbonyl stretching region, shown in Figure 4, illustrate the effect of heating an 80:20 wt % PVPh–EVA(45) blend sample originally cast from THF. At room temperature the spectrum is characterized by a major band at 1738 cm^{-1} (the carbonyl stretching frequency of EVA(45) in the amorphous state) and a relatively weak shoulder at about 1710 cm^{-1} (hydrogen-bonded carbonyls). Up to 70 °C very little change in the spectrum is observed. At 90

°C, however, there is an increase in the relative intensity of the band attributed to hydrogen-bonded carbonyls over that of the non-hydrogen-bonded species. A much larger increase is observed at 110 °C, which continues up to 130 °C. Between 130 and 190 °C, the trend is reversed and there is a systematic decrease in the relative intensity of the hydrogen-bonded to non-hydrogen-bonded carbonyl bands.

Although the above results appear somewhat confusing, we believe there is a simple explanation based on the following argument. It is often tacitly assumed that intimate mixing of two polymers can best be achieved by preparing a film from the evaporation of a common solvent. In fact, for samples used in transmission infrared spectroscopy one usually has little choice but to cast films from solvents to ensure that the samples are thin enough to be in a range where the Beer–Lambert law is obeyed.[12] Nevertheless, it is well-known that solvent type and rate of evaporation can have major effects upon the phase behavior of polymer blends. Patterson[15] describes the case where phase separation may easily occur in a ternary system (i.e., two miscible polymers in a common solvent) if there are significant differences in the strengths of the respective polymer–solvent interactions. In our PVPh blends with PVAc and the EVA's, we would anticipate major differences in the relative polymer–solvent interaction strengths of the two classes of polymers with the cyclic ether THF (hydroxyl–ether intermolecular interactions appear to be quite strong[5] in comparison to ester carbonyl–ether interactions[7]). Accordingly, it is reasonable to assume that the films of the PVPh–EVA(45) blends cast from THF are phase separated, but given the opportunity, the two polymers would prefer to be intimately mixed. The glass transition temperatures (T_g) of PVPh and EVA(45) are approximately +130 and −16 °C, respectively, while the predicted T_g of a miscible 80:20 wt % PVPh–EVA(45) blend is about 87 °C. Consequently, although the phase-separated blend would presumably prefer to revert to a single phase, there is insufficient mobility below the T_g and the structure is effectively "frozen in".

Given the above scenario, we are now in a position to rationalize the results obtained in the heating studies shown in Figure 4. Little change in the relative intensity of the hydrogen-bonded carbonyl band is observed up to 90 °C but there is a large increase at 110 °C which continues to about 130 °C. These observations can readily be explained on the basis of the T_g of the system. Above 130 °C, the relative intensity of the hydrogen-bonded carbonyl band decreases and this is a consequence of the increased thermal energy, which serves to reduce the average strength of the intermolecular interaction and decrease the number of interactions that, on average, occur.

This hypothesis is further substantiated by the FT-IR results obtained upon cooling the same sample from 190 °C to ambient temperature as shown in Figure 5. As the sample is cooled the relative intensity of the hydrogen-bonded carbonyl band increases at the expense of the non-hydrogen-bonded species over the entire temperature range. (Note particularly the marked contrast between the room-temperature spectra of the film cast from THF (Figure 4) and the heat-treated sample (Figure 5)). Furthermore, the frequency of the maxima in the bands associated with both the hydrogen-bonded and non-hydrogen-bonded carbonyls decreases systematically upon cooling. The effect is much greater, however, for the hydrogen-bonded carbonyls (about 6.5 cm^{-1} from 190 °C to room temperature) than the corresponding non-hydrogen-bonded species (ca. 2 cm^{-1}). The latter is entirely consistent with the results published previously for the frequency dependence upon temperature for pure EVA(45).[8]

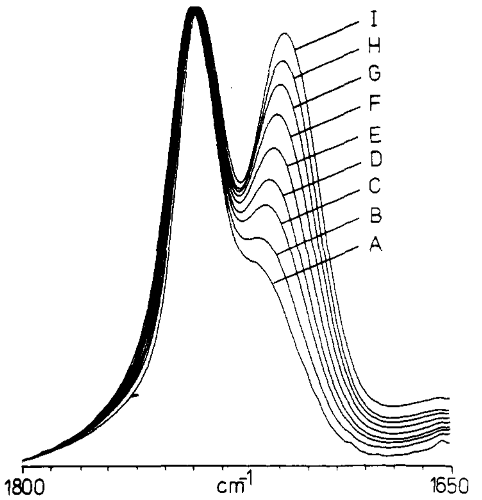


Figure 5. FT-IR spectra in the region 1800–1650 cm^{-1} of an 80:20 wt % PVPh–EVA(45) blend cast from THF, heated to 190 °C, and recorded as a function of decreasing temperature: (A) 190 °C, (B) 170 °C, (C) 150 °C, (D) 130 °C, (E) 110 °C, (F) 90 °C, (G) 70 °C, (H) 50 °C, and (I) room temperature.

Table I

T, °C	non-H-bonded carbonyls freq	non-H-bonded carbonyls area	H-bonded carbonyls freq	H-bonded carbonyls area[a]	frac of H-bonded carbonyls, %
	(a) Films Cast from THF (Figure 4)				
30	1737.1	943	1708.3	250	15.0
50	1737.6	922	1709.4	254	15.5
70	1738.0	961	1709.8	244	14.5
90	1738.3	913	1710.6	302	18.1
110	1738.7	802	1710.5	508	29.7
130	1739.1	714	1710.9	662	38.2
150	1739.5	771	1711.9	640	35.6
170	1739.9	815	1712.8	453	27.0
190	1740.0	904	1713.8	390	22.3
	(b) Films after Heat Treatment (Figure 5)				
190	1740.0	904	1713.8	390	22.3
170	1739.8	857	1712.9	477	27.1
150	1739.6	796	1711.9	560	31.9
130	1739.4	751	1711.2	622	35.6
110	1739.2	701	1710.4	671	39.0
90	1738.8	664	1709.4	723	42.1
70	1738.4	635	1708.5	752	44.1
50	1738.0	616	1707.8	780	45.8
30	1737.4	522	1707.3	739	48.6

[a] Adjusted by a factor of a_1/a_2 (see text).

As temperature decreases (Figure 5), two major effects are observed and both are relevant to the subject of the miscibility and phase behavior of polymer blends. The first is that the average overall strength of the intermolecular hydrogen-bonding interaction increases. This is indicated by the decrease in frequency of the hydrogen-bonded carbonyl band (approximately 6.5 cm^{-1} from 190 °C to room temperature (see Table I)). The second major effect is that the fraction of hydrogen-bonded carbonyl groups increases with decreasing temperature. One must recognize that in the time scale of our infrared experiments, we are observing an average structure. The polymer blend is in a dynamic state and presumably hydrogen bonds are being formed and broken quite rapidly. However, on average, at a given temperature, the infrared spectral features will reflect the fraction of hydrogen-bonded to non-hydrogen-bonded carbonyl groups.

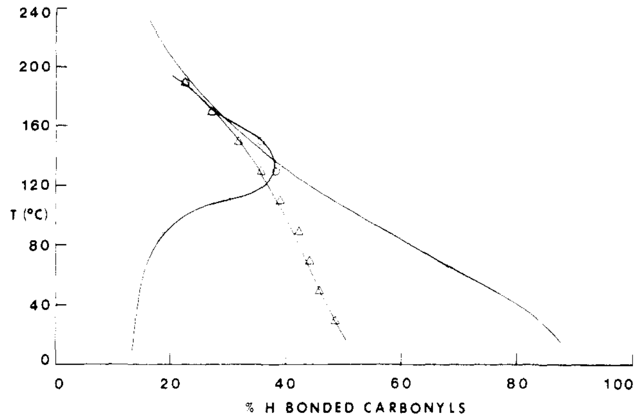


Figure 6. Graph of temperature vs. fraction of hydrogen-bonded carbonyls for an 80:20 wt % PVPh–EVA(45) blend. (○) Sample cast from THF at room temperature and heated to 190 °C; (△) same sample cooled from 190 °C. The solid line represents the theoretical calculations (see text).

Incidentally, a second cycle of reheating to 190 °C and subsequently cooling back to room temperature yield spectra that are essentially identical with those shown in Figure 5.

To obtain a quantitative measure of the fraction of hydrogen-bonded carbonyls present in a sample of the PVPh–EVA(45) blend, we require knowledge of the respective absorptivities, a_1 and a_2 for the 1738- and 1708-cm^{-1} bands, or at least, the ratio of the two absorptivities, a_2/a_1. Fortunately, we can obtain a measure of the absorptivity ratio from the infrared spectra shown in Figures 4 and 5. Consider the two spectra acquired at room temperature. Using curve fitting techniques,[16] we can obtain the relative areas of the 1738- and 1708-cm^{-1} bands in both spectra. Recall that these spectra were recorded on the same sample and the total concentration of carbonyl groups in the infrared beam remains constant. However, a fraction of the non-hydrogen-bonded carbonyls in the solvent-cast film (Figure 4) convert to hydrogen-bonded species upon heat treatment (Figure 5). Let us denote the intensity (area) of the 1738- and 1708-cm^{-1} bands in the solvent-cast film as I_1 and I_2, respectively, and in the corresponding heat-treated film as I_1' and I_2'. Now

$$a_2(I_1 - I_1') = a_1(I_2' - I_2)$$

and

$$\frac{a_1}{a_2} = \frac{I_1 - I_1'}{I_2' - I_2}$$

Thus we should be able to measure the absorptivity ratio and determine the fraction of hydrogen-bonded carbonyl groups in the blend. Naturally, errors in the measurement of the absorptivity ratio will be minimized for samples where there are large differences in the relative intensities of the hydrogen-bonded to non-hydrogen-bonded species in the two spectra. Such is the case for the spectra recorded between room temperature and 90 °C. A value of absorptivity ratio of 1.5 ± 0.1 is calculated which does not appear to be a strong function of temperature. Accordingly, we are now in a position to estimate the fraction of hydrogen-bonded carbonyl groups in the 80:20 wt % PVPh–EVA(45) blends as a function of temperature. The results are presented in Table I and displayed graphically in Figure 6 for a sample cast from THF solution, heated to 190 °C, and subsequently cooled to room temperature.

There are several features of the graph shown in Figure 6 that deserve mention. Upon heating of the sample cast from THF at ambient temperature, the fraction of hydrogen-bonded carbonyl groups increases significantly as the effective T_g of the system is approached and then decreases. The rationale for this behavior has been discussed above. At 190 °C, only 22% of the available carbonyl groups are hydrogen bonded. As the temperature is reduced, this figure increases until there are about half of the carbonyl groups hydrogen bonded at room temperature. The molar concentration of the blend is about 86.5:13.5 PVPh–EVA(45), and one question that must be addressed is why are only approximately half of the carbonyl groups hydrogen bonded when there is a large molar excess of the PVPh?

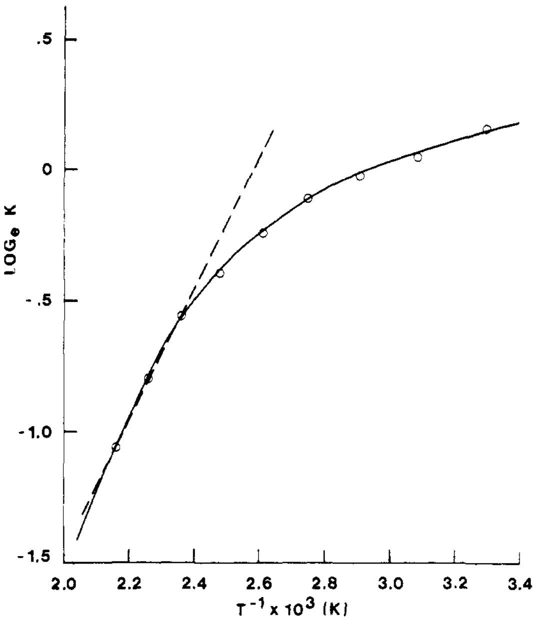


Figure 7. Graph of ln K vs. T^{-1} based on the data obtained from the 80:20 wt % PVPh–EVA(45) blend.

It did not escape our attention that we may be observing an equilibrium process and that the system had not attained equilibrium conditions, especially below the effective T_g of the system. In other words, in passing through the effective T_g of the system upon cooling, we are essentially trapping the system in a nonequilibrium state which reflects the distribution of hydrogen bonds associated with a higher temperature. Only above the T_g can we expect equilibrium to be approached. Nevertheless, as we have obtained an estimation of the fraction of hydrogen-bonded carbonyl groups for the 80:20 PVPh–EVA(45) blend as a function of temperature, we decided to attempt to obtain an effective equilibrium constant, K, and thus a measure of the strength of the intermolecular interaction.

A 1:1 complex is assumed with the molar concentration of PVPh and EVA(45) designated as [–OH] and [–C=O], respectively, and f defined as the fraction of hydrogen-bonded carbonyl groups. Simplistically

$$[\text{-OH}] + [\text{-C=O}] \rightleftharpoons [\text{-OH}\cdots\text{O=C-}] \qquad \text{(I)}$$

$$x = f[\text{-C=O}] \qquad \text{(II)}$$

$$K = x/([\text{-OH}] - x)([\text{-C=O}] - x) \qquad \text{(III)}$$

A plot of ln K against T^{-1} is shown in Figure 7. A reasonable straight line may be drawn through the points associated with the three highest temperatures (above T_g), and from the slope an estimation of the heat of formation of the complex ΔH may be obtained from

$$\ln K = (-\Delta H/RT) + C \qquad \text{(IV)}$$

A value of approximately 5.1 kcal mol^{-1} is calculated by a least-squares fit. This is in very good agreement with the literature values reported for low molecular weight phenol–methyl acetate and phenol– and ethyl acetate mixtures, which range from 4.8 to 5.7 kcal mol^{-1}.[17] We realized that as only three points were used to define a straight line and subsequently determine ΔH, significant errors can be introduced. Nevertheless, we believe the agreement between our experimental result and those of the literature values for low molecular analogues cannot be entirely fortuitous. Accordingly, this gives us confidence to employ ΔH values obtained from low molecular species for analogous polymeric materials.

Below the effective T_g of the system there is a marked deviation from a linear relationship in the plot of ln K vs. T^{-1} (Figure 7). This is consistent with the premise that a nonequilibrium state exists in the samples below T_g. (It should also be mentioned that deviations from linearity will occur if ΔH is temperature dependent. In fact, as demonstrated above, the spectral evidence suggests that it is. However, we do not believe that temperature dependence alone is sufficient to cause such a marked deviation from linearity.)

Using the experimentally determined values of ΔH = 5.1 kcal mol^{-1} and the intercept $C = -6.55$ (eq IV), one can theoretically calculate the fraction of hydrogen-bonded carbonyl groups as a function of blend composition and temperature (eq II and III). Naturally this assumes a system that has reached equilibrium and that ΔH is temperature independent. The theoretical relationship for an 80:20 wt % (86.5:13.5 molar) PVPh–EVA(45) blend as a function of temperature is shown by the solid line in Figure 6. Below 90 °C the experimental results are significantly less than theoretically predicted. This implies that at room temperature, for example, the equilibrium fraction of hydrogen-bonded carbonyl groups should be greater than that observed for the sample cooled from 190 °C to room temperature.

If the above explanation is correct, it should be theoretically possible to increase the fraction of hydrogen-bonded carbonyl groups in actual samples of the blend at room temperature. To date we have been unable to do so. Annealing experiments at room temperature were performed but the fraction of hydrogen-bonded carbonyls remains constant within experimental error over periods of up to 1 month. This is hardly surprising, as below the effective T_g mobility is severely restricted. An alternative approach is to expose a film of the blend that has been previously heated to 190 °C and subsequently cooled to room temperature to solvent vapor. The premise here is that as the solvent is imbibed into the film, the T_g will be depressed, which, in turn, increases mobility and permits the system to attain equilibrium. Accordingly, blend films were exposed to a variety of solvents of different chemical structures and polarity (benzene, tetrahydrofuran, methylene chloride, and acetone) in the anticipation that one might drive the system toward equilibrium. However, in all cases the fraction of hydrogen-bonded carbonyl groups *decreased*, eventually reaching the level observed for the original THF-cast film. Thus exposure of PVPh–EVA(45) blends of the solvents mentioned above leads to phase separation, evidently a consequence of the thermodynamics of specific terniary systems described by Patterson.[15]

Studies similar to those described above were performed on the miscible 80:20 wt % PVPh–PVAc and PVPh–EVA(70) blends. The effects due to solvent casting from THF were also apparent in these blends but to a much lesser degree. However, each blend was heat treated to 190 °C and cooled to room temperature. Spectra were recorded throughout this temperature range, and with the identical procedure described for the PVPh–EVA(45) blend, the fraction of hydrogen-bonded carbonyl groups were calculated as a function of temperature. The results are presented in Table II and compared to those of the EVA(45) blend graphically in Figure 8. In comparison to the PVPh–EVA(45) blend, the fraction of hydrogen-bonded carbonyl groups in the EVA(70) and PVAc blends is significantly greater at all temperatures. It should also be emphasized that the molar equivalence of the 80:20 wt % PVPh–EVA(70) and PVPh–PVAc blends is approximately 80 and 74% PVPh, respectively. Hence, in relative terms, there is less of a molar excess of PVPh in these blends compared to the corresponding EVA(45) blend.

Table II

T, °C	frac of H-bonded carbonyls, %	T, °C	frac of H-bonded carbonyls, %
	(a) PVAc		
190	61.6	90	67.9
170	62.7	70	68.3
150	65.3	50	68.4
130	67.4	30	74.4
110	68.1		
	(b) EVA(70)		
190	56.9	90	70.0
170	57.3	70	70.5
150	64.2	50	71.1
130	66.0	30	72.9
110	68.7		
	(c) EVA(25)		
190	2.1	70	6.2
150	3.0	30	6.4
110	3.8		

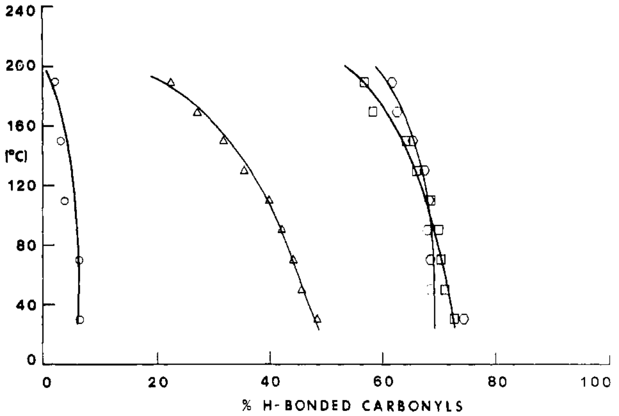


Figure 8. Graph of temperature vs. fraction of hydrogen-bonded carbonyls for samples of 80:20 wt % blends heated to 190 °C and measured as a function of decreasing temperature. (○) PVPh–EVA(25); (△) PVPh–EVA(45); (□) PVPh–EVA(70); (○) PVPh–PVAc.

A comment concerning the constant C (eq IV) is in order. If we assume that the $-\Delta H/RT$ term is constant over a limited temperature range for the formation of the specific intermolecular hydrogen-bonding interactions involving the phenolic hydroxyl with the acetate carbonyl group (i.e., regardless of whether the acetate group is in PVAc or any of the EVA's), it follows that ln K and the fraction of hydrogen-bonded carbonyl groups is determined solely by the value of C. When the value of C is adjusted to less negative values, the fraction of hydrogen-bonded carbonyl groups increases at any given temperature. For example, at 190 °C (well above T_g for all of the blend systems) changing the value of C from -6.55 to -4.85 increases the fraction of hydrogen-bonded carbonyl groups from 22 to 58%. This is in the range observed for the

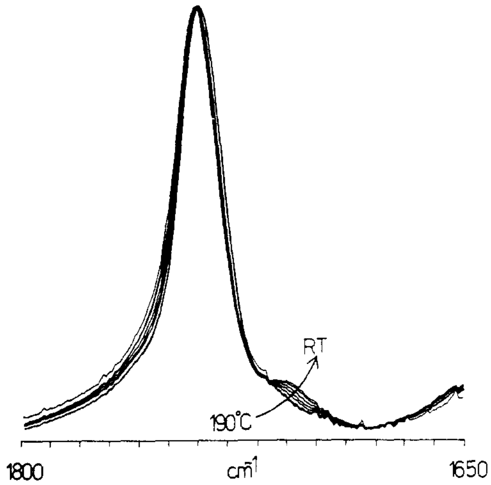


Figure 9. FT-IR spectra in the region 1800–1650 cm^{-1} of an 80:20 wt % PVPh–EVA(25) blend recorded from 190 °C to room temperature.

PVPh–EVA(70) and PVPh–PVAc blends as shown in Figure 8.

In simple terms, from classical thermodynamics, C is related to $\Delta S/R$, an entropic contribution. It is reasonable to assume that the immediate environment of a particular carbonyl group will be dependent upon the copolymer composition, sequence distribution, molecular weight, molecular weight distribution, and chainlike nature of the copolymer. In other words, at any instance in time, the probability that an EVA(45) carbonyl group is in close proximity to a phenolic hydroxyl group is less than that of an analogous EVA(70) or PVAc carbonyl group for equivalent molarity. Accordingly, for a particular degree of hydrogen bonding there is a greater restriction on the number of distinguishable degrees of freedom for the EVA(45) chain relative to those of the EVA(70) and PVAc polymer chains. As entropy is related to the number of accessible degrees of freedom, this predicts a lower entropic contribution to the equilibrium constant with decreasing vinyl acetate concentration in the copolymer. This, in turn, corresponds to an increasingly negative value of C. Further work is necessary to determine whether we can calculate the entropic contribution to the equilibrium constant from primarily probabilistic considerations. This is currently being explored from studies of all the blends across the whole composition range.

The results displayed in Figure 8 are also relevant to the phase behavior of polymer blends. It is reasonable to assume that a lower critical solution temperature (LCST) should occur in the vicinity of 200–250 °C for the 80:20 wt % PVPh–EVA(45) blend when the fraction of hydrogen-bonded carbonyl groups drops below a critical value. Unfortunately, this is also in the temperature range where serious polymer degradation occurs, which makes independent verification difficult at best. On the other hand, the LCST's of the PVPh blends with EVA(70) and PVAc, assuming they could be attained, are most likely to be well in excess of 300 °C, based upon the observed dependence of the fraction of hydrogen-bonded carbonyl groups with temperature. Similar trends have been previously reported for PVC–EVA blends. The LCST's reported for 80:20 wt % blends of PVC–EVA(45) and PVC–EVA(70) occur at about 110[8] and 200 °C,[18] respectively. (It is realized that this is somewhat simplistic as molecular weight can have a marked effect upon the position of the LCST). Nevertheless, it is evident that it is not just the strength of the intermolecular interaction that is important to miscibility. An overriding factor is the number of these interactions that can be achieved, which is a function of temperature and probability.

Finally, and in marked contrast to the results presented above, FT-IR temperature studies of the 80:20 wt % PVPh–EVA(25) blend suggest that this system is to all extents and purposes incompatible. Incidentally, the very appearance of the film strongly suggests an incompatible blend. Figure 9 shows the spectra obtained after the sample had been heated to 190 °C and cooled to room temperature. A very weak infrared band is detected at about 1710 cm^{-1}, which marginally increases in intensity upon cooling to room temperature. Curve fitting reveals that at room temperature less than 7% of the carbonyl groups are hydrogen bonded as shown in Table II and displayed in Figure 8.

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Registry No. PVPh, 24979-70-2; PVAc, 9003-20-7; EVA copolymer, 24937-78-8.

References and Notes

(1) Coleman, M. M.; Zarian, J. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 837.
(2) Varnell, D. F.; Coleman, M. M. *Polymer* **1981**, *22*, 1324.
(3) Varnell, D. F.; Runt, J. P.; Coleman, M. M. *Macromolecules* **1981**, *14*, 1350.
(4) Varnell, D. F.; Runt, J. P.; Coleman, M. M. *Polymer* **1983**, *24*, 37.
(5) Coleman, M. M.; Moskala, E. J. *Polymer* **1983**, *24*, 251.
(6) Moskala, E. J.; Coleman, M. M. *Polymer Commun.* **1983**, *24*, 207.
(7) Varnell, D. F.; Moskala, E. J.; Painter, P. C.; Coleman, M. M. *Polym. Eng. Sci.* **1983**, *23*, 658.
(8) Coleman, M. M.; Moskala, E. J.; Painter, P. C.; Walsh, D. J.; Rostami, S. *Polymer* **1983**, *24*, 1410.
(9) Patterson, D.; Robard, A. *Macromolecules* **1978**, *11*, 690.
(10) Kraus, S. *J. Macromol. Sci., Rev. Macromol. Chem.* **1972**, *7*, 251.
(11) Coleman, M. M.; Varnell, D. F. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1403.
(12) Coleman, M. M.; Painter, P. C. *J. Macromol. Sci., Rev. Macromol. Chem.* **1978**, *C16*, 1975.
(13) Bellamy, L. J. "The Infrared Spectra of Complex Molecules"; Chapman and Hall: New York, 1980.
(14) Walsh, D. J.; Higgins, J. S.; Rostami, S. *Macromolecules* **1983**, *16*, 388.
(15) Patterson, D. *Polym. Eng. Sci.* **1982**, *22*, 64.
(16) Painter, P. C.; Snyder, R. W.; Starsinic, M.; Coleman, M. M.; Kuehn, D. W.; Davis, A. *Appl. Spectrosc.* **1981**, *35* (5), 475.
(17) Pimentel, G. C.; McClellan, A. L. "The Hydrogen Bond"; W. H. Freeman: San Francisco, 1960.
(18) Nolley, E.; Paul, D. R.; Barlow, J. W. *J. Appl. Polym. Sci.* **1979**, *23*, 589.