Studies of the phase behaviour of poly(vinyl phenol)–poly(n-alkyl methacrylate) blends

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The results of theoretical and experimental studies of poly(4-vinyl phenol) (PVPh) blends with a series of poly(n-alkyl methacrylates) are presented. PVPh is miscible with poly(methyl methacrylate), poly(ethyl methacrylate) and poly(n-propyl methacrylate) over the entire composition range at temperatures between ambient and 200°C. In contrast, PVPh–poly(n-butyl methacrylate) blends phase separate at temperatures below 200°C. Quantitative analyses of the fraction of hydrogen bonded carbonyl groups were obtained by *FT*i.r. spectroscopy for all the PVPh blends–poly(n-alkyl methacrylates) as a function of composition and temperature. The data obtained from the miscible blend systems was employed to determine values of the equilibrium constant describing inter-association, K_A, and the enthalpy of hydrogen bond formation, h_A. Theoretical fractions of hydrogen bonded carbonyl groups and spinodal phase diagrams were calculated using a recently reported association model. The results compare very favourably to experiment.

(Keywords: poly(4-vinyl phenol) blends; phase behaviour; theoretical and experimental studies)

INTRODUCTION

We have previously presented a theoretical model to describe the free energy changes occurring in binary polymer mixtures containing strong directionally specific interactions such as hydrogen bonds[1–3]. More recently, we have obtained our original result in a more formal manner using a Flory lattice model[4]. At the same time, we have conducted numerous experimental studies concerned with assessing the predictive capabilities of the model[5–10]. In selecting blend candidates for these studies, we have found it beneficial to concentrate on those systems in which one component's chemical structure, and thus the overall free energy of mixing, may be systematically varied. This can be accomplished simply through the use of copolymers or, alternatively, homologous series. In certain systems, this ability to progressively alter the free energy of mixing results in the detection of miscibility limits which then serve as the basis for comparison with model predictions. Using this approach, we have been able to assess the model's ability at predicting trends in the miscibility behaviour of a number of systems including blends of polyethers with (ethylene–methacrylic acid) copolymers[6] and a series of polyisophthalamides[2], and blends of poly(4-vinyl phenol) (PVPh) with a series of polyacetates, polylactones, polyacrylates[8], and polyethers[9]. In addition, we have presented limited results for blends of PVPh with a series of poly(alkyl methacrylates)[10].

In this paper, we provide results of more extensive research conducted on this latter system which focuses on the series of poly(alkyl methacrylates) containing linear pendent groups. As in our previous studies, the primary characterization tool in this research was Fourier transform infrared spectroscopy (*FT*i.r.). While the use of *FT*i.r. for the determination of important model parameters has been illustrated in the past[10], its potential application as a sensitive probe for detection of phase separation in these polymer blends will also be demonstrated.

EXPERIMENTAL

The poly(4-vinyl phenol) (PVPh) and poly(n-alkyl methacrylates) employed in this study have been described previously[10]. Their molecular weights and glass transition temperatures are summarized in *Table 1*. The poly(n-alkyl methacrylates) were prepared via group transfer polymerization and are amorphous materials with relatively narrow molecular weight distributions ($M_w/M_n < 1.25$).

Blends of various compositions were prepared by co-dissolving appropriate amounts of the components in methyl isobutyl ketone to yield 2% (w/v) solutions. Thin films for *FT*i.r. and light scattering studies were obtained by casting the blend solutions onto potassium bromide windows or microscope cover slides, respectively, at room temperature. The solvent was removed slowly under ambient conditions for a minimum of 24 h. The samples were then dried in a vacuum desiccator for an additional day before being placed in a vacuum oven at 110°C for 4 h to completely remove the residual solvent. To

Table 1 Description of polymers

Polymer	T_g (°C)	M_n
Poly(4-vinyl phenol) (PVPh)	140	1500–7000
Poly(methyl methacrylate) (PMMA)	105	31 000
Poly(ethyl methacrylate) (PEMA)	65	8400
Poly(propyl methacrylate) (PPMA)	35	10 000
Poly(butyl methacrylate) (PBMA)	21	55 000

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minimize water absorption, samples were stored under vacuum desiccation while awaiting study. All blends prepared in this manner were optically transparent.

Samples for the determination of cloud points were heated in a Mettler FP82 hot stage regulated by a FP80 control unit. A He/Ne laser was used as the light source and the scattered intensity was measured by a photomultiplier tube situated at 90° to the incident radiation and recorded on a strip chart. The scattering intensity was recorded as a function of temperature in the range of 110–200°C using a heating rate of 2°C min^{-1}. The cloud point was taken as the temperature at which there was observed a significant increase in scattering intensity.

Infrared spectra were obtained on a Digilab FTS-60 Fourier transform infrared spectrometer using a minimum of 64 coadded scans at a resolution of 2 cm^{-1}. Spectra recorded at elevated temperatures were obtained using a heating cell mounted inside the sample chamber. Temperature was regulated by a Micristar 828D digital process controller which has a reported accuracy of ±0.1°C. All films were sufficiently thin to be within the absorbance range where the Beer–Lambert law is obeyed[11].

RESULTS AND DISCUSSION

Experimental determination of the fraction of hydrogen-bonded carbonyl groups

The use of *FT*i.r. spectroscopy to investigate the degree of molecular level mixing in polymer blends possessing intermolecular hydrogen-bonding interactions is now firmly established[12,13]. The technique is particularly well suited to blends, such as the PVPh/poly(n-alkyl methacrylate) system studied here, in which one of the components contains a carbonyl group. The carbonyl stretching region of the *FT*i.r. spectra of these blends is characterized by two bands which may be attributed to absorption by 'free' and hydrogen-bonded carbonyl groups. Quantitative analysis of these carbonyl bands provides a direct measure of the degree of mixing in a particular blend sample. While the presence of a significant fraction of hydrogen-bonded groups indicates a 'well mixed' system, it does not necessarily imply the existence of a thermodynamically stable single-phase mixture. Information concerning the phase behaviour of these blends may be obtained from equations describing the stoichiometry of the system and by monitoring trends in the carbonyl region as a function of temperature[1–3,8]. However, this requires a knowledge of the equilibrium constants pertaining to self-association and inter-association, respectively.

As an illustration of the typical trends observed, the scale-expanded *FT*i.r. spectra in the carbonyl region of an 80:20 PVPh–PEMA blend recorded as a function of increasing temperature are shown in *Figure 1a*. The 'free' and hydrogen-bonded carbonyl bands are well resolved and centred at approximately 1729 and 1702 cm^{-1}, respectively. The room temperature spectrum displays a preponderance of hydrogen-bonded carbonyl groups which indicates a highly mixed system at 25°C. As the temperature is raised to 200°C, however, the intensity of the 'free' band increases at the expense of the hydrogen-bonded band. Upon cooling back to room temperature, a spectrum is obtained whose carbonyl region is nearly identical to that recorded prior to heating (*Figure 1b*). Similar spectral trends have previously been reported for single-phase polymer systems whose miscibility has been verified by other methods[13,14].

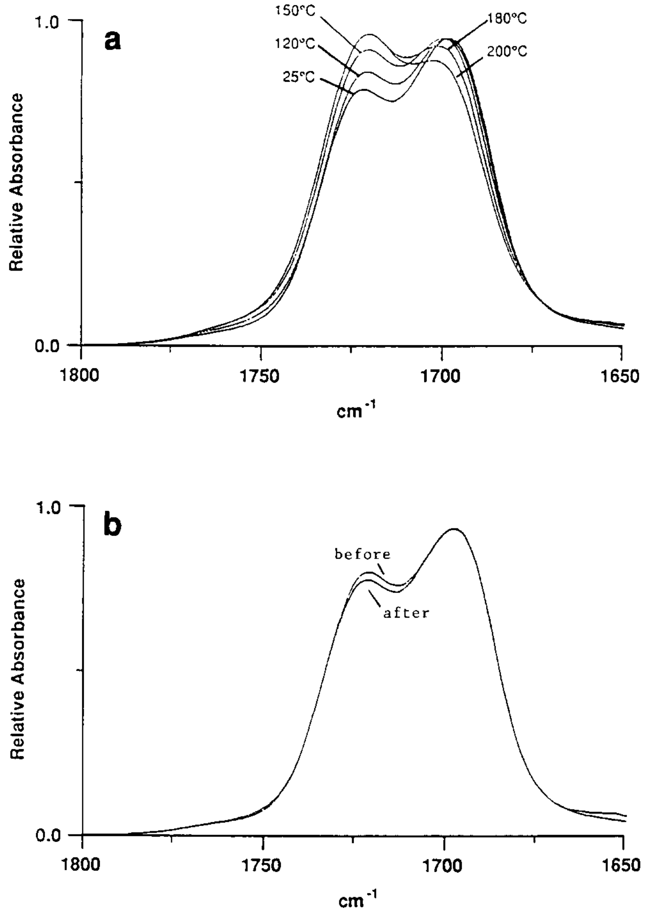

Figure 1 *FT*i.r. spectra in the carbonyl region of an 80:20 PVPh–PEMA blend recorded (a) as a function of increasing temperature and (b) at room temperature before and after heating to 200°C

At equilibrium, the ability to recover the initial fraction of hydrogen bonded carbonyl groups upon heating and subsequent cooling is a necessary requirement and implies, but does not prove, the existence of a single-phase system throughout the temperature range studied. For a single-phase system the observed decrease in the bonded fraction at high temperatures simply reflects the effect of temperature on the equilibrium state of the system. *FT*i.r. results obtained for PVPh–PEMA blends at compositions containing 60, 50, 40, and 20 wt% PVPh indicated identical trends to those discussed above. Quantitative determination of the fraction of hydrogen-bonded carbonyl groups present at a given temperature and composition were obtained from a least-squares fit of two Gaussian bands to the carbonyl stretching absorptions. The results are summarized in *Table 2* for all blend compositions and temperatures studied. In calculating the fraction of hydrogen-bonded carbonyl groups, band areas were corrected for absorption coefficient differences by applying the previously determined ratio, $a_{hb}/a_f = 1.5$, where a_{hb} and a_f represent the absorption coefficients of the hydrogen-bonded and 'free' carbonyl bands, respectively[13]. The results in *Table 2* quantitatively confirm the trends evident from visual inspection of the spectra. For all blend compositions, the fractions of hydrogen-bonded carbonyl groups obtained before and after heating to

Table 2 Curve-fitting results for PVPh–PEMA blends

Temperature (°C)	Fraction of H-bonded carbonyl groups Blend composition PVPh:PEMA 80:20	60:40	50:50	40:60
25↑	0.605	0.493	0.431	0.349
110	0.590	0.489	0.432	0.345
120	0.588	0.485	0.430	0.344
130	0.583	0.481	0.427	0.340
140	0.577	0.476	0.423	0.338
150	0.570	0.471	0.420	0.336
160	0.563	0.467	0.415	0.331
170	0.558	0.463	0.412	0.330
180	0.553	0.457	0.409	0.327
190	0.548	0.452	0.405	0.322
200	0.542	0.445	0.401	0.314
25↓	0.595	0.484	0.428	0.339

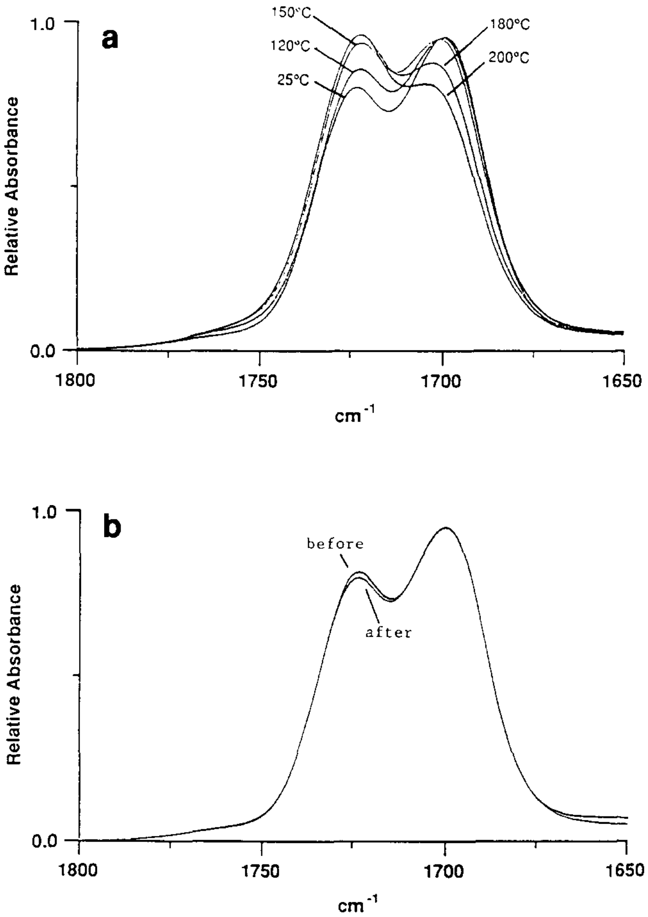

Figure 2 *FT*i.r. spectra in the carbonyl region of an 80:20 PVPh–PPMA blend recorded (a) as a function of increasing temperature and (b) at room temperature before and after heating to 200°C

200°C were within 1%, well within the experimental errors involved in these calculations.

*FT*i.r. investigations of PVPh–PPMA blends revealed trends analogous to those observed in the PVPh–PEMA system. These trends are illustrated in the scale-expanded *FT*i.r. spectra obtained for the 80:20 PVPh–PPMA blend shown in *Figure 2a* and *b*. The complete curve-fitting results are reported in *Table 3*. Again, the fraction of hydrogen-bonded carbonyl groups present before and after heating were within 1% for all blend compositions. In addition, the fractions of hydrogen-bonded groups, for a given composition, were similar to those reported for PVPh–PEMA blends. The results for these two systems imply miscibility over the entire composition and temperature range investigated.

Overall trends observed in the *FT*i.r. spectra of PVPh–PMMA blends were identical to those reported above for the miscible PVPh–PEMA and PVPh–PPMA systems. *FT*i.r. spectra obtained for an 80:20 PVPh–PMMA blend are illustrated in *Figure 3a* and *b*. However, since the glass transition temperatures of both PVPh and PMMA are >100°C, there is only a very

Table 3 Curve-fitting results for PVPh–PPMA blends

Temperature (°C)	Fraction of H-bonded carbonyl groups Blend composition PVPh:PPMA 80:20	60:40	50:50	40:60
25↑	0.586	0.511	0.458	0.375
110	0.579	0.507	0.461	0.371
120	0.578	0.507	0.456	0.369
130	0.575	0.502	0.452	0.367
140	0.570	0.497	0.446	0.364
150	0.564	0.493	0.441	0.362
160	0.558	0.489	0.437	0.360
170	0.555	0.484	0.433	0.358
180	0.549	0.479	0.426	0.356
190	0.544	0.473	0.421	0.356
200	0.539	0.467	0.414	0.352
25↓	0.582	0.509	0.454	0.375

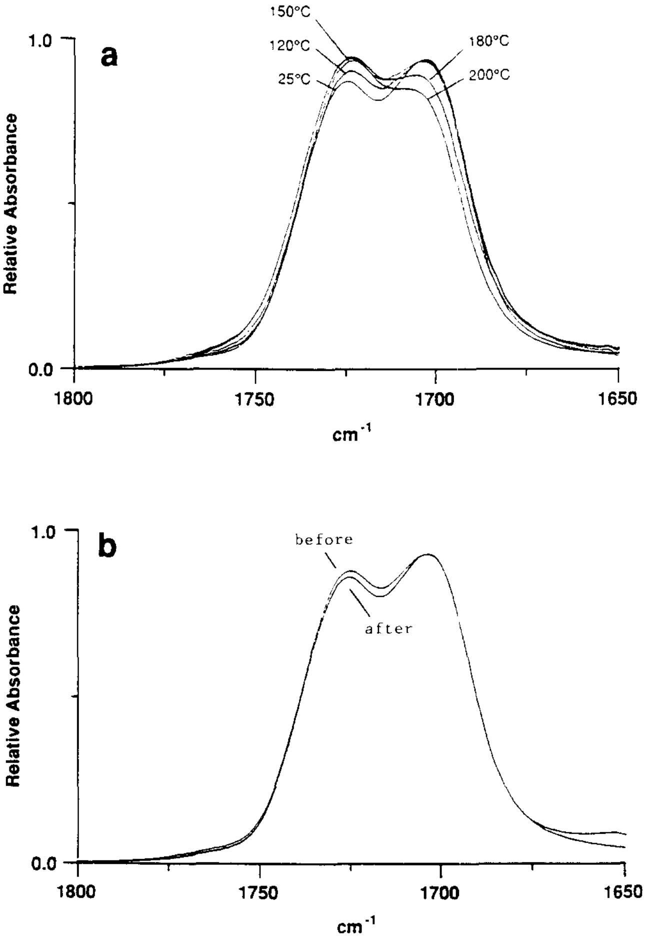

Figure 3 *FT*i.r. spectra in the carbonyl region of an 80:20 PVPh–PMMA blend recorded (a) as a function of increasing temperature and (b) at room temperature before and after heating to 200°C

limited temperature range over which equilibrium conditions can be achieved, resulting in relatively poor reproducibility of the curve-fitting data. Accordingly, we decided to restrict quantitative analysis to blends containing PEMA and the higher homologues, systems where the predicted glass transition temperatures of miscible mixtures are substantially lower.

In marked contrast, the *FT*i.r. results obtained for PVPh–PBMA blends differed significantly from those reported thus far. The trends observed in the carbonyl region of the *FT*i.r. spectra of an 80:20 PVPh–PBMA blend are illustrated in *Figure 4a* and *b*. Although the initial room temperature spectrum of this blend is comparable to those recorded for the previously discussed systems, a much more dramatic decrease in the hydrogen-bonded carbonyl band is observed at elevated temperatures. In addition, the initial state of the system is not recovered upon cooling back to room temperature. This is substantiated by the curve-fitting results reported in *Table 4*. In the 80:20 blend, over 15% of the original hydrogen-bonded carbonyl groups were lost upon heating to 200°C (compared to ≈5% in the corresponding PVPh–PEMA and PVPh–PPMA blends) and less than one-half of these groups were recovered upon subsequent cooling to room temperature. The overall trends observed in these *FT*i.r. results suggest the occurrence of phase separation in PVPh–PBMA blends at elevated temperatures. This conclusion, as well as those drawn for the other PVPh/poly(n-alkyl methacrylates) systems, is consistent with the thermal analysis and cloud point studies of previous investigators[15].

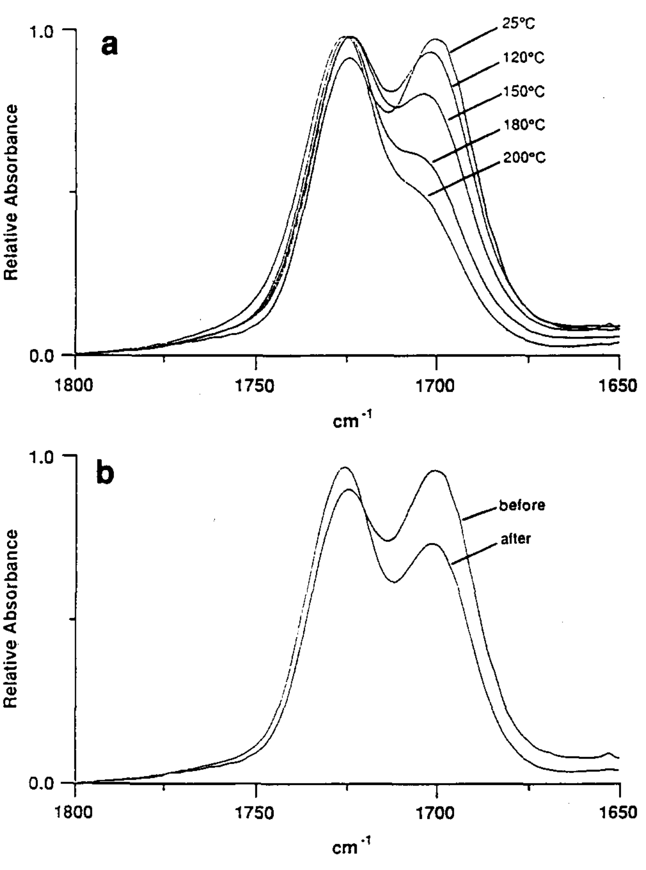

Figure 4 *FT*i.r. spectra in the carbonyl region of an 80:20 PVPh–PBMA blend recorded (a) as a function of increasing temperature and (b) at room temperature before and after heating to 200°C

Table 4 Curve-fitting results for PVPh–PBMA blends

Temperature (°C)	Fraction of H-bonded carbonyl groups Blend composition PVPh:PBMA 80:20	60:40	50:50	40:60
25↑	0.526	0.492	0.456	0.383
110	0.516	0.493	0.454	0.380
120	0.511	0.488	0.449	0.377
130	0.504	0.482	0.443	0.373
140	0.496	0.475	0.437	0.369
150	0.483	0.466	0.430	0.363
160	0.464	0.448	0.423	0.357
170	0.446	0.427	0.403	0.344
180	0.426	0.409	0.382	0.327
190	0.402	0.388	0.360	0.311
200	0.353	0.361	0.337	0.292
25↓	0.418	0.384	0.362	0.325

Theoretical considerations: determination of association parameters

We turn our attention now to the determination of association parameters which will allow calculation of theoretical fractions of hydrogen-bonded carbonyl groups and, ultimately, spinodal phase diagrams for the series of PVPh–poly(n-alkyl methacrylates) blends. Equations describing the stoichiometry of a polymer mixture containing a self-associating component B and a second component A which does not self-associate but may associate with B have been derived previously[2] and are given by:

$$\Phi_A = \Phi_{0A} + K_A \Phi_{0A} \Phi_{B1} \left[\left(1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \left(\frac{1}{(1 - K_B \Phi_{B_1})} \right) \right] \quad (1)$$

$$\Phi_B = \Phi_{B_1} \left[\left(1 - \frac{K_2}{K_B} \right) + \frac{K_2}{K_B} \left(\frac{1}{(1 - K_B \Phi_{B_1})^2} \right) \right] \left[1 + \frac{K_A \Phi_{0A}}{r} \right] \quad (2)$$

where Φ_B and Φ_A are the volume fractions of components B and A, respectively, Φ_{B_1} and Φ_{0A} are the volume fractions of the respective 'free monomers', and r is the ratio of molar volumes, V_A/V_B. The self-association equilibrium constants K_B and K_2 describe the formation of B n-mers and B dimers, respectively, and the association equilibrium constant K_A describes the formation of B_nA complexes.

As discussed in a previous publication[8], the self-association constants for PVPh, K_B and K_2 may be determined from the equilibrium constants for phenol after appropriate compensation for differences in molar volume. Utilizing these equilibrium constants, obtained by Whetsel and Lady[16], gross trends in phase behaviour were successfully predicted for a number of PVPh blends containing polyacrylates, polyacetates, and polylactones[8]. Accordingly, these same self-association equilibrium constants will be used here. Values of 66.8 and 21.0 were determined for K_B and K_2 (at 25°C) of PVPh, respectively. The minor discrepancies in these values and those used previously are a result of the slightly different PVPh molar volumes employed in the two studies. The equilibrium constants are assumed to obey a van't Hoff relationship over the temperature range of interest. The previously determined enthalpies of hydrogen-bond formation, $h_B = 5.2$ kcal mol^{-1} and $h_2 = 5.6$ kcal mol^{-1}, are also employed here. Constant h_B and h_2 values will be assumed for the entire temperature range considered.

Using equations (1) and (2) in conjunction with the expression for the compositional variation of the theoretical fraction of hydrogen-bonded carbonyl groups, f_B (refs 2, 3)

$$f_B = 1 - \Phi_{0A}/\Phi_A$$
$$= 1 - \left\{\frac{1}{[1 + K_A\Phi_{B1}[(1 - K_2/K_B) + (K_2/K_B)(1/(1 - K_B\Phi_{B_1}))]]}\right\} \qquad (3)$$

the value of K_A (given values for K_B, K_2 and r), at a given temperature, may be determined from a least-squares fit of f_B to the experimental fractions of hydrogen-bonded carbonyl groups reported in the previous section. By considering only experimental data obtained at temperatures favouring equilibrium conditions, it will be shown that consistent values for K_A and the corresponding enthalpy of hydrogen-bond formation, h_A, may be determined for the miscible PVPh–PEMA and PVPh–PPMA systems. Because the attainment of an equilibrium state may be reasonably presumed only at temperatures above the glass transition temperatures of both blend components, K_A determinations will be restricted to temperatures above the T_g of PVPh (≈140°C).

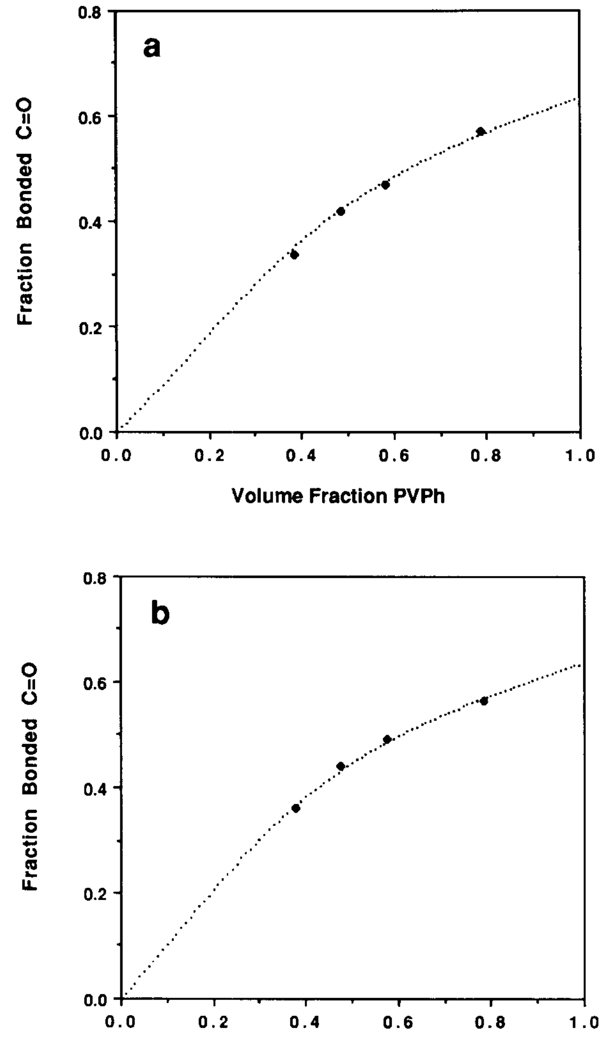

Figure 5 Comparison of the theoretical ($K_A = 5.6$) and experimental fractions of hydrogen-bonded carbonyl groups for (a) PVPh–PEMA and (b) PVPh–PEPA blends at 150°C as a function of the volume fraction of PVPh. ·····, Theoretical; ●, experimental

Table 5 Determination of K_A

Temperature (°C)	K_A PEMA	K_A PPMA
150	5.62	5.76
160	5.02	5.18
170	4.56	4.71
180	4.15	4.28
190	3.80	3.92
200	3.47	3.60

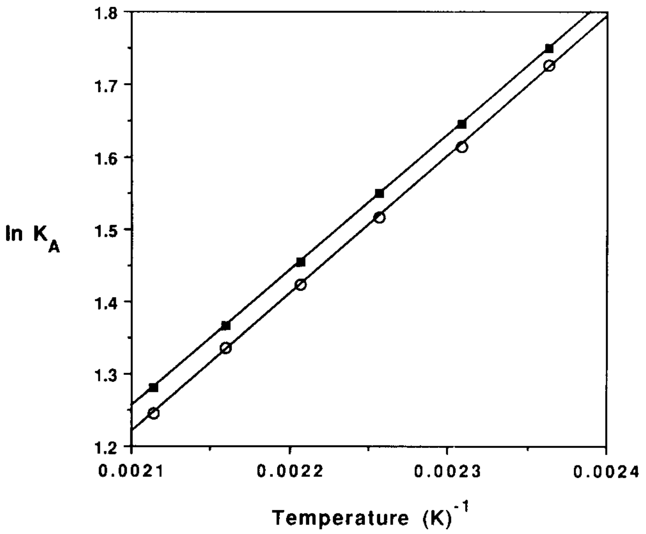

Figure 6 Plots of $\ln K_A$ *versus* $1/T$ for PVPh–PEMA (○) and PVPh–PPMA (■) blends

Initially, the value of K_A at 150°C was determined for the PVPh–PEMA system from the least-squares fit of equation (3) to the curve-fitting results reported in *Table 2*. The fine agreement of the experimentally determined fractions of hydrogen-bonded carbonyl groups with those predicted by the 'best fit' theoretical curve is shown in *Figure 5*. A K_A value of 5.6 was indicated at this temperature, which was identical to the value reported previously[10]. The reproducibility of the K_A determinations in these blends is encouraging. The results of all K_A determinations for PVPh–PEMA blends in the temperature range between 150–200°C are summarized in *Table 5*. The plot of ln K_A *versus* $1/T$ for this data is shown in *Figure 6*. The linearity of the plot illustrates the validity of a van't Hoff relationship over the temperature range studied. The slope of the curve corresponds to a heat of hydrogen-bond formation, h_A of 3.8 kcal mol^{-1}. Extrapolation of the van't Hoff plot to room temperature yields a K_A value of 37.2 at 25°C.

Similar K_A determinations were performed for PVPh–PPMA blends using the infrared curve-fitting data contained in *Table 3*. The results for all temperatures are shown in *Table 5* and indicate K_A values comparable to those obtained for the PVPh–PEMA system. A van't Hoff plot of this data is again linear (*Figure 6*) and indicates an h_A value of 3.7 kcal mol^{-1}. A room temperature K_A value of 37.0 was determined from the results.

These values are in excellent agreement with those obtained for the PVPh–PEMA blends. The similarity in the h_A values of the two systems is expected due to the identical nature of the intermolecular hydrogen-bonding interaction present in both systems. In addition, because the association model references all equilibrium constants to the molar volume of the self-associating component of the blend (i.e. PVPh), the correspondence in the determined K_A values of the PVPh–PEMA and PVPh–PPMA systems is theoretically predicted[2,3].

Based on the above results, average K_A and h_A values of 37.1 and 3.75 kcal mol^{-1}, respectively, will be used in subsequent calculations. These values differ somewhat from those used in prior investigations ($h_A = 4.3$ kcal mol^{-1} and $K_A = 46.8$–66.2) where the h_A value was not determined directly but was obtained from low-molecular-weight phenol-ester mixtures[8].

Theoretical versus *experimental fractions of H-bonded carbonyl groups*

Prior to the calculation of spinodal phase diagrams for the PVPh–poly(alkyl methacrylate) systems, it is interesting to compare the experimental fractions of hydrogen-bonded carbonyl groups present in these blends with theoretical predictions calculated as a function of both blend composition and temperature.

A comparison of the compositional dependence of the experimental and theoretical fractions of hydrogen-bonded carbonyl groups in PVPh–PEMA and PVPh–PPMA blends at 150°C has already been presented (*Figure 5*). Similar comparisons at 200°C are presented in the thesis of Serman[17]. In all cases, the experimental fractions of hydrogen bonded carbonyl groups at each blend composition are in excellent agreement with theoretical predictions. More comprehensive comparisons are shown in *Figure 7*, which illustrate the theoretical and experimental hydrogen-bonded carbonyl fractions for all PVPh–PEMA and PVPh–PPMA blend compositions at temperatures between 110°C and 200°C. The overall results clearly illustrate the ability of the association model to accurately describe the composition and temperature dependence of the fraction of hydrogen bonded carbonyl groups present in these blends. The excellent agreement of the theoretical and experimental results obtained for the PVPh–PEMA and PVPh–PPMA blends implies complete miscibility in these systems at temperatures up to 200°C. These findings are consistent with the conclusions drawn earlier on the basis of thermally reversible spectral trends.

In contrast, a comparison of the theoretical and experimental fractions of hydrogen bonded carbonyl groups in PVPh–PBMA blends at 200°C is shown in *Figure 8a*. Unlike the previous examples, the experimental hydrogen bonded fractions obtained for all PVPh–PBMA blend compositions at this temperature were significantly lower than their predicted values. The deviations in the theoretical and experimental results suggest phase separation in these blends. This phase instability may be confirmed by cloud point measurements as shown in *Figure 8b*. Phase separation is also suggested in the plots of temperature *versus* the fraction of hydrogen bonded carbonyl groups for each blend composition, as shown in *Figure 9*.

As temperature is increased a point is reached in each composition at which the experimental fractions begin to decrease more rapidly than predicted. These points of deviation presumably correspond to the onset of phase separation in these blends. For the PVPh-rich blends, phase separation appears to occur at significantly lower temperatures than determined by the corresponding cloud point measurements. For example, for the 80:20 blend (*Figure 9a*), the experimental bonded fraction lies below the theoretical curve over the entire temperature range, indicating that phase separation occurs below 110°C. It is important to recognize, however, that the i.r. probe size is considerably smaller than that of light scattering although it is not clear at this stage whether or not i.r. spectroscopy is sensitive to the large scale fluctuations that occur before the onset of phase separation as the spinodal boundary is approached. In any event, these results illustrate the potential application of *FT*i.r. spectroscopy as a sensitive tool for the detection of phase separation in hydrogen bonded polymer blends.

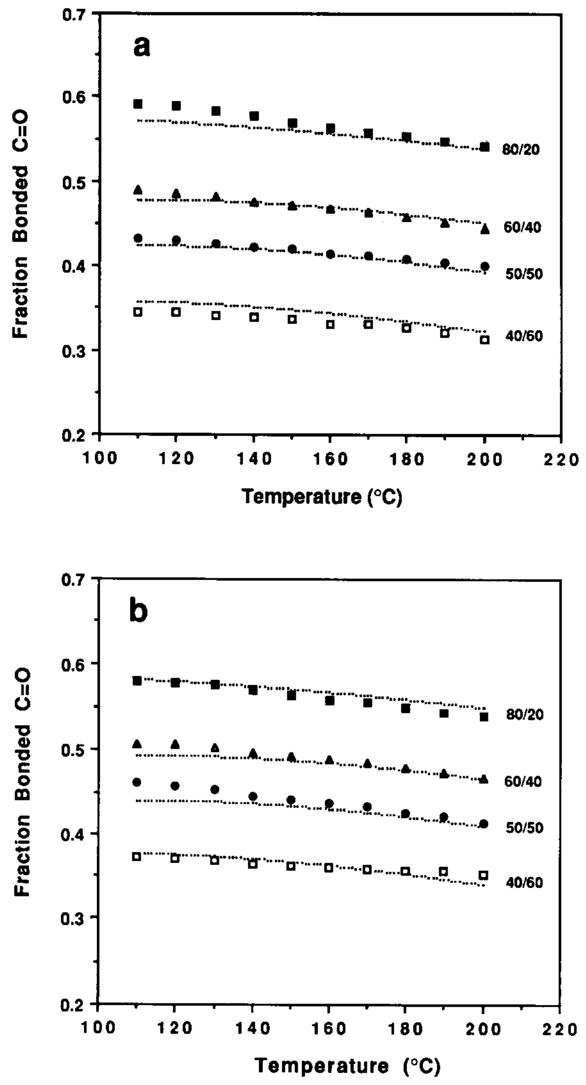

Figure 7 Comparison of the theoretical and experimental fractions of hydrogen-bonded carbonyl groups for different compositions of (a) PVPh–PEMA and (b) PVPh–PPMA blends as a function of temperature. (····, Theoretical)

Calculation of spinodal phase diagrams

In our model, the free energy change obtained upon mixing two polymer components that are capable of

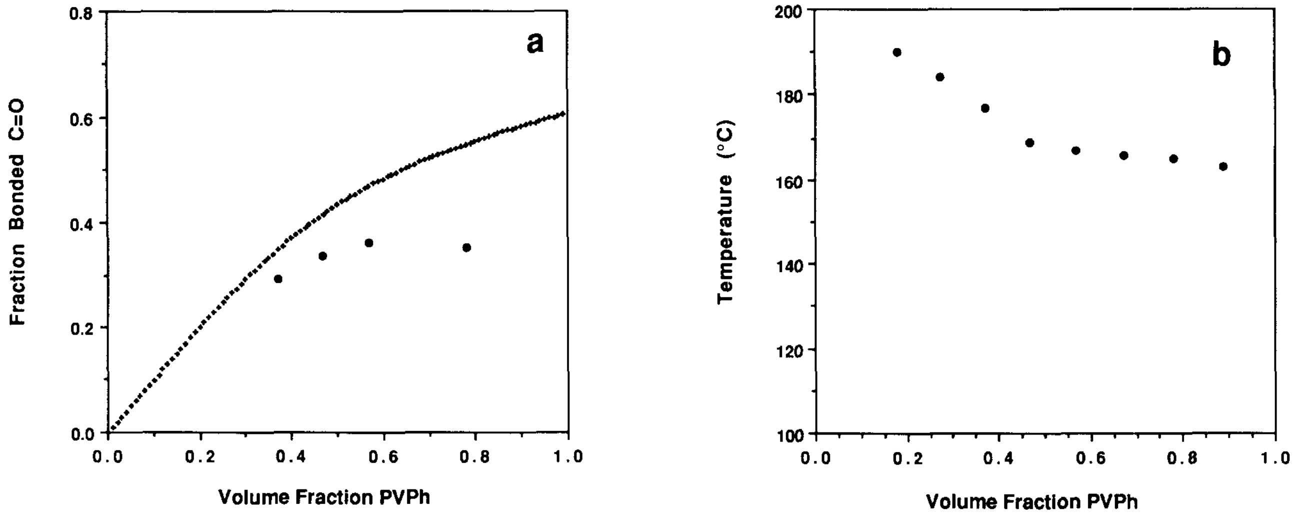

Figure 8 (a) Comparison of the theoretical (+) and experimental (●) fractions of hydrogen-bonded carbonyl groups for PVPh–PBMA blends at 200°C as a function of the volume fraction of PVPh. (b) Cloud point curve for PVPh–PBMA blends

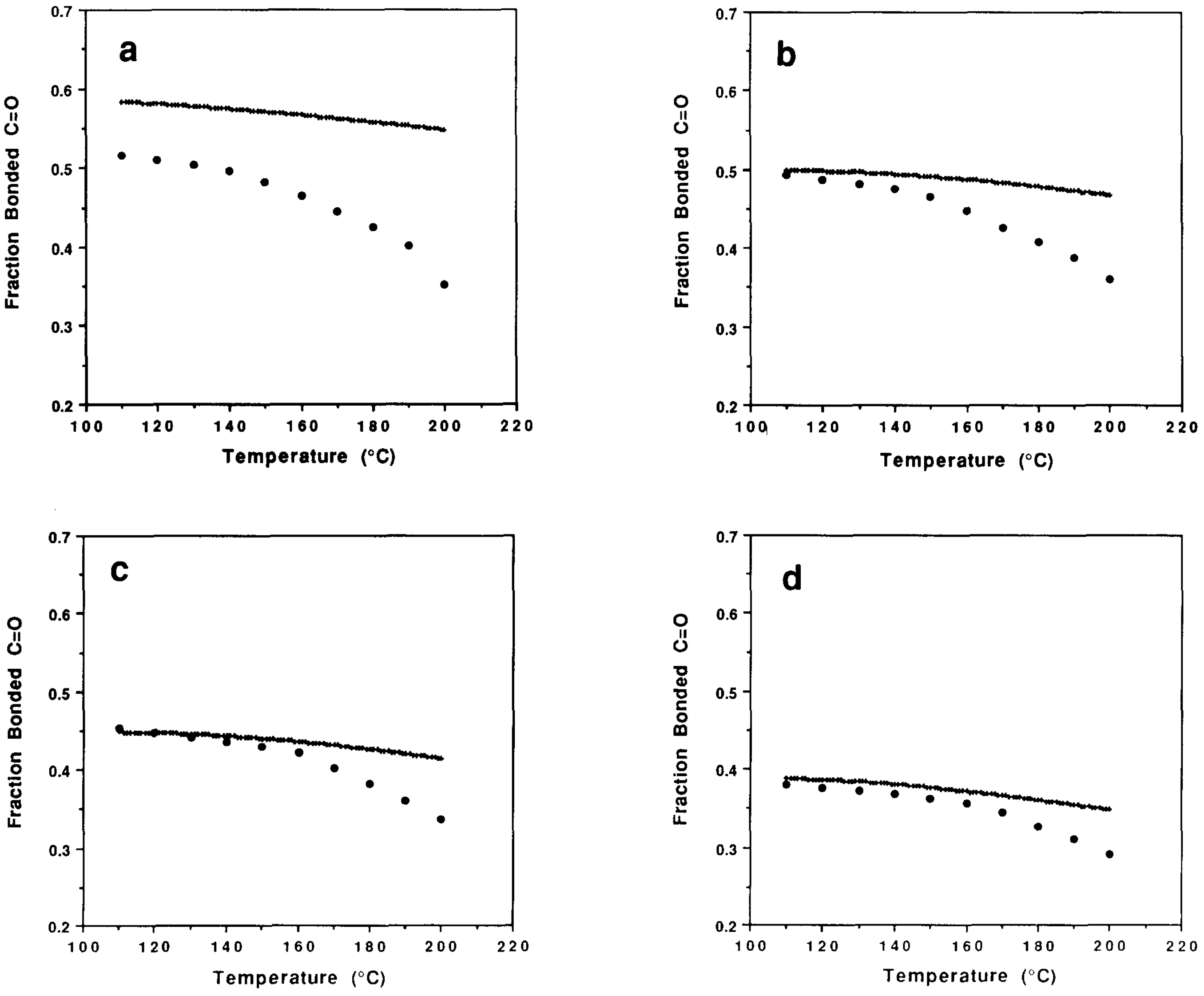

Figure 9 Comparison of the theoretical (+) and experimental (●) fractions of hydrogen-bonded carbonyl groups for (A) 80:20, (B) 60:40, (C) 50:50 and (D) 40:60 PVPh–PBMA blends as a function of temperature

hydrogen-bonding may be approximated by:

$$\Delta G_M/RT = (\Phi_A/N_A)\ln\Phi_A + (\Phi_B/N_B)\ln\Phi_B + \chi_{AB}\Phi_A\Phi_B + \Delta G_H/RT \qquad (4)$$

where the initial three terms of the expression are identical to the original Flory–Huggins equation and ΔG_H represents the free energy associated with the change in the distribution of hydrogen bonds. This free energy contribution is then given by:

$$\begin{aligned}\Delta G_H/RT = {} & \Phi_B \ln\left[\frac{\Phi_{B_1}}{\Phi^0_{B_1}\Phi_B^{1/\bar{n}^0_H}}\right] + \frac{\Phi_A}{r}\ln[\Phi_{0A}/\Phi_A] \\ & + \Phi_B[(\Gamma^0_1/\Gamma^0_2) - (\Gamma_1/\Gamma_2)] \\ & + \Phi_B(\Gamma_1/\Gamma_2)\left[\frac{K_A\Phi_{0A}/r}{1 + K_A\Phi_{0A}/r}\right] \qquad (5)\end{aligned}$$

where

$$\Gamma_1 = [(1 - K_2/K_B) + (K_2/K_B)(1/(1 - K_B\Phi_{B_1}))]$$

$$\Gamma_2 = [(1 - K_2/K_B) + (K_2/K_B)(1/(1 - K_B\Phi_{B_1})^2)]$$

and

$$\bar{n}^0_H = \Gamma^0_2/\Gamma^0_1$$

whose parameters are described in more detail elsewhere[1–4]. In addition to the association parameters already determined, the model requires values for the molar volumes and degrees of polymerization of both components as well as an estimate of the interaction parameter, χ_{AB}, for the different systems.

The values for the molar volumes and solubility parameters were calculated from group contributions tabulated by us in a recent publication[18]. Interaction parameters of the various systems were then determined from solubility parameter differences via the Scatchard–Hildebrand relation[19] using a reference volume equal to the molar volume of PVPh. A value of 500 was used for the degrees of polymerization, N_A and N_B of both components. A summary of all parameters employed in the spinodal calculations is shown in *Table 6*.

Theoretical spinodal phase diagrams for the PVPh–poly(n-alkyl methacrylate) blends were calculated from the locus of points whose numerically determined second derivatives of free energy, with respect to blend composition, were equal to zero. The results of such calculations for temperatures between −100°C and 250°C are shown in *Figure 10* using the lower value of the solubility parameter for PVPh of 10.6 (cal cm^{-3})$^{0.5}$. As indicated in the figure, blends of PVPh with PMMA and PEMA are predicted to be thermodynamically stable throughout this entire temperature range except for a small region of immiscibility below −50°C. Results obtained for the PVPh–PPMA and PBMA systems predict the emergence of a closed immiscibility loop at high temperatures and high PVPh compositions, as well as an increase in temperature of the lower phase boundary compared to that of the PMMA and PEMA blends. For PPeMA, PHMA and higher homologues blends, a larger two-phase region is predicted, resulting from the merger of the upper and lower phase boundaries, with the breadth of the two-phase region becoming progressively larger. The trend observed here, a decrease in miscibility with increasing size of the poly(n-alkyl methacrylate) pendent group, is analogous to that reported previously for blends of PVPh with a series of poly(alkyl acrylates)[8]. Importantly, these calculations correctly predict the composition and temperature ranges of the lower critical boundary for the PVPh–PBMA blends.

It is important to recognize that for blends on the edge of miscibility, where the favourable ΔG_H term and unfavourable χ term are finely balanced, the exact locations of the theoretical spinodals are very sensitive to the values of the interaction parameters employed in the calculations. As an example, *Figure 11* illustrates the effects of relatively small changes in the solubility parameter of PVPh on the spinodal calculations for PVPh–PBMA blends. Upon decreasing the solubility parameter of PVPh from 11.0 to 10.6 (cal cm^{-3})$^{0.5}$, which is within the margin of error for calculated solubility parameters[17,18], an immiscible blend with a two-phase region extending throughout the whole temperature range transforms to one with separate upper and lower immiscibility regions. In other words, a decrease of only 0.4 (cal cm^{-3})$^{0.5}$ is sufficient to yield a window of miscibility which extends throughout the

Table 6 Summary of model parameters

Polymer	Molar volume (cm^3 mol^{-1})	Solubility parameter (cal. cm^{-3})$^{0.5}$	Interaction parameter χ_{AB}	Degrees of polymerization $N_A = N_B$
PVPh	100.0	10.6–11.0	–	
PMMA	84.9	9.1	0.38–0.61	
PEMA	101.4	8.9	0.49–0.74	
PPMA	117.9	8.8	0.55–0.82	500
PBMA	134.4	8.7	0.61–0.89	
PPeMA	150.9	8.6	0.68–0.97	
PHMA	167.4	8.5	0.74–1.06	

Association parameters

	Equilibrium constants	Enthalpy of H-bond formation (kcal mol^{-1})	
K_B	66.8	h_b	5.2
K_2	21.0	h_2	5.6
K_A	37.1	h_A	3.75

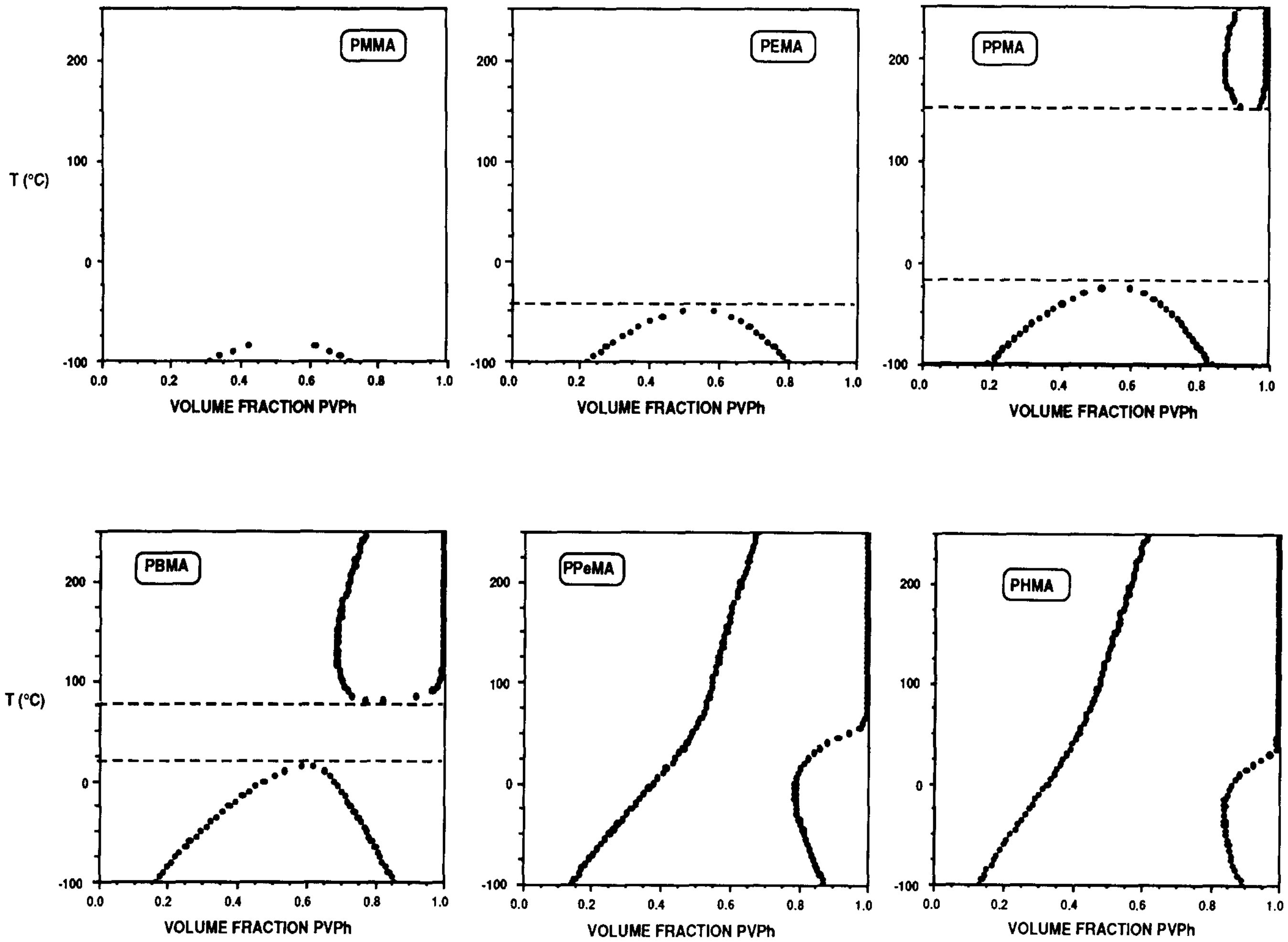

Figure 10 Theoretical spinodal phase diagrams for PVPh–poly(n-alkyl methacrylate) blends using a PVPh solubility parameter value of 10.6 (cal cm^{-3})$^{0.5}$

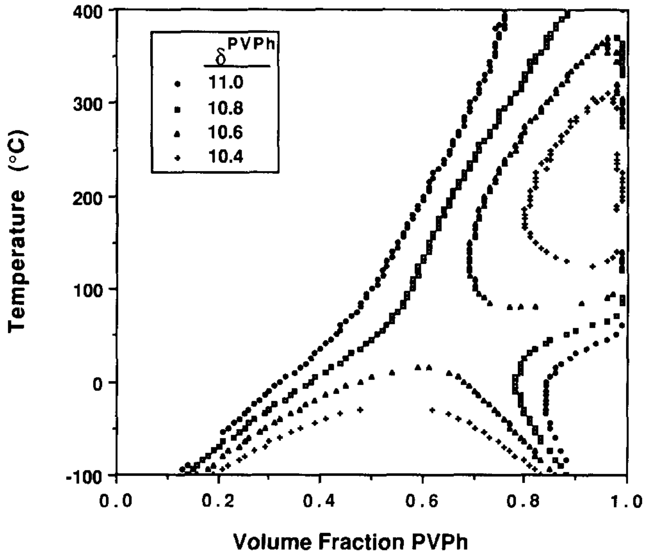

Figure 11 Effect of PVPh solubility parameter on calculated spinodal phase diagrams for PVPh–PBMA blends

entire composition range at ambient temperature. Since the estimation of the non-hydrogen bonded solubility parameter of PVPh, (or any strongly self-associated polymer for that matter), is subject to the most error in our scheme[18], it is perfectly valid to consider the interaction parameter χ_{AB}, or the non-hydrogen bonded solubility parameter of PVPh from which it is calculated, as adjustable parameters. Thus, by adjusting the solubility parameter of PVPh in this manner, theoretical phase diagrams in excellent agreement with experimental observations may be obtained for all PVPh–poly(n-alkyl methacrylate) blends considered. What is probably most surprising is that our crude and simple method of determining the solubility parameter of PVPh from non-hydrogen bonded group contributions[18] has yielded results that are close to that required to satisfactorily predict the gross phase behaviour of a number of different polymer blend systems.

Finally, in this simple scheme we have ignored free volume effects. In blends where interactions are weak these dominate in determining a lower critical solution temperature. In systems where strong self-association occurs, however, free volume appears to play only a minor role. We will present a complete discussion of these arguments in a separate publication.

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