Phenoxy blends: an approach to the miscibility by *FT*i.r. and chemical modification of the interacting sites

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In this work, *FT*i.r. spectroscopy has been used in order to verify the proposed influence of the hydroxyl group, present in each monomeric unit of the phenoxy (PH) resin, in the observed miscibility of this polymer with a variety of other polymer families such as polyoxides or polyesters. Two different approaches have been used for this purpose. First, *FT*i.r. studies at different temperatures have been carried out on mixtures of PH with polyoxides, in order to demonstrate the higher strength of the hydrogen bonds in the mixture with respect to those existing between pure PH molecules. Second, chemical modification of the PH resin, with a controlled elimination of the repetitive hydroxyl, has been carried out intending to relate the percentage of hydroxyl substitution to the observed miscibility of PH. In the second approach, mixtures of PH and modified PH with poly(*N*-vinyl-2-pyrrolidone) have been studied.

(Keywords: blends; *FT*i.r. spectroscopy; miscibility)

INTRODUCTION

It is well known that in most miscible polymer blends it is usually necessary to have some sort of attractive forces between unlike segments. These attractive forces can be due to dipole moments. In this case, strictly speaking, the system would not be random, in that unlike segments would have an increased propensity to be adjacent to one another. They are not in the usual sense of the word associated, however, and it is possible to assume that for such weak interaction the modification in the calculated entropy of mixing, according to the Flory–Huggins theory, is not significant.

Stronger interactions, particularly hydrogen bonds, are different and cannot be dealt with by a simple approximation. Both the Flory–Orwoll–Vrij–Eichinger (FOVE)[1] equation-of-state theory and the Lattice–Fluid (LF) model[2] have explained the properties of polymer blends and specially lower critical solution temperature phenomena on the basis of the effect of the finite compressibility of the mixture. However, in their original formulation, neither model took into account specific interactions as responsible for the experimental observed magnitudes. Strong interactions should induce some degree of order in the mixture. Therefore, it is not surprising that FOVE and LF models have failed in explaining the properties of systems with specific interactions, the breakdown being clearer when we proceed from non-polar systems to strongly polar solutions.

In recent years different approaches[3–5] have been proposed to rationalize the behaviour of such systems. A different specific weight has been attributed to the two factors which seem to control the miscibility and phase separation of the blend: specific interaction and finite compressibility.

From a different point of view, Lai *et al.*[6,7] have proposed a group contribution method based on the enthalpy of mixing of model compounds for the a priori estimation of the miscibility of a polymer blend. Given that specific interactions seem to be responsible for the miscibility in the majority of cases, they have modified the Guggenheim quasi-chemical method introducing the local non-randomness in the form of a non-random factor Γ_{ij} defined by Panayiotou and Vera[8].

In this paper, we report data of several blends with a common component. The phenoxy (PH) resin, a copolymer of bisphenol A and epichlorhydrin, has repeatedly been proven to be miscible with polyoxides[9], poly(vinyl ether)s[10], polyesters[11], polysulphones[12], polyamides[13], etc.

Some years ago Robeson *et al.*[9] observed that PH resin was miscible with poly(ethylene oxide) (PEO) but not with poly(propylene oxide). In the case of poly(methylene oxide) (PMO) its enormous capacity of crystallizing, even in the presence of important amounts of a second amorphous component, hinders the classical macroscopic glass transition temperature (T_g) analysis of its miscibility with PH resin. However, some experimental evidence seems to lead to the conclusion that both polymers are immiscible, as will be shown later.

PH and PEO blends are stated to be miscible over the whole range of compositions and temperatures investigated. Glass transition temperatures in the paper by Robeson *et al.* cited above and those obtained in our own group[14] can be adjusted without difficulties to a unique Gordon–Taylor equation, with an adjustable *K*

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parameter equal to 0.55. PEO melting point depressions, due to the presence of PH, were used to calculate the interaction energy density *B*. Hoffmann–Weeks plots were drawn with PEO melting points measured at low crystallization degrees. These conditions tried to ensure true equilibrium melting temperature (T_m) values. At 74°C the *B* value was $-25\,\mathrm{J\,cm^{-3}}$ reflecting the existence of strong specific interactions in our blend[14].

In this work, the importance of these strong interactions in the differences of the behaviour between PH/PEO and PH/PMO blends has been studied by *FT*i.r. at various temperatures. Blends of PH and PEO were first studied using *FT*i.r. by Coleman and Moskala[15] in a tentative way. They only studied blends of different compositions at room temperature. The main conclusion was that the hydrogen-bonded hydroxyl mode shifted to lower frequencies as a function of PEO concentration. The implication of this shift is that the hydrogen bonding interaction is stronger than the corresponding self-associated hydrogen bonding in pure PH.

The other way to illustrate the possible influence of PH hydroxyl groups in the miscibility of this polymer with other families, consists of a chemical elimination of this functional group. In this work we have studied the evolution of the miscibility of a benzoylated PH sample with poly(*N*-vinyl-2-pyrrolidone) (PVP) when the hydroxyl group is progressively esterified. Blends of PH and PVP have been studied in this laboratory[13]. The results indicated that the blend was miscible over the entire composition range. The T_g–composition relationship showed a peculiar convex behaviour, with a Gordon–Taylor parameter of 1.25.

*FT*i.r. studies and chemical modification of the PH resin can demonstrate that the repetitive hydroxyl unit of the PH resin is responsible for the miscibility of the systems studied. A tentative analysis of the results in the light of the group contribution method described above is also given.

EXPERIMENTAL

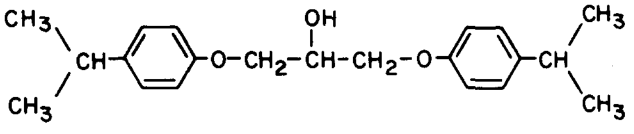
Materials

The polymers used in this work were commercial products. The PH samples (PKHH, Union Carbide) were purchased from Quimidroga (Barcelona, Spain). Their average molecular weights were determined by g.p.c.[16] in tetrahydrofuran (THF) at 30°C ($M_w = 50\,700\,\mathrm{g\,mol^{-1}}$ and $M_n = 18\,000\,\mathrm{g\,mol^{-1}}$). PEO was purchased from Polysciences (cat. no. 6511). Its average viscosity molecular weight ($M_v = 365\,000\,\mathrm{g\,mol^{-1}}$) was obtained in benzene at 25°C, using the Mark–Houwink equation[17]:

$$[\eta] = 3.97 \times 10^{-4} M_v^{0.686}$$

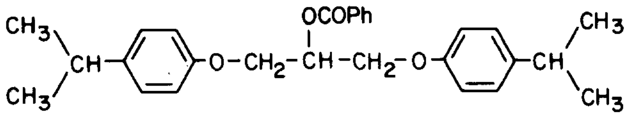
PVP was purchased from C. Barcia SA (Barcelona, Spain). Its nominal molecular weight was $40\,000\,\mathrm{g\,mol^{-1}}$. PMO was a commercial sample of Delrin.

1,3-Bis (4-isopropylphenoxy)-2-propanol (IPPHP) was synthesized by adding NaOH (40%) to 4-isopropyl phenol (1:1). The mixture was stirred for 20 min at 50°C. Epichlorohydrin (1:3 mol) was added and allowed to stand in these conditions for 20 min and then refluxed for 3 h.



The mixture was washed with ethyl ether (three times) and the organic phase was washed successively with 10% aqueous NaOH and water and dried over anhydrous Na_2SO_4. The solvent was evaporated and the product was recrystallized from hexane and characterized by i.r., ^1H and ^{13}C n.m.r.

In order to synthesize 1,3-bis(4-isopropylphenoxy)-2-propyl benzoate (BIPPHP), an excess of benzoyl chloride was added to a solution of IPPHP in anhydrous pyridine.



The mixture was refluxed for 2 h and then poured into a 10% Na_2CO_3 solution, washed with ethyl ether and the organic layer washed successively with a solution of HCl (10%) and water and dried over anhydrous Na_2SO_4. Ethyl ether was evaporated and the product was purified by recrystallization from hexane/THF (10:1) and characterized by i.r., ^1H and ^{13}C n.m.r.

2-Ethoxyethyl ether (diethylene glycol diethyl ether, DEGDEE) and 1-methyl-2-pyrrolidone (MP) were purchased from Aldrich and used without further purification.

Films of PH, PEO and PH/PEO blends were cast from 1% chloroform solutions (by weight) onto potassium bromide windows at room temperature. After most of the solvent had evaporated, films were transferred to a vacuum desiccator to completely remove the residual solvent. Films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law was obeyed (<0.6 absorbance units).

Samples of PH/PEO blends for d.s.c. studies were prepared from dioxane solutions and evaporation of the solvent. Samples of PH/PMO were prepared from solution in dimethylsulphoxide and precipitation in methanol.

Phenoxy resin modification

PH resin benzoylation was carried out by a slightly different method from that of Reinking *et al.*[18]. PH resin (4.08 g, 0.0144 mol) was dissolved in anhydrous pyridine (30 ml, 0.372 mol) and benzoyl chloride (5 ml, 0.0431 mol) was then added. After the addition of benzoyl chloride, the mixture was refluxed for 1.5 h to insure complete reaction. The benzoylated polymer was isolated by pouring the reaction mixture into a 0.5% aqueous Na_2CO_3 solution, in order to remove residual benzoyl chloride. The dried polymer was dissolved in THF, precipitated twice in hexane and dried for 48 h in a vacuum oven at 50°C. In this manner, 100% benzoylated polymer was obtained. By using less than one equivalent of benzoyl chloride, partially benzoylated polyhydroxyethers were obtained.

Instrumental methods

Characterization of the modified products was carried out from n.m.r. spectra obtained at room temperature, in a Varian VXR 300 spectrometer, using deuterated chloroform as the solvent and tetramethyl silane as the internal reference.

The i.r. spectra of pure and modified PH resin and blends were obtained in a Nicolet 5DXC spectrometer. A SPECAC high temperature cell, mounted in the spectrometer, was used to obtain spectra above room temperature with an accuracy of ±2°C.

Glass transition temperatures, melting heats and T_m measurements were carried out in a Perkin Elmer DSC 2C. The calorimeter was operated at a heating rate of 20 K min^{-1}. Calibration was achieved using an indium standard. The T_gs were determined at the onset of the transition.

Heats of mixing of model compounds of the blends were measured in a Calvet type calorimeter (Setaram C-80D model) with appropriate mixing cells.

RESULTS AND DISCUSSION

Phenoxy/polyoxide blends

Data for PH/PMO obtained via d.s.c. are summarized in *Table 1*. The PMO T_g and heat of fusion data have been taken from reference 19. From our data, it is clear that PH resin restricts PMO crystallization. On the other hand, due to experimental difficulties inherent to the determination of the T_g of PMO (190 K), only one T_g was observed for the compositions investigated. In all cases, these T_gs were very near that of pure PH, indicating a phase-separated mixture. This hypothesis can be supported by visual observation of opaque mixtures when the blend is processed at a high temperature or maintained as a film at temperatures above the T_g and the T_m of the components.

Figure 1 shows the i.r. spectra of pure PH at different temperatures in the region 3800–3250 cm^{-1}. A very broad band is observed centred at 3400 cm^{-1} which is attributed to a wide distribution of hydrogen-bonded hydroxyl stretching frequencies. The spectral contribution seen at 3570 cm^{-1} is associated with free hydroxyl groups. When the temperature is increased there is a progressive change in the appearance of this broad band. Starting with a band centred at 3400 cm^{-1} with a small shoulder at 3570 cm^{-1}, the situation evolves to a sharp band centred at this second frequency. This is consistent with breaking of the hydrogen bonds of the PH resin, as a consequence of the higher thermal level, which modifies the ratio of free to self-associated hydroxyl groups.

Table 1 D.s.c. results for PH/PMO blends

PH composition (wt%)	T_g (K)	T_m (K)	ΔH_f (J g^{-1})	PMO crystallization (%)
100	369	–	–	–
90	367	439	13.4	41.0
75	358	439	33.2	40.6
50	364	440	74.4	45.5

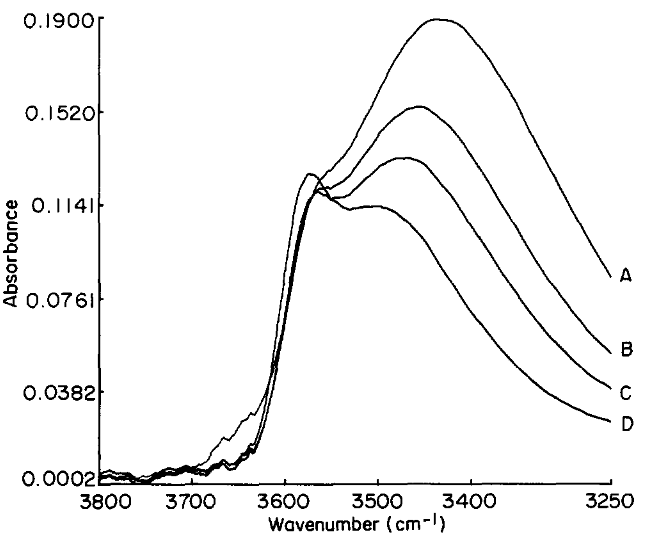


Figure 1 *FT*i.r. spectra in the range 3800–3250 cm^{-1} of PH resin recorded at: (A) 25°C; (B) 75°C; (C) 100°C; (D) 150°C

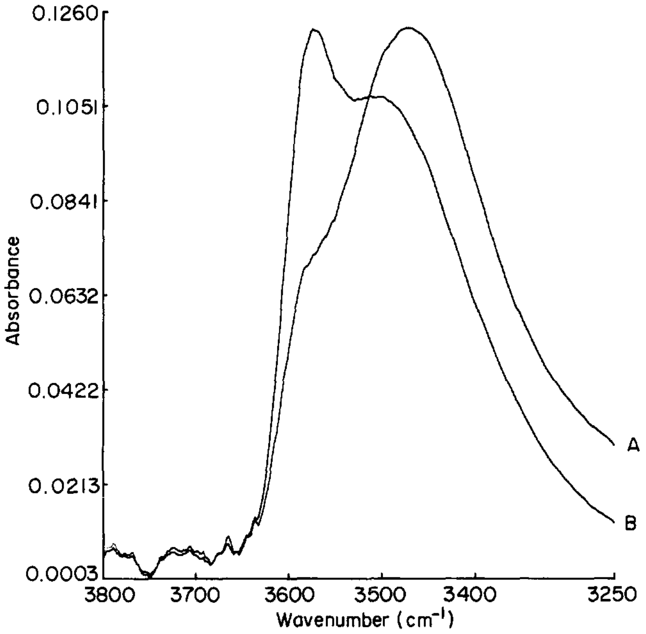


Figure 2 *FT*i.r. spectra recorded at 150°C in the range 3800–3250 cm^{-1} for: (A) PH/PEO (50:50) blend; (B) pure PH

The influence of the temperature in this region of the PH spectrum will be useful in the study of the different behaviour of the PH/PEO and PH/PMO blends. *Figure 2* shows the spectrum of a 50:50 PH/PEO blend at a temperature (150°C) high enough to be above the T_g of the system and the melting point of the PEO. A first comparison with pure PH spectra reveals important differences in the bands corresponding to the free and associated hydroxyl groups. Whereas at 150°C in pure PH, the free hydroxyl group band was the largest, in PH/PEO blends this relation is inverted, the associated hydroxyl band being the largest in this case. This seems to indicate that whereas in pure PH a temperature of 150°C was enough to break the hydrogen bonds, this is not the case in PH/PEO blends, indicating a stronger interaction between hydroxyl groups in PH with the PEO ether groups. Similar results have been obtained for other PH/PEO compositions.

The importance of such specific interactions in the miscibility of the mixture is even clearer in the *FT*i.r. spectra of PH/PMO blends. Irrespective of the reasons which lead to immiscible behaviour in PH/PMO blends, the *FT*i.r. spectra reflect a very different behaviour with temperature, if they are compared with those observed for PH/PEO blends. As can be seen in *Figure 3*, at 200°C the behaviour of the broad hydroxyl band in PH/PMO resembles that of the pure PH, in agreement with the immiscible behaviour experimentally observed.

In an attempt to rationalize this different phase behaviour, heats of mixing of model compounds have been measured. Heats of mixing of DEGDEE and IPPHP were measured at 89°C, a temperature at which model compound mixtures and also the PH/PEO (50:50) blend are in the liquid state. Results are shown in *Table 2*.

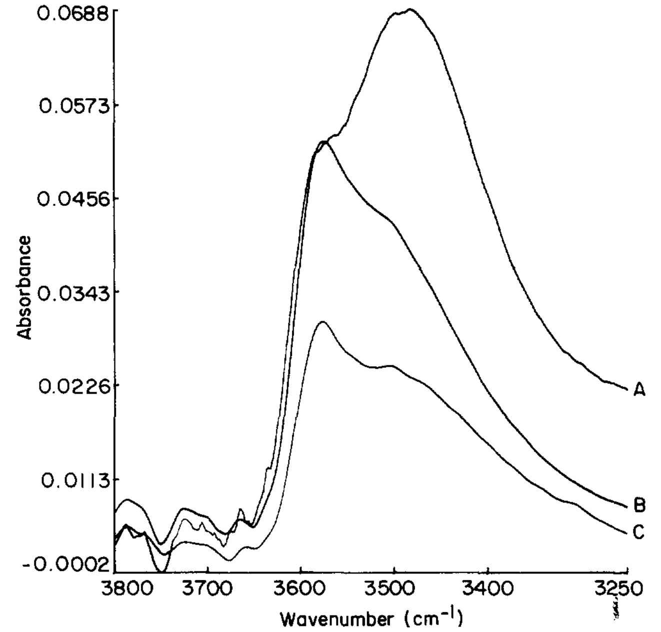


Figure 3 *FT*i.r. spectra recorded at 200°C in the range 3800–3250 cm^{-1} for: (A) PH/PEO (50:50) blend; (B) PH/PMO (50:50) blend; (C) pure PH

Table 2 Heats of mixing between PH/PEO model compounds at 89°C

PH model composition	ΔH (J g^{-1})
0.25	−3.33
0.50	−4.92
0.75	−4.42

Assuming an enthalpic character for the interaction energy density (B)[6]:

$$\Delta H_m/V = B\phi_1\phi_2$$

the experimental value yields a B value of -19.7 J cm^{-3} for a 50:50 blend, which seems consistent with the results of the melting point depression in the polymer blends[14]. However, this is a very bare approximation, incapable of explaining the dramatic differences between PH/PEO and PH/PMO miscibility where the only difference is the CH_2/CO relation.

There are other cases in which the relation between functional groups of one of the components can play an important role in the miscibility[11]. Lai *et al.*[6] have explained miscibility windows in blends of poly(vinyl chloride) and polyesters on the basis of the contribution of inter- and intramolecular interactions between the different groups in which the component repetitive units are arbitrarily divided. Using a Guggenheim quasi-chemical approach, modified by the introduction of non-randomness factors, it is possible to calculate B values on the basis of group contribution tables. Fortunately, the different groups implicated in PH/polyoxide blends have been determined in the original papers of Lai *et al.*[6,7]. Consequently, we can calculate B values for PH/polyoxides as a function of the CH_2/CO ratio. *Figure 4* shows these calculations at 60°C.

A minimum in B is found for a CH_2/CO ratio equal to two. This is the PEO ratio, the only member of the family for which there is clear evidence of miscibility. However, the B value so found is positive in all cases, meaning that only a qualitative indication of the best conditions for miscibility have been predicted. Lai *et al.*[7] have had similar inaccuracies in reproducing the experimental miscibility window in PH/polyester blends. They attributed the discrepancies to the necessity of taking into account the self-association between PH molecules and to the inaccuracies inherent to calculating group contributions between the hydroxyl and other functional groups. They calculated this contribution from model compounds very different to the structure of the PH molecule. As far as the first argument is concerned, we have calculated B at temperatures other than 60°C. At 140 and 200°C B is negative for PEO and positive for PPO and PBO, but very negative for PMO. We have concluded that more experimental work with model compounds similar to PH is necessary for a more accurate test of the feasibility of the model. This argument is supported by the fact that if the heats of mixing for mixtures of DEGDEE and the IPPHP model compound are calculated, according to the group contributions tabulated by Lai *et al.*[6,7], the enthalpy of mixing is small but positive over the whole range of concentration, in contrast to the experimental values encountered and reported in this work.

Miscibility of the chemically modified phenoxy

The macroscopic criterium of the T_g has also been used for monitoring the evolution of the miscibility as a function of blend composition. In *Figure 5*, T_gs of 50:50

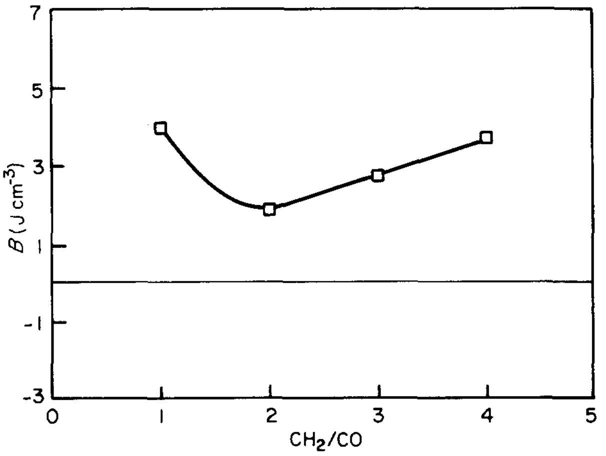


Figure 4 Interaction energy densities (B) for PH/polyoxides *versus* CH_2/CO ratio at 60°C

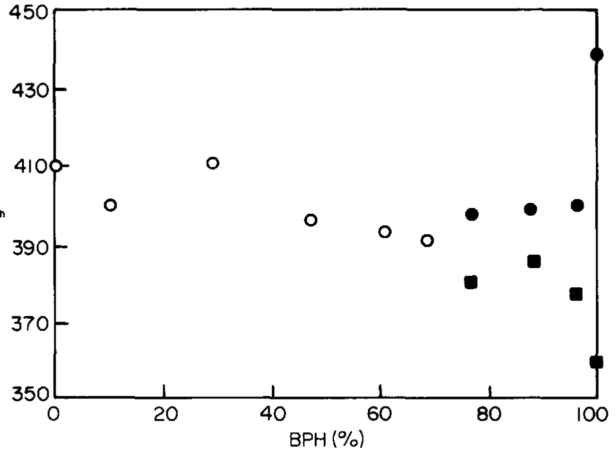


Figure 5 T_g for PVP/PH-BPH (50:50) blends *versus* BPH composition in the copolymer: (○) miscible compositions; (●, ■) T_gs of the two-phase compositions

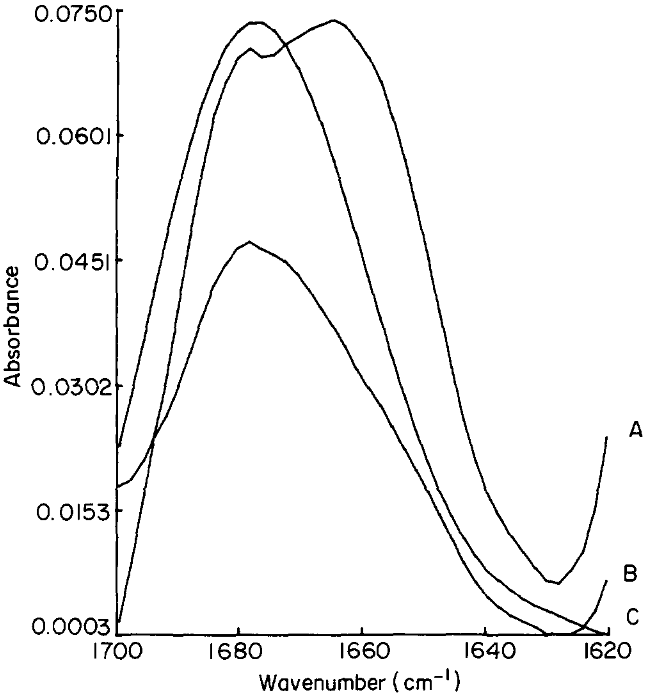


Figure 6 *FT*i.r. spectra recorded at room temperature in the range 1700–1620 cm^{-1} for: (A) PVP/PH (10:90); (B) PVP/BPH (10:90); (C) pure PVP

Table 3 Heats of mixing of 50:50 mixtures of model compounds of PH, BPH and PVP at 94°C

Mixture	Heat of mixing (J g^{-1})
IPPHP/BIPPHP	1.83
IPPHP/MP	−18.9
BIPPHP/MP	−3.63

blends of PVP and a phenoxy-benzoylated phenoxy (PH-BPH) copolymer of different compositions are shown. As can be seen, PVP remains miscible with PH at low degrees of esterification. However, when this substitution is 70% or more, two T_gs appear, indicating that the hydroxyl content is not enough to make PVP miscible.

*FT*i.r. experiments seem to confirm again the extent of the interactions through the hydroxyl groups. *Figure 6* shows the corresponding spectra of PVP/PH (10:90), PVP/totally benzoylated PH (10:90) and pure PVP. Pure PVP is characterized in the carbonyl stretching region by a rather broad band centred at 1680 cm^{-1}. This band is a mixed mode containing contributions from the carbonyl stretching and N-C stretching vibrations. Upon mixing PVP with PH or slightly modified PH a second band is observed near 1660 cm^{-1} which is easily assigned to hydrogen-bonded PVP carbonyl groups. However, in the case of highly benzoylated PH/PVP blends, the i.r. spectra are similar to that obtained for pure PVP.

Model compounds of PH (IPPHP), BPH (BIPPHP) and 1-methyl-2-pyrrolidone (MP) as a model compound of PVP have been mixed at 94°C in a 50:50 mixture in the Calvet calorimeter. The results are shown in *Table 3*.

These results show, at least qualitatively, that there is a great difference between the interactions of the functional groups involved in the PVP unit with those in PH and BPH. A group contribution calculation of the evolution of *B* with copolymer composition is not currently possible because the contributions of the groups in the PVP molecule have not been tabulated.

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