Miscible polyacetal–poly(vinyl phenol) blends: 1. Predictions based on low molecular weight analogs

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A chemical analog of poly(vinyl phenol) mixes exothermically with analogs of polyacetal and poly(ethylene oxide), suggesting miscibility in the case of blends of poly(vinyl phenol) with polyacetal and with poly(ethylene oxide). The interaction parameter corresponding to the poly(vinyl phenol) and the poly(ethylene oxide) analog mixtures agrees well with an interaction parameter reported for the polymer mixtures, which was based on the melting point depression of poly(ethylene oxide) in blends with poly(vinyl phenol). *FT*i.r. spectroscopy indicates the presence of strong hydrogen bonding between phenol and ether groups in these analog mixtures. Application of the binary interaction model predicts that a rather wide range of styrene–vinyl phenol copolymers would exhibit miscibility with polyacetal.

(Keywords: polyacetal; poly(vinyl phenol); blends; miscibility)

INTRODUCTION

Since the combinatorial entropy of mixing high molecular weight polymers is small, miscibility between high molecular weight polymers usually requires exothermic mixing[1]. Direct measurements of the heat of mixing of polymers are generally not practical[1,2]. However, Paul and Barlow[1] and Walsh and Rostami[2] have shown that the heats of mixing of low molecular weight model compounds are closely related to the heat effect on mixing polymers that contain the same functional groups. Paul and Barlow[3] have used the interaction parameters derived from low molecular weight chemical analogs in a binary interaction model to predict heat effects in the corresponding polymer blends.

Analog calorimetry and the binary interaction model have been primarily applied to blends where interactions are not very strong or directionally specific. When hydrogen bonding or electron donor–acceptor interactions exist, mixing thermodynamics may not be well described by a mean-field approach that considers only enthalpic contributions. Such interactions undoubtedly create excess entropic effects. It is also questionable whether strong interactions in analog mixtures are quantitatively similar to those in polymer blends. A recent study of blends of PMMA with copolymers of styrene and acrylic acid identified differences in the degree of hydrogen bonding among analogs and polymers[4,5].

Two approaches are available to represent the thermodynamics of strongly interacting blends. Coleman and Painter have developed an association model for blends of polymers that hydrogen-bond[6–8]. Sanchez and Balasz[9] have incorporated directionally specific interactions into a compressible lattice model[9]. Both models recognize entropic, as well as enthalpic, effects.

We are interested in defining the capabilities of analog calorimetry and the binary interaction model for predicting the phase behaviour of blends that exhibit strong interactions. The poly(vinyl phenol)–polyacetal system has been chosen as a test case.

Qin *et al.*[10] recently reported miscibility in blends containing PVP and another polyether, PEO. Analysis of melting point depression indicated a large exothermic interaction. *FT*i.r. identified a high level of hydrogen bonding as the driving force for miscibility.

As the first member of the polyether family, polyacetal contains the highest fraction of electron donor sites, and has the potential to interact strongly with PVP. However, polyacetal is highly crystalline, has a high melting point, and is resistant to most solvents. This suggests a high degree of self-association, which must be overcome to form miscible blends. No miscible blends involving polyacetal have been reported. In contrast, PVP is miscible with a variety of oxygen-containing polymers[11]. In copolymers with styrene only a small percentage of vinyl phenol groups are required to achieve miscibility[12] with, for example, PMMA.

In this paper, analog calorimetry and the binary interaction model have been applied to predict miscibility between polyacetal and PVP, and between polyacetal and copolymers of styrene and vinyl phenol. The approach of Coleman and Painter is also used to model polyacetal–PVP. Interaction parameters derived from analog heats and reported from melting point depression analysis in polymer blends are compared for the PEO–PVP system. *FT*i.r. spectroscopy of the analog solutions indicates the presence of strong hydrogen bonding between phenol and ether analogs.

In the second paper of this series, experimental evidence of miscibility between polyacetal and PVP will be presented based on thermomechanical properties of blends, and interaction parameters derived from polymers will be compared with those derived from their analogs. The third paper of this series will discuss blends of polyacetal with a copolymer of styrene and vinyl phenol.

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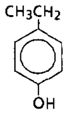
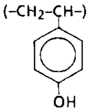
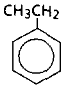
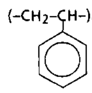
Table 1 Analog and polymer structures

Analog	Structure	Polymer	Structure
4-Ethylphenol 4EP		Poly(vinyl phenol) PVP	
Dimethoxymethane DMM	$CH_3\text{-}O\text{-}CH_2\text{-}O\text{-}CH_3$	Polyacetal PAc	$(\text{-}CH_2\text{-}O\text{-})_n$
Ethylbenzene EB		Polystyrene PS	
Ethyleneglycoldimethylether EGDME	$CH_3\text{-}O\text{-}CH_2CH_2\text{-}O\text{-}CH_3$	Poly(ethylene oxide) PEO	$(\text{-}CH_2\text{-}CH_2\text{-}O\text{-})_n$
Tetraethyleneglycoldimethylether TEGDME	$CH_3\text{-}O\text{-}(CH_2\text{-}CH_2\text{-}O)_4CH_3$	Poly(ethylene oxide) PEO	$(\text{-}CH_2\text{-}CH_2\text{-}O\text{-})_n$

EXPERIMENTAL

Calorimetry

The analogs used were obtained from Aldrich and are given in *Table 1*. All chemicals were used as received. Heats of mixing at 25°C for each system at several compositions were measured in a flow calorimeter from Hart Scientific.

Dimethoxymethane and ethyl benzene are both liquids at room temperature and heats of mixing were measured directly. The heats were fitted to the van Laar expression to generate binary interaction parameters

$$\Delta H/V = B_{12}\phi_1\phi_2 \qquad (1)$$

where ϕ_1 and ϕ_2 are volume fractions.

Since 4-ethyl phenol (4EP) is a solid at room temperature, highly concentrated solutions of 4EP in the other analogs were prepared. The heats of mixing these solutions against the pure liquid second analog were measured. From these dilution experiments an apparent interaction parameter was calculated:

$$B_{\text{app}} = \Delta H/(V\phi_A\phi_B) \qquad (2)$$

where solution B comprises analog 1 in analog 2 at composition ϕ_1. Solution A is pure analog 2. By assuming a parabolic shape to the heat of mixing curve B_{12} is calculated from B_{app}

$$B_{12} = B_{\text{app}}/\phi_1^2 \qquad (3)$$

The B_{12} values are given in *Table 2*. The heats of mixing are represented as a function of volume fraction in *Figure 1*.

FT*i.r. spectroscopy*

Solutions of 4EP in CCl_4 at the concentrations of 0.01 M, 0.1 M and 1 M were prepared for i.r. measurements to study the free OH stretching frequency. The hydrogen bond interactions between 4EP and the analogs of polyacetal and PEO, DMM and TEGDME, were investigated by taking the i.r. spectra of the 4EP–ether mixtures in CCl_4. To ensure that the hydrogen bonding between 4EP and DMM (or TEGDME) is the dominant intermolecular interaction in the 4EP–ether mixtures, 0.01 M was selected as the concentration for 4EP. The concentrations of the ethers in the mixtures were 0.1 M, 0.5 M and 1 M. The i.r. spectra of DMM and TEGDME were measured in CCl_4 at the concentrations of 0.1 M and 1 M to locate the overtone/combination bands of these ethers in the 3700–3000 cm^{-1} region. Identification of these overtone/combination bands allows unambiguous assignment of the hydrogen-bonded OH bands.

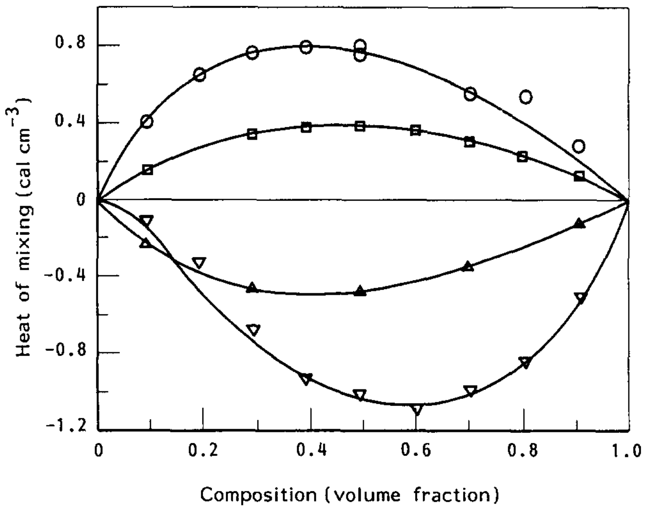


Figure 1 Heats of mixing of analogs as functions of volume fraction of component listed first: □, DMM versus EB; ○, 70 wt% 4EP in EB versus EB; ▽, 64% 4EP in EGDME versus EGDME; △, 50% 4EP in DMM versus DMM

The i.r. spectra were obtained on a Nicolet 20DXB *FT*i.r. spectrometer with a spectral resolution of 2 cm^{-1} and 100 scans co-addition. The path length of the i.r. cell is 0.5 mm for all spectra with the exception of 1 M 4EP, for which a 0.025 mm fixed-path cell was used.

RESULTS AND DISCUSSION

Analog calorimetry

The enthalpy of mixing versus composition curve, shown in *Figure 1*, exhibits an approximately parabolic shape, as required by the van Laar treatment. The maximum in the EGDME–4EP curve is shifted from the midpoint composition. For this system, the B_{12} values calculated from equation (3) exhibit a slight concentration dependence. The average value is reported in *Table 2*.

The endothermic heats for DMM–EB and 4EP–EB indicate that blends of PS with PAc and with PVP would be immiscible. The B_{12} value characterizing the interaction between EB and 4EP is rather large and positive. This suggests that miscibility windows in blends involving

Table 2 Interaction parameters

Analog 1	Analog 2	Polymer pair	B_{12} (cal cm^{-3})^c	$\Delta\nu_{OH}$ (cm^{-1})	$\Delta H_{\text{H-bond}}$ (kcal mol^{-1})
4EP	DMM	PVP–PAc	−7.6	221	5.34
4EP	EB	PVP–PS	6.9		
DMM	EB	PAc–PS	1.5		
4EP	EGDME	PVP–PEO	−10.0		
4EP	TEGDME	PVP–PEO		249	5.64
4EP^a	–	PVP–PVP		135	4.47
4EP^b	–	PVP–PVP		279	5.93

^{a}Self-associated through dimers
^{b}Self-associated through multimers
^{c}One thermochemical calorie equals 4.184 J

styrene–vinyl phenol random copolymers arise in part from the unfavourable interaction between these monomer units.

The large exothermic heats between 4EP and the two ethers (DMM and EGDME) suggest a strong driving force for miscibility between PVP and both PAc and PEO. *FT*i.r. spectroscopy, as described below, identifies hydrogen bonds between the phenolic hydroxyl group of PVP and the ether oxygens of PAc and PEO as the origin of this favourable interaction. However, the B_{12} values are not entirely determined by the extent of hydrogen bonding between the ethers and phenol. Mixing involves a change from two pure components to a homogeneous combination of the two. The enthalpy change reflects the difference in enthalpy of the mixture from the average of the two components. Therefore, the strength of interaction in the mix must be viewed relative to the interactions between the like molecules that it replaces.

The B_{12} values can be converted to Flory–Huggins χ interaction parameters if a reference volume is assumed:

$$\chi_{12} = B_{12}V_{\text{ref}}/(RT) \qquad (4)$$

To maintain consistency with the χ parameter reported previously for PEO–PVP, V_{ref} is set equal to the repeat unit molar volume of PVP (100.0 cm^3)[10]. For PVP–PAc we estimate χ values of −1.3 and −0.9 at 25 and 170°C, respectively. The latter temperature is approximately the melting point of polyacetal. For PVP–PEO we calculate χ values of −1.7 and −1.4 at 25 and 60°C, respectively. Belfiore reports $\chi = -1.5$ based on analysis of the melting point depression of PEO in blends with PVP over the range 70 to 50°C. This is in excellent agreement with the χ value that was derived from the analog heats.

FT*i.r. spectroscopy*

Figure 2 shows the i.r. spectra of 4EP in CCl$_4$ at various concentrations. The stretching frequency of the free OH group at 3614 cm^{-1} is in good agreement with the previously reported spectral range for phenols[13]. No self-association is observed for the 0.01 M solution. The broad band near 3480 cm^{-1} in the spectrum of the 0.1 M solution suggests the presence of the dimeric 4EP formed through hydrogen bonding[13,14]. Further self-association occurs in the more concentrated solution of 1 M, as indicated by the very broad i.r. band near 3335 cm^{-1}.

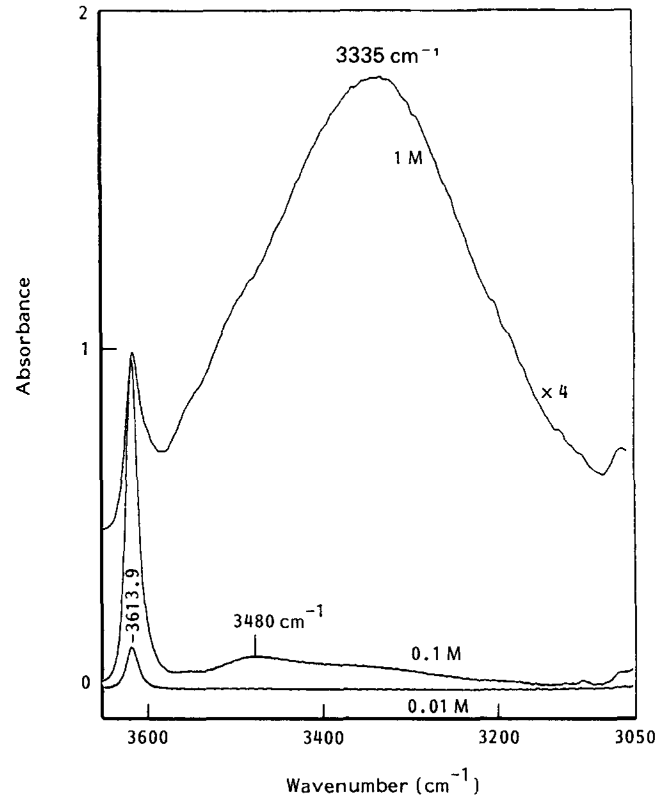


Figure 2 The *FT*i.r. spectra of 4-ethyl phenol in carbon tetrachloride. The spectra of the 0.01 M and 0.1 M solutions were measured in a 0.5 mm fixed-path cell while the spectrum of the 1 M solution was measured in a 0.025 mm fixed-path cell. A 4× multiplication was applied to the 1 M spectrum before plotting

Figure 3 illustrates the i.r. spectra of 4EP–DMM mixtures. The broad band near 3393 cm^{-1} can be reasonably attributed to the hydrogen-bonded OH absorption since it is not observed in the spectrum of 0.01 M 4EP solution and is very weak in the spectrum of 1 M DMM solution. The intensity of this hydrogen-bonded band increases at the expense of the free OH intensity as the DMM concentration increases.

Similar results are found for 4EP–TEGDME mixtures (*Figure 4*) for which the hydrogen-bonded OH band occurs near 3365 cm^{-1}. However, the intensity of the free OH band decreases at a much faster rate with the ether concentration for TEGDME than for DMM. This is probably due to the fact that there are more basic sites per molecule in TEGDME than in DMM. In addition, Drago *et al.*[15,16] have demonstrated that the hydrogen-bond dissociation energy can be estimated from the frequency shift of the OH stretching from the free OH frequency by the correlation

$$-\Delta H\ (\text{kcal/mol}) = 0.0103\Delta\nu_{OH}\ (\text{cm}^{-1}) + 3.08$$

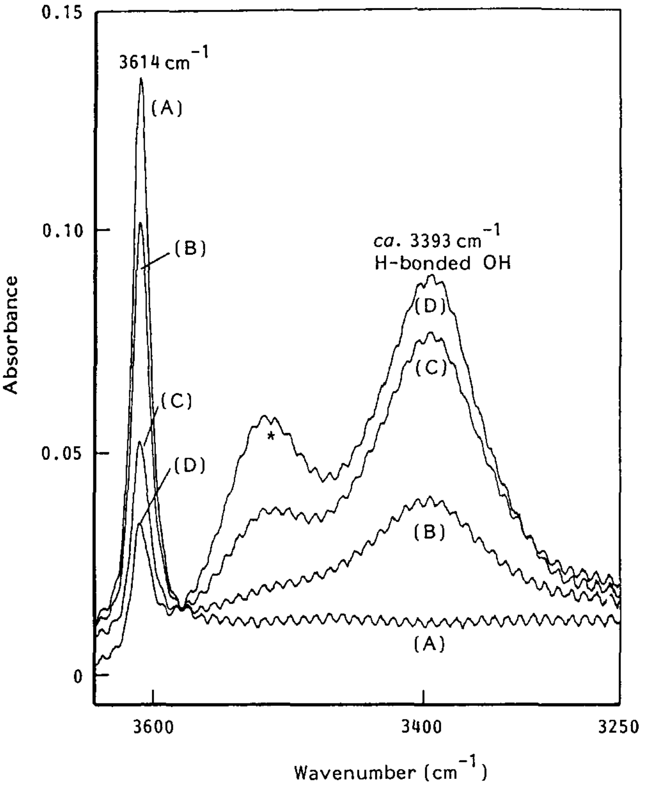


Figure 3 The *FT*i.r. spectra of 0.01 M 4EP–DMM mixtures in carbon tetrachloride. The concentration of 4EP is 0.01 M for all mixtures: (A) No DMM; (B) 0.1 M DMM; (C) 0.5 M DMM; (D) 1 M DMM; asterisk indicates i.r. band due to DMM

Table 2 summarizes the frequency shifts and the hydrogen bond dissociation energies for 4EP–DMM and 4EP–TEGDME systems, and for 4EP self association. The ΔH values calculated from the above equation appear to agree with the literature values for similar systems[14].

Application of the binary interaction model

The heat of mixing of a premixed solution of analogs 1 and 2 with analog 3 simulates the enthalpic effect in mixing a random copolymer with a homopolymer[17]. The heats in such a ternary system can often be estimated from a binary interaction model:

$$B = B_{13}\phi_1 + B_{23}\phi_2 - B_{12}\phi_1\phi_2 \qquad (5)$$

where B is the observed heat effect in mixing the solution and ϕ_1 and ϕ_2 represent the compositions of the premix.

Blends of styrene–vinyl phenol copolymers with PAc can be modelled by using the B_{ij} values listed in *Table 2*. For VP ($i = 1$), S ($i = 2$) and Ac ($i = 3$) the interaction parameters are $B_{12} = 6.9$, $B_{13} = -7.6$, and $B_{23} = 1.5$ cal cm^{-3}. Analysis using equation (5) shows that vinyl phenol levels of 10 vol% or greater in a copolymer with styrene produce net exothermic mixing ($B < 0$) in blends with polyacetal. Thus, on this basis, one would anticipate miscibility between polyacetal and styrene–vinyl phenol copolymers that contain at least 10 vol% vinyl phenol.

The model predicts that miscibility is driven by the combination of a strong favourable interaction between acetal and vinyl phenol units, a relatively weak unfavourable interaction between acetal and styrene units, and a strong unfavourable interaction between vinyl phenol and styrene units.

To test the applicability of equation (5) to hydrogen-bonding systems, we measured the heats of mixing dilute solutions of 4EP in EB against DMM. A 4% solution of 4EP in EB mixes exothermically to form DMM-poor mixtures and endothermically to form DMM-rich mixtures, as shown in *Figure 5*. Such 'S'-shaped heat-of-mixing curves are uncommon and characteristic of two types of systems. The first are mixtures near the critical point of one or both components. Examples are carbon dioxide with decane and dimethylacetamide with dichlorodifluoromethane[18].

The second class are mixtures of a component that

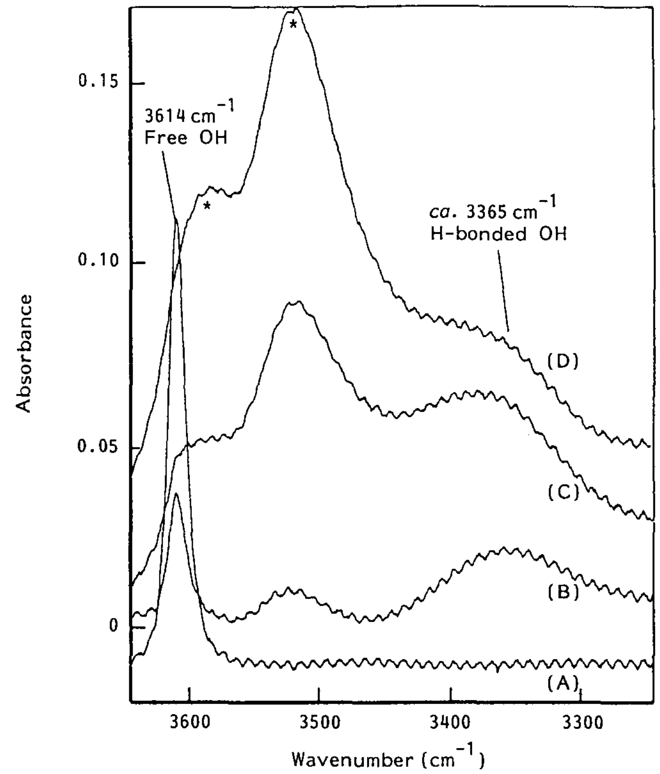


Figure 4 The *FT*i.r. spectra of 0.01 M 4EP–TEGDME mixtures in carbon tetrachloride. The concentration of 4EP is 0.01 M in all mixtures: (A) No TEGDME; (B) 0.1 M TEGDME; (C) 0.5 M TEGDME; (D) 1 M TEGDME; asterisk indicates i.r. band due to TEGDME

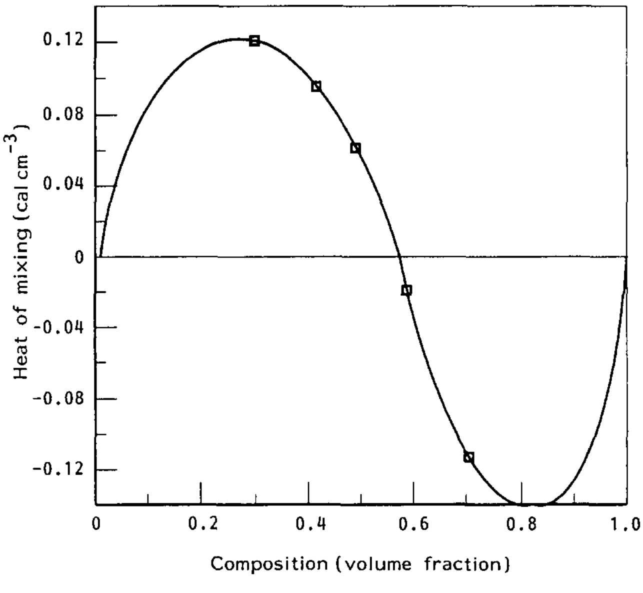


Figure 5 Heat of mixing of 4% 4EP in EB versus DMM as function of volume fraction of the 4EP–EB solution

self-associates in the pure state and a component that does not self-associate, but specifically interacts with the first component. The heat of mixing arises from three contributions: (1) dispersive forces, which are endothermic; (2) the loss of self-association through dilution, which is endothermic; and (3) the specific interaction between dissimilar molecules, which is exothermic. If only the dispersive contribution is parabolic then the three terms can combine to produce exothermic mixing at high concentrations of the self-associating component and endothermic mixing at low concentrations of the self-associating component. Examples of such systems are ketones mixed with benzene or carbon tetrachloride[19], esters mixed with chlorinated solvents[20], and *N*-ethylurethane mixed with TEGDME.

Since the binary interaction model assumes all heats of mixing are parabolic, it cannot predict 'S'-shaped behaviour. In this case, the binary interaction model slightly overestimates the amount of phenol needed to produce exothermic mixing, consistent with results on similar systems measured in our laboratory. The model, therefore, provides a conservative basis from which to predict the phase behaviour of homopolymer and copolymer blends.

Application of the Coleman and Painter approach

Coleman and Painter recently proposed an association model to represent the phase behaviour of polymer blends where one polymer self-associates and the second polymer associates with the first[6,8]. Unlike the binary interaction model, this approach explicitly considers both enthalpic and excess entropic contributions to the excess Gibbs energy. Coleman and Painter have applied this model successfully to blends of PVP and polymers containing ester groups[21,22]. This model should apply as well to blends of PVP with polyethers. However, the requisite equilibrium constant and enthalpy to characterize the hydrogen bonding between polyethers and PVP are unavailable.

Recently Coleman and Painter presented a simplified approach to screen for miscible blends, which embodies the main effects in their rigorous model[23]. The unfavourable dispersive contribution to mixing is estimated from non-hydrogen-bonding solubility parameters. This is compared to the expected favourable contribution characteristic for a given class of specific interaction. From group contributions the estimated solubility parameters for PAc and PVP are 10.5 and 11.0, respectively. The estimated solubility parameter for PAc falls within the range of values reported in the literature[24]. Strong hydrogen bonding should readily overcome this relatively small difference in solubility parameters. Therefore, this approach predicts miscibility between PAc and PVP.

CONCLUSIONS

Low molecular weight analogs of polyacetal and poly(vinyl phenol) exhibit large exothermic heats of mixing. *F*Ti.r. spectroscopy indicates that this specific interaction arises from hydrogen bonding between the ether oxygens and the hydroxyl group of the phenol. These results suggest a strong thermodynamic driving force for polyacetal and poly(vinyl phenol) to form miscible blends.

Low molecular weight analogs of PEO and PVP also show large exothermic heats of mixing. This is consistent with the reported miscibility of PEO–PVP blends. A χ parameter estimated from the analog heats is in excellent agreement with a χ value derived from analysis of melting point depression in the blends.

Application of the binary interaction model of Paul predicts that copolymers of styrene and vinyl phenol containing approximately 10% vinyl phenol units will be thermodynamically miscible with polyacetal. The binary interaction parameters are derived from the heat-of-mixing measurements. This approach slightly overestimates the amount of phenol needed to produce exothermic mixing of analog solutions.

Analysis using the recently proposed approach of Coleman and Painter also predicts a strong driving force for miscibility between PAc and PVP.

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