Poly(vinyl phenol)–polyether blends

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Spinodal phase diagram calculations are presented for poly(vinyl phenol)–polyether blends. Equilibrium constants corresponding to self-association and inter-association were transferred from those reported in the literature for low molecular weight model analogues after adjusting to account for differences in molar volume of the model and the polymer repeat. The results are in good agreement with the trends observed experimentally.

INTRODUCTION

In two recent publications we have described equations derived from a simple association model that may be used to determine the free energy changes and phase behaviour of binary polymer mixtures in systems where relatively strong intermolecular interactions are involved, typically hydrogen bonds[1,2]. In brief, the overall equation may be obtained formally using a Flory lattice model[3] and has the form of the classic Flory–Huggins relationship, but with an added term, $\Delta G_H/RT$, to account for the presence of favourable intermolecular interactions:

$$\frac{\Delta G^M}{RT} = \frac{\Phi_A}{N_A} \ln \Phi_A + \frac{\Phi_B}{N_B} \ln \Phi_B + \Phi_A \Phi_B \chi + \frac{\Delta G_H}{RT} \quad (1)$$

where Φ_A and Φ_B, and N_A and N_B = the volume fractions and degrees of polymerization of polymers A and B, respectively, and χ is the polymer–polymer interaction parameter.

If we disregard free volume effects and the very small contribution from combinatorial entropy contained in the first two natural log terms, miscibility rests on the balance between the number and strength of favourable interactions, included in the $\Delta G_H/RT$ term, and unfavourable 'physical' interactions, embodied in a conventional χ parameter. The latter parameter, which is restricted to values of $\geqslant 0$, may be estimated from non-hydrogen-bonded solubility parameters[4], while the contribution from the $\Delta G_H/RT$ term, which assumes values of $\leqslant 0$, may be readily calculated[5] if one knows the molar volumes of the chemical repeat units, V_B and V_A; equilibrium constants describing self-association, K_B (K_2) and inter-association, K_A, and the corresponding interaction enthalpies, h_B (h_2) and h_A.

In specific cases, e.g. the amorphous polyurethane–polyether[6] and ethylene-co-methacrylic acid–polyether[7] blend systems, equilibrium constants describing both self-association and inter-association can be measured directly in the solid state using infra-red spectroscopy from a quantitative analysis of the fraction of hydrogen-bonded carbonyl groups in the pure self-associated

polymer and blends, respectively. However, as we have discussed previously, for strongly self-associating polymers containing hydroxyl, amine or similar groups, it is not presently feasible to measure K_B using samples in the solid state directly from the mid infra-red region of the spectrum[5,8]. K_B for poly(4-vinyl phenol) (PVPh) can be obtained indirectly from the results of solution studies of the model compound phenol[9] by scaling to the polymer repeat after correcting for molar volume differences[5]. In the case of blends of PVPh with carbonyl-containing polymers such as polyacrylates, polymethacrylates, polyesters and polyacetates, values of the inter-association equilibrium constant, K_A, can be measured directly using the equations describing the blend stoichiometry and a quantitative analysis of the fraction of hydrogen-bonded carbonyl groups determined from the carbonyl region of the infra-red spectrum[5,10].

In this communication we go one step further and present spinodal calculations for PVPh blends with poly(alkyl ethers) and poly(vinyl alkyl ethers) where both the equilibrium constants describing self-association and inter-association are scaled from literature values of low molecular weight models. The results compare favourably with experimental observations and support the concept of transferable equilibrium constants determined from appropriate model compounds to analogous polymeric blend systems.

EXPERIMENTAL TRENDS IN MISCIBILITY

The poly(4-vinyl phenol) (PVPh) and polytetrahydrofuran (PTHF) mentioned in this study have been described previously[5,7,11]. Poly(vinyl n-butyl ether) (PVBE) was polymerized cationically in our laboratories from the monomer vinyl butyl ether (Aldrich Chemical Co.). To our knowledge, previous published experimental studies of PVPh blends with poly(alkyl ethers) and poly(vinyl alkyl ethers) have been limited to those of Moskala et al.[11]. Based on a qualitative analysis of the hydroxyl stretching region of the i.r. spectrum, blends of PVPh with poly(ethylene oxide) (PEO), poly(vinyl methyl ether) (PVME) and poly(vinyl ethyl ether) (PVEE) were found to exhibit a high degree of molecular

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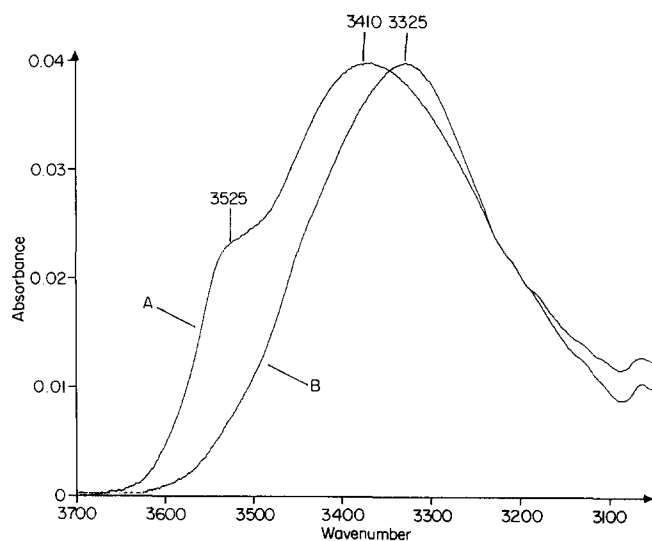
Figure 1 *FT*i.r. spectra in the hydroxyl stretching region from 3100 to 3700 cm⁻¹: curve A, pure PVPh; curve B, 20:80 wt% blend of PVPh and PTHF

mixing. From additional recent i.r. studies we can now add PVPh blends with polytetrahydrofuran (PTHF) to this list (see *Figure 1*). All the blends were observed to be optically clear over the entire composition range, suggesting miscible systems. I.r. bands attributed to the hydrogen-bonding interaction between the phenolic hydroxyl of PVPh and the ether oxygen of the respective polyether were readily identified. The relative contribution of these bands increases with increasing concentration of the polyether in the blend, consistent with a system of competing equilibria where one would anticipate an increase in the relative number of hydroxyl–ether interactions. The interaction may be characterized a strong hydrogen-bonding interaction, as the frequency difference (Δv) between the 'free' hydroxyl band (3525 cm⁻¹) and the hydroxyl–ether interaction, which is a measure of the relative strength of the interaction, varies from about 200 cm⁻¹ for PVME, PVEE and PTHF to 235 cm⁻¹ in the case of PEO. Unlike the corresponding phenolic hydroxyl interaction with carbonyl groups of polyesters, polyacrylates, methacrylates etc.[5,11], the hydroxyl–ether interaction is significantly stronger than that of the self-association of PVPh ($\Delta v = 155$ cm⁻¹).

In marked contrast, blends of PVPh with poly(vinyl isobutyl ether) (PVIBE) were shown by Moskala to be immiscible[11]. To eliminate the possibility of steric complications arising from the branched side group, we synthesized the linear analogue, poly(vinyl n-butyl ether) (PVBE). Nonetheless, the result is the same and PVPh–PVBE blends are immiscible as indicated by their opacity and the i.r. spectral data shown in *Figure 2*. Even in the presence of a large excess of PVBE the spectrum of the blend in the hydroxyl stretching region is essentially the same as that of pure PVPh. There is no evidence of a band attributable to hydroxyl–ether interactions, which implies minimal molecular mixing and a two-phase system.

To summarize the major experimental trends:

1 PVPh blends are miscible in the amorphous state with PEO and PTHF.

2 PVPh blends are miscible with PVME and PVEE but immiscible with PVBE and PVIBE.

Now the question remains, can we predict these trends from our theoretical spinodal calculations using equilibrium constants and interaction enthalpies derived from literature values of low molecular weight models?

DETERMINATION OF MODEL PARAMETERS

The self-association parameters of PVPh are independent of the second blend component and consequently those employed previously for blends of PVPh with polyacrylates and the like[5] are directly applicable to the PVPh–polyether system (see *Table 1*). (There are some very minor differences in the absolute values of the equilibrium constants, K_2 and K_B, the non-hydrogen-bonded solubility parameter and the molar volume, however, which reflect our own recent refinements to the calculations of group molar attraction and molar volume constants[4,10].)

Conversely, the inter-association parameters, K_A and h_A, for the PVPh–polyether blend system are expected to differ from that of the PVPh–polyacrylate (methacrylate etc.) systems[5] due to the dissimilar nature of the respective hydrogen-bonding interactions. As mentioned previously, K_A for the PVPh–polyacrylate systems and the like were obtained from a least-squares fit of the theoretical model to the experimentally determined fractions of hydrogen-bonded carbonyl groups present in miscible blends as a function of composition[5,10]. Unfortunately, this procedure is not applicable to the PVPh–polyether blend system. Unlike the carbonyl stretching vibration, the C–O–C stretching vibration is not a localized mode and is conformationally sensitive, which precludes quantitative analysis of the fraction of hydrogen-bonded ether groups in the blend[12]. Nevertheless, as in the case of the self-association parameters of PVPh, values of K_A and h_A for PVPh–polyether blends may be estimated from inter-association parameters determined from i.r. studies of model mixtures. Powell and West investigated the thermodynamics of phenol–diethyl ether mixtures in carbon tetrachloride solution using a near i.r. spectrophotometric method[13] and obtained a value of 23 kJ mol⁻¹ for h_A and 8.83 dm³ mol⁻¹ for the concentration equilibrium constant, K_A^c. Conversion of the concentration-based equilibrium constant to
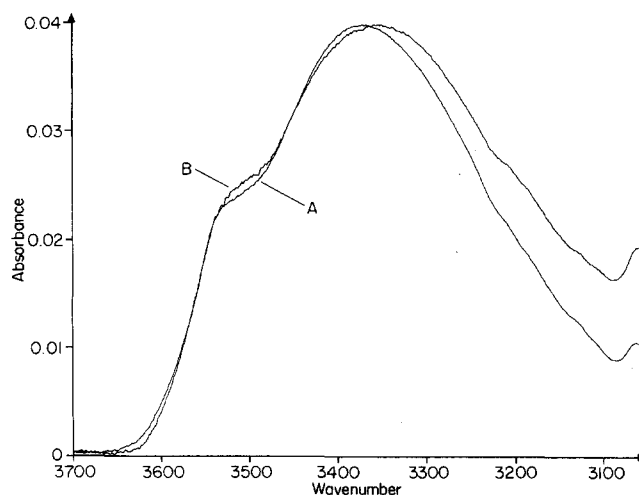
Figure 2 *FT*i.r. spectra in the hydroxyl stretching region from 3100 to 3700 cm⁻¹: curve A, pure PVPh; curve B, 20:80 wt% blend of PVPh and PVBE

Table 1 Parameters used in theoretical spinodal calculations

Polymer	Molar volume $(dm^3 mol^{-1})$	Solubility parameter $(kJ dm^{-3})^{0.5}$	Interaction parameter PVPh χ_{AB}	Degrees of polymerization $N_A = N_B$
PVPh	0.1000	22.5	–	
PVME	0.0553	17.3	1.09	
PVEE	0.0718	17.1	1.18	
PVPE	0.0883	16.9	1.27	
PVBE	0.1048	16.7	1.36	
PViBE	0.1055	16.3	1.55	
PMO	0.0216	21.4	0.05	500
PEO	0.0381	19.2	0.44	
PTMO	0.0546	18.4	0.68	
PTHF	0.0711	18.0	0.82	
PPeMO	0.0876	17.5	1.01	
PHxMO	0.1041	17.3	1.09	
PHpMO	0.1206	17.1	1.18	
POMO	0.1371	17.1	1.18	

	Association parameters		
Equilibrium constants		Enthalpy of H-bond formation $(kJ mol^{-1})$	
K_B	66.8	h_B	5.2
K_2	21.0	h_2	5.6
K_A	88.3	h_A	5.4

Table 2 Parameters used in theoretical spinodal calculations for STVPh-PVBE blends

Polymer	Molar volume $(dm^3 mol^{-1})$	Solubility parameter $(kJ dm^{-3})^{0.5}$	Interaction parameter χ_{AB}	Degrees of polymerization $N_A = N_B$
PVBE	0.1048	34.4	–	500
STVPh[75]	0.1361	44.5	1.33	367
STVPh[50]	0.2083	42.8	1.43	240
STVPh[25]	0.4250	41.2	1.93	118

	Association parameters		
Polymer	K_2	K_B	K_A
STVPh[75]	15.4	49.1	64.9
STVPh[50]	10.1	32.1	42.4
STVPh[25]	4.9	15.7	20.8

the dimensionless parameter defined in the association model and correcting for molar volume differences[1] leads to a value for K_A of 88.3.

The solubility parameters and molar volumes of the polyethers were calculated from our recently reported group molar attraction, and molar volume constants (see Table 2 of ref. 4). Values of 2.25 $(kJ dm^{-3})^{0.5}$ and 0.1 $dm^3 mol^{-1}$ for the non-hydrogen-bonded solubility parameter and molar volume, respectively, were employed for PVPh[4,10]. Interaction parameters for the various PVPh-polyether blends were estimated from the equation:

$$\chi_{AB}^{PVPh} = \frac{V_r}{RT} [\delta_A - \delta_B]^2 \tag{2}$$

employing V_B, the molar volume of the self-associating species, PVPh, as the reference volume[5]. A value of 500 was used in the calculations for the degree of polymerization of both PVPh and the polyethers.

SPINODAL CALCULATIONS—PVPh BLENDS WITH POLY(VINYL ALKYL ETHERS)

Using an identical procedure to that reported previously[5], theoretical spinodal phase diagrams were calculated from -100 to $250°C$ for PVPh blends with a homologous series of linear aliphatic poly(vinyl alkyl ethers), starting with PVME and systematically adding methylene groups to the side group to form PVEE, poly(vinyl n-propyl ether) (PVPE), PVBE, poly(vinyl pentyl ether) (PVPeE) and poly(vinyl hexyl ether) (PVHE). Calculations were also performed for PVIBE.

Only a single-phase region was calculated for PVME blends with PVPh, implying that they are theoretically miscible throughout the entire temperature range considered. For blends of PVPh with PVEE (*Figure 3a*) and PVPE (*Figure 3b*), a two-phase region is calculated for blends rich in PVPh at temperatures exceeding $170°C$ and $80°C$, respectively. For PBME and PVIBE blends
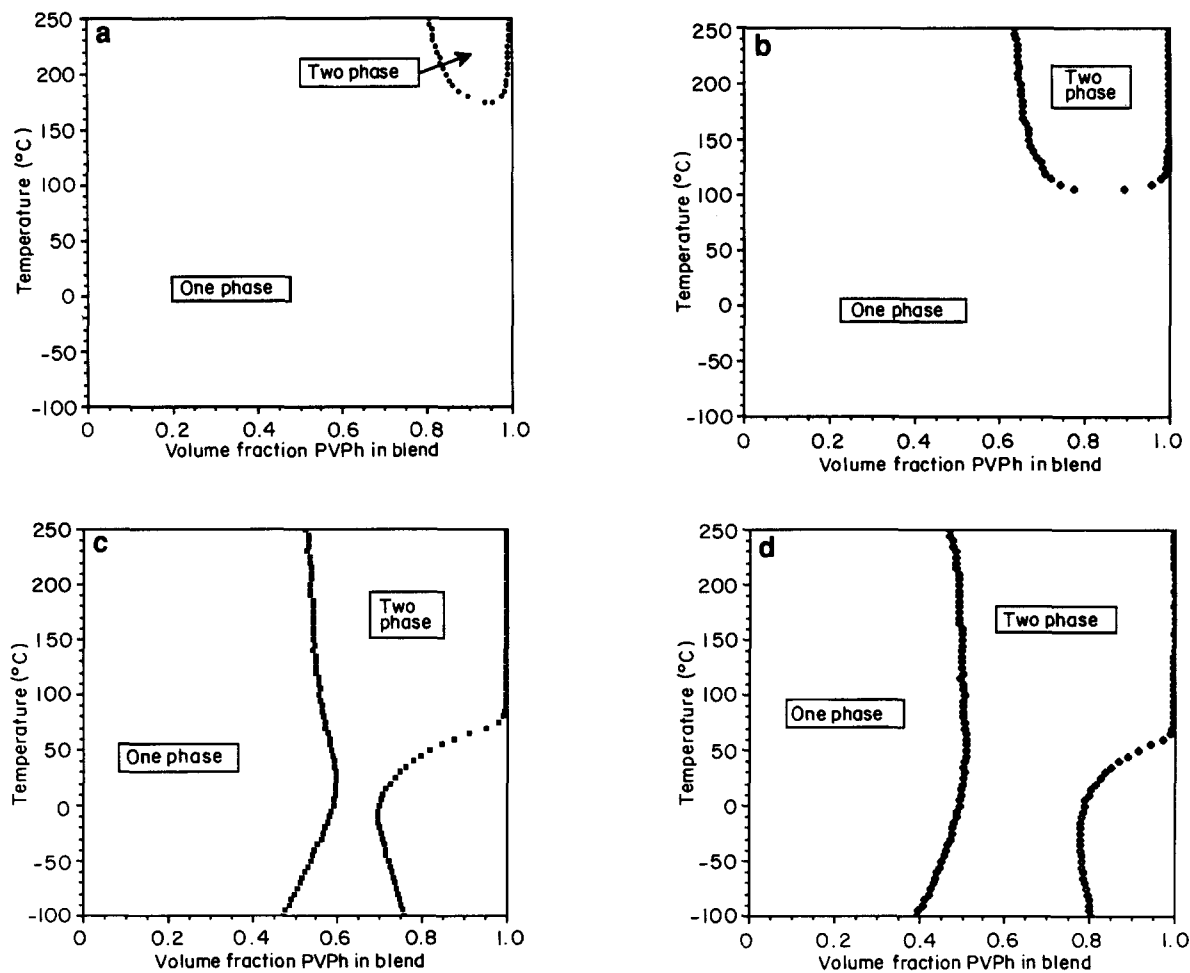
Figure 3 Calculated spinodal phase diagrams for PVPh blends with: (a) PVEE; (b) PVPE; (c) PVBE; (d) PVIBE

(*Figures 3c,d*) an hourglass-shaped phase diagram typical of immiscible polymer blends is calculated. Further addition of CH_2 groups to the side group in the poly(vinyl alkyl ether) repeat just serves to enlarge the two-phase region. In summary, the results of these calculations indicate that PVPh blends should be miscible with PVME, PVEE and PVPE, but immiscible with PVBE and higher homologues in the amorphous state at ambient temperature.

In considering the ramifications of these results two factors are particularly important. First, as the number of CH_2 groups in the repeat of the polyether is increased the ratio of the molar volumes, $r = V_A/V_B$, increases, since V_B is constant. All other things being equal this is unfavourable to mixing, as it results in a decrease in the contribution from the $\Delta G_H/RT$ term (equation (1))[1,2,5]. Second, the solubility parameter of the polyether decreases in magnitude with increasing number of CH_2 groups (see *Table 1*). Accordingly, the magnitude of χ increases as the difference between the PVPh and polyether solubility parameters widens. This also is unfavourable to mixing as the contribution from the $\chi\Phi_A\Phi_B$ term increases.

MISCIBILITY WINDOWS

As an alternative to showing conventional phase diagrams of volume fraction of PVPh in the blend *versus* temperature, it is perhaps more convenient, especially for scouting purposes, to display a type of 'miscibility

window' where the volume fraction of PVPh in the blend is plotted against a hypothetical 'copolymer' of varying composition at a particular temperature, as illustrated in *Figure 4*. It is important to recognize that we make no distinction between the average repeat in a random copolymer and the actual repeat in a homopolymer. If there is a favourable interaction between components of a blend, miscibility will ultimately depend upon the balance between the number and strength of such favourable interactions, which is embodied in the $\Delta G_H/RT$ term, and unfavourable 'physical' interactions, which are described by a conventional average χ parameter for copolymers[14]. For example, PVPE is isomorphous to a random copolymer of two methylenes and vinyl methyl ether unit as depicted below:
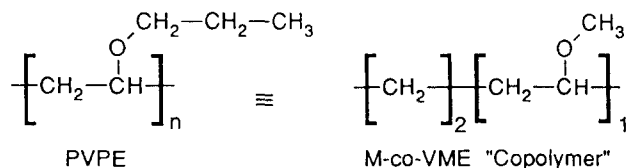
Accordingly, we can readily calculate a 'miscibility window' at 25°C for PVPh blends with hypothetical methylene-co-vinyl methyl ether (M-co-VME) copolymers containing different concentrations of methylene varying from 0% (PVME) to essentially 100% (polyethylene). Naturally, specific concentrations of methylene in the 'copolymer' correspond to the 'homopolymers'
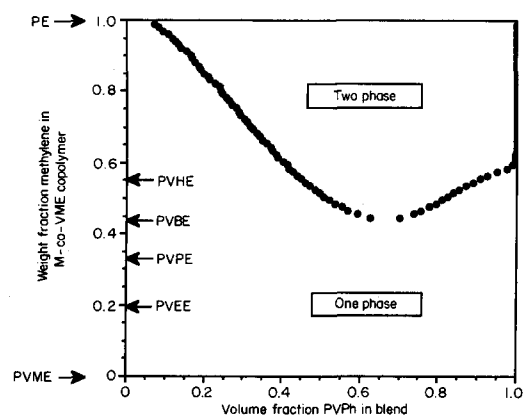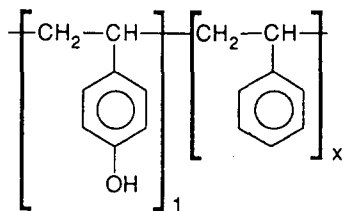
Figure 4 'Miscibility window' for PVPh blends with hypothetical M–co–VME copolymers at 25°C

PVEE, PVPE, PVBE, PVHE etc. As miscibility is defined as a single-phase across the entire composition range, it can be seen from the room temperature 'miscibility window', illustrated in *Figure 4*, that blends of PVPh with M-co-VME polymers containing greater than about 45 wt% of methylene (roughly corresponding to PVBE) are predicted to be immiscible. This is in good agreement with experiment.

STYRENE-CO-VINYL PHENOL BLENDS WITH POLYETHERS—THE EFFECT OF DILUTION

Let us suppose that we wish to find a miscible PVBE blend. The above calculations suggest, and we have experimentally confirmed, that PVBE is immiscible with PVPh. If one accepts the idea that polymer–polymer miscibility is primarily determined by the balance between the unfavourable $\chi\Phi_A\Phi_B$ and favourable $\Delta G_H/RT$ contributions (equation (1)), then it follows that if we can alter the balance slightly in favour of the latter it should be possible to find a miscible PVBE system. This we can achieve by copolymerization of vinyl phenol with an appropriate 'inert diluent' (comonomer) such as styrene, ethylene, butadiene etc.

Consider a styrene-co-vinyl phenol (STVPh) copolymer containing an average chemical repeat defined in such a manner that it contains one vinyl phenol unit, as illustrated below:

$$\left[\!\!\begin{array}{c} CH_2-CH \\ \\ \bigcirc \\ \\ OH \end{array}\!\!\right]_1 \left[\!\!\begin{array}{c} CH_2-CH \\ \\ \bigcirc \end{array}\!\!\right]_x$$

The value of χ is determined by the interplay of two factors (equation (2)): the magnitude of the reference volume, V_B, which increases with the concentration of the inert diluent in the copolymer, and the difference between the solubility parameters ($\Delta\delta$) of PVBE (δ_A) and the STVPh copolymer (δ_B). The solubility parameters of the STVPh copolymers change with copolymer composition and are estimated from the corresponding values of the pure polymers[4] (PVPh = 22.5 and PS = 19.4 (kJ dm^{-3})$^{0.5}$ using the relationship of Scott[14]:

$$\delta_B = \delta_B^{STVPh[x]} = \Phi_{PS}\delta_{PS} + \Phi_{PVPh}\delta_{PVPh}$$

In the particular case of PVBE–STVPh blends the two factors tend to offset one another and χ remains essentially constant up to a concentration of about 60% styrene in the STVPh copolymer. At greater concentrations of styrene, the magnitude χ increases in an exponential fashion[15].

On the other hand, the contribution from the $\Delta G_H/RT$ term is a function of (a) the magnitude of the equilibrium constants describing self-association and inter-association and (b) the ratio of the molar volumes of the respective polymer chemical repeating units, $r = V_A/V_B$. As discussed previously, if the values of the equilibrium constants for the pure PVPh–PVBE blend system are known (*Table 1*), it is simple to calculate the corresponding equilibrium constant values for the STVPh–PVBE blends from the ratio of the molar volumes of the PVPh and STVPh chemical repeats for a specific STVPh[x]–PVBE blend[15]. The magnitudes of K_2 and K_B vary with the composition of the STVPh copolymer, but the ratio of these two equilibrium constants to K_A is theoretically predicted to be constant[1]. This is because all the equilibrium constants are defined in terms of chemical repeat units and are related to the equivalent equilibrium constants in terms of the self-associating interacting unit used to define the lattice cell size[1,3]. The adjustment for the different size of the chemical repeat units enters through the factor $r = V_A/V_B$. Since the molar volume of PVBE is constant, it follows that as the molar volume of the STVPh repeat increases with increasing styrene content in the copolymer, the value of r decreases. This is favourable to mixing[1,5,15].

Dilution of PVPh with styrene affects both self-association and inter-association and although the concentration of phenolic hydroxyl sites are reduced by dilution with the styrene comonomer, the absolute magnitude of the $\Delta G_H/RT$ term (equation (1)) increases. Since we wish to compare the free energy of mixing blends of comparable molecular weight we must also adjust the values of N_A and N_B in the STVPh blends to reflect the increased molar volume of the average repeat of the STVPh copolymer, which we use to define a reference volume. This we do by multiplying N_A and N_B by the factor $V_B^{PVPh}/V_B^{STVPh[x]}$.

Figure 5, which is in the same form as *Figure 4*, shows the corresponding 'miscibility window' calculated for hypothetical M-co-VME blends with STVPh copolymers containing 25, 50 and 75 wt% styrene. For convenience,
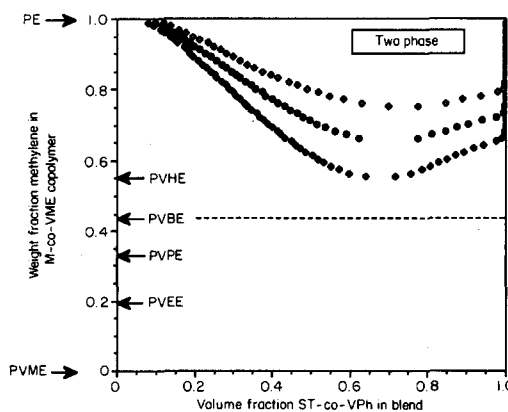

Figure 5 'Miscibility window' for STVPh blends with hypothetical M–co–VME copolymers at 25°C. ◆, STVPh[75]; ●, STVPh[50]; ◇, STVPh[25]

we have designated the three STVPh copolymers as 'homopolymers' having the parameters shown in *Table 2*, since we consider random copolymers to be equivalent to homopolymers having an average chemical repeat of the type illustrated above. As we dilute PVPh with styrene, the single-phase region ('miscibility window') increases and PVBE is predicted to be miscible with all three hypothetical STVPh copolymers. It is important to recognize that the calculations show that there is a limit to this trend—at about 80% styrene the trend reverses and the two-phase region starts to increase again. At ≈90% styrene PVBE is once again predicted to be immiscible and at ≈95% styrene blends with all poly(vinyl alkyl ethers) are predicted immiscible.

As a crude test of the above concept we synthesized a copolymer by free radical polymerization of styrene and p-tert-butoxycarbonyloxystyrene[16]. From [1]H n.m.r. analysis it was determined that the copolymer contained approximately 52 mol% styrene. Subsequent hydrolysis of the t-BOC group yielded a STVPh copolymer containing about 48 wt% styrene.

Figure 6B shows the i.r. spectrum of the pure STVPh[48] copolymer in the hydroxyl stretching region from 3100 to 3700 cm⁻¹. Comparison of this spectrum with that of pure PVPh (*Figure 2a*), makes the effect of dilution by the styrene comonomer on the magnitude of the equilibrium constants describing self-association (*Table 2*) immediately apparent. The fraction of 'free' phenolic hydroxyls (3525 cm⁻¹) increases at the expense of those that are hydrogen-bonded. In addition, the number average length of the hydrogen-bonded phenolic 'chains' decreases which is partially responsible for the shift in the peak frequency of the broad hydrogen-bonded band from 3360 to 3410 cm⁻¹. *Figure 6B* shows the corresponding i.r. spectrum of a 20:80 STVPh[48]–PVBE blend. Comparing *Figure 2B* and *Figure 6B*, it is immediately apparent that unlike the PVPh–PVBE sample, significant molecular mixing has occurred between the STVPh[48] copolymer and PVBE (note the major component at 3325 cm⁻¹ attributed to the phenolic hydroxyl–ether oxygen interaction). This agrees with our theoretical predictions and is very encouraging, but it is only considered a preliminary result. It does, however,
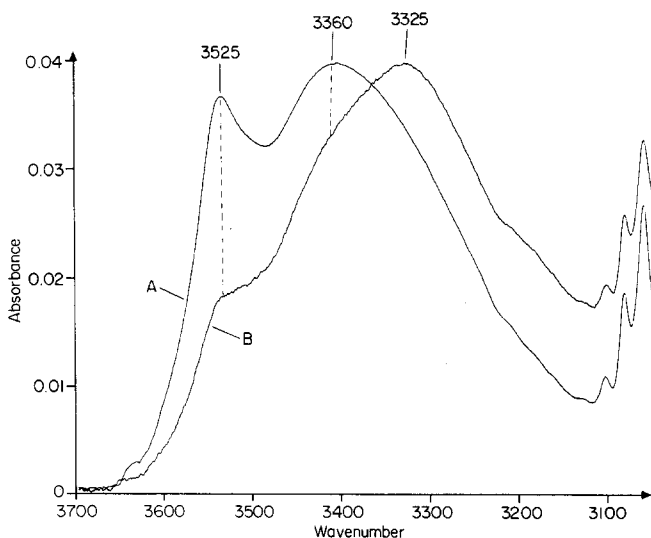

Figure 6 *FT*i.r. spectra in the hydroxyl stretching region from 3100 to 3700 cm⁻¹: A, pure STVPh[48]; B, 20:80 wt% blend of STVPh[48] and PVBE

point the way to more rigorous testing of our model. We have embarked on a programme to synthesize well characterized copolymers of vinyl phenol to test the predictions exemplified by the calculations presented in *Figure 5*.

SPINODAL CALCULATIONS—PVPh BLENDS WITH POLY(ALKYL ETHERS)

Theoretical spinodal phase diagrams, similar to those shown in *Figure 3*, were calculated from −100 to 250°C for PVPh blends with a hypothetical homologous series of linear aliphatic amorphous polyethers starting with poly(methylene oxide) (PMO) and then systematically adding methylene groups to form PEO, poly(trimethylene oxide) (PTMO), PTHF, poly(pentamethylene oxide) (PPeMO), poly(hexamethylene oxide) (PHxMO), poly(heptamethylene oxide) (PHpMO) and poly(octamethylene oxide) (POMO). For the first four polymers in the series, PMO to PTHF, no spinodal information was calculated implying that blends with PVPh were theoretically miscible throughout the entire temperature range considered. For blends of PVPh with PPeMO (five CH_2 groups) (*Figure 7a*), a small two-phase region is calculated for blends very rich in PVPh at temperatures exceeding 150°C. This two-phase region expands for the corresponding PHxMO (six CH_2 groups) (*Figure 7b*) and the lower critical solution temperature (LCST) reduces to about 80°C. These phase diagrams are similar to those calculated above for the PVEE and PVPE blends (*Figure 3a,b*) and reflects a similar polar:non-polar ratio of the respective chemical repeats. For PHpMO (seven CH_2 groups) (*Figure 7c*) there is a further expansion of the two-phase region, a further reduction of the LCST to about 50°C and the appearance of a second low-temperature two-phase region with an upper critical solution temperature (UCST) of about −70°C. Finally, in the case of PVPh blends with POMO (eight CH_2 groups) (*Figure 7d*) the two-phase regions merge to form the classic hourglass-shaped phase diagram typical of immiscible polymer blends. Again, further addition of CH_2 groups to the repeat just serves to enlarge the two-phase region. In summary, assuming equilibrium conditions, the results of these calculations indicate that PVPh blends should be miscible with linear aliphatic polyethers containing approximately 1–7 methylene groups in the chemical repeat in the amorphous state at ambient temperature.

Figure 8 shows the 'miscibility window' calculated for PVPh blends with hypothetical methylene-co-methylene oxide (M-co-MO) copolymers containing different concentrations of methylene ranging from 0% (PMO) to 100% (polyethylene). Again it follows that specific concentrations of methylene in the 'copolymer' correspond to the 'homopolymers' PEO, PPrO, PTHF, PHMO, POMO etc. In this case blends of PVPh with M-co-MO polymers containing more than about 70 wt% of methylene (roughly corresponding to PHpMO) are predicted to be immiscible. Experimentally, poly(alkyl ethers) containing up to four methylene groups (PTHF) are known to be miscible with PVPh, which agrees with the results of our calculations. Whether or not we have accurately predicted the maximum number of CH_2 groups that can be tolerated in miscible blends with PVPh will have to wait for the synthesis and availability of the relevant poly(alkyl ethers).
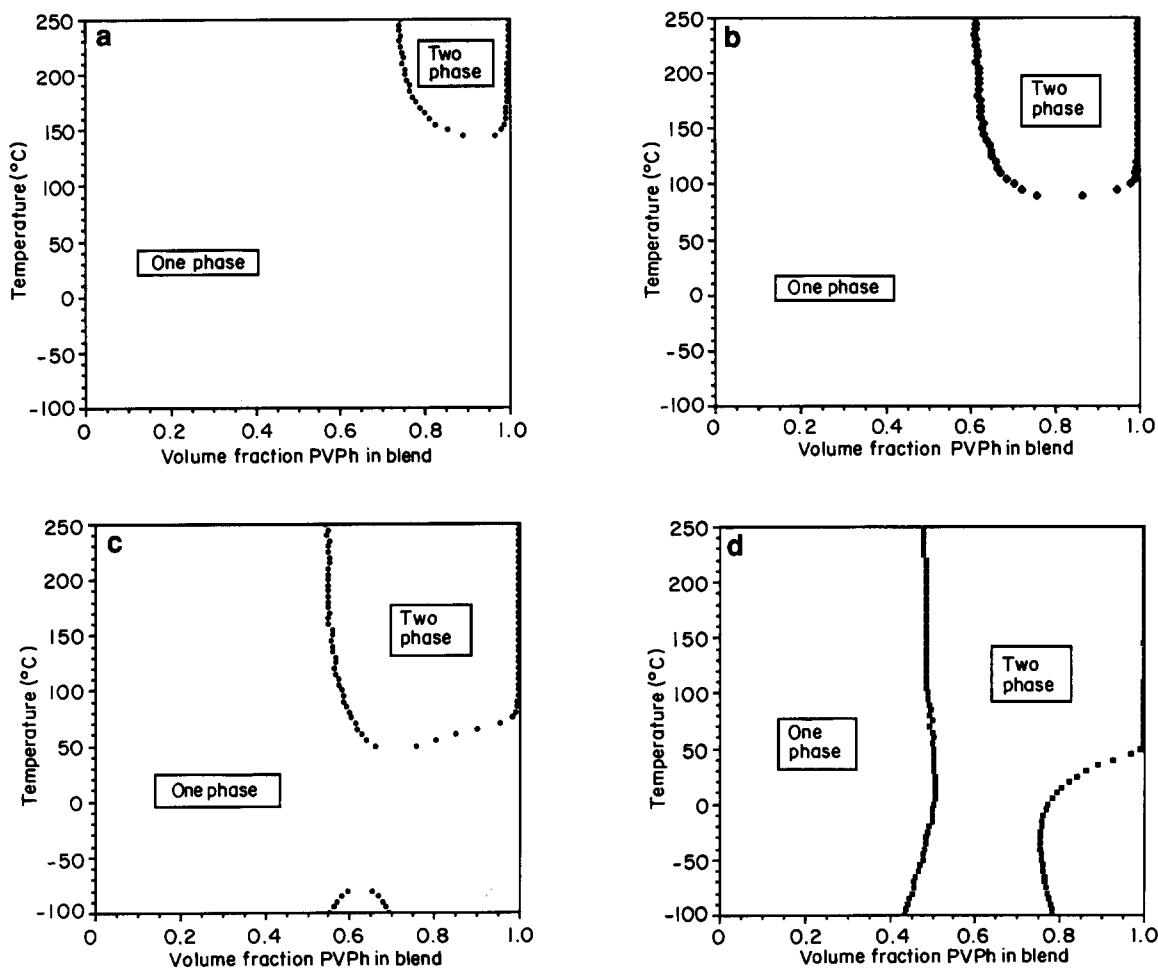
Figure 7 Calculated spinodal phase diagrams for PVPh blends with (a) PPeMO; (b) PHxMO; (c) PHpMO; (d) POMO
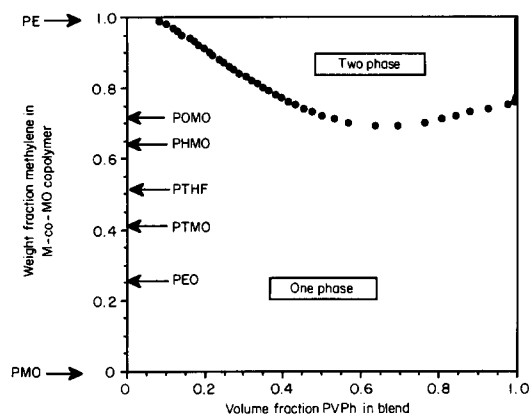

Figure 8 'Miscibility window' for PVPh blends with hypothetical M–co–MO copolymers at 25°C

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REFERENCES

1 Painter, P. C., Park, Y. and Coleman, M. M. *Macromolecules* 1989, **22**, 570
2 Painter, P. C., Park, Y. and Coleman, M. M. *Macromolecules* 1989, **22**, 580
3 Painter, P. C., Graf, J. and Coleman, M. M. *J. Chem. Phys.* 1990, **92**, 6166
4 Coleman, M. M., Serman, C. J., Bhagwagar, D. E. and Painter, P. C. *Polymer* 1990, **31**, 1187
5 Coleman, M. M., Lichkus, A. M. and Painter, P. C. *Macromolecules* 1989, **22**, 586
6 Coleman, M. M., Hu, J., Park, Y. and Painter, P. C. *Polymer* 1988, **29**, 1659
7 Coleman, M. M., Lee, J. Y., Serman, C. J., Wang, Z. and Painter, P. C. *Polymer* 1989, **30**, 1298
8 Skrovanek, D. J., Howe, S. E., Painter, P.C. and Coleman, M. M.*Macromolecules* 1985, **18**, 1676
9 Whetsel, K. B. and Lady, J. H. 'Spectrometry of Fuels', (Ed. H. Friedle), Plenum, London, 1970
10 Serman, C. J. Ph.D. Thesis, The Pennsylvania State University, 1989
11 Moskala, E. J., Varnell, D. F. and Coleman, M. M. *Polymer* 1985, **26**, 228
12 Coleman, M. M. and Painter, P. C. *Appl. Spectrosc. Revs.* 1984, **20** (3 & 4), 255
13 Powell, D. L. and West, R. *Spectrochim. Acta* 1964, **20**, 983
14 Scott, R. L. *J. Polymer Sci.* 1952, **9**, 423
15 Serman, C. J., Xu, Y., Painter, P. C. and Coleman, M. M. *Macromolecules* 1989, **22**, 2015
16 Frechet, J. M. J., Eichler, E., Ito, H. and Willson, C. G. *Polymer*