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Self-association *versus* interassociation in hydrogen bonded polymer blends:
1. Determination of equilibrium constants from miscible poly(2,6-dialkyl-4-vinyl phenol) blends

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Equilibrium constants that describe the self-association of poly(2,6-dimethyl-4-vinyl phenol) and poly(2,6-diisopropyl-4-vinyl phenol) together with their interassociation to complimentary (co)polymers that contain carbonyl moeties, such as methacrylates and acetoxy groups, have been determined from i.r. studies of miscible polymer blend systems containing poly(n-butyl methacrylate) and an ethylene-*co*-vinyl acetate copolymer. A comparison of these equilibrium constant values with those previously determined for analogous poly(4-vinyl phenol) (PVPh) blends reveals that interassociation is accentuated over self-association in the case of the partially hindered poly(2,6-dialkyl-4-vinyl phenol)s. This is a favourable trend for polymer blend miscibility. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polymer blends; hydrogen bonding; equilibrium constants)

INTRODUCTION

As we have previously discussed in a series of papers published over the past decade, a digest of which is presented in our 1991 monograph[1] and recent review article[2], the free energy of mixing two high molar mass (co)polymers that contain functional groups attached to the polymers capable of forming specific interactions may be expressed by the following equation:

$$\frac{\Delta G_m}{RT} = \left\{\frac{\Phi_A}{M_A}\ln\Phi_A + \frac{\Phi_B}{M_B}\ln\Phi_B\right\} + \Phi_A\Phi_B\chi + \frac{\Delta G_H}{RT} \qquad (1)$$

where Φ_A and Φ_B, and M_A and M_B, are the volume fractions and degrees of polymerization of polymers A and B, respectively. For high molar mass (co)polymers the contribution from combinatorial entropy (the first two bracketed terms) is very small and the free energy of mixing can be viewed simply as a balance between two major opposing contributions to the free energy mixing (the last two terms of equation (1)), which we refer to as 'weak' (or 'physical') and 'strong' (or 'chemical') forces. The former is unfavourable to mixing and is expressed in terms of a Flory χ parameter which we estimate from non-hydrogen bonding solubility parameters, calculated from group contributions[1]. The latter, the 'chemical' contribution in equation (1), which is denoted by $\Delta G_H/RT$ and calculated from spectroscopically determined equilibrium constants and enthalpies of hydrogen bond formation, is generally favourable to mixing and arises from the change in the distribution of hydrogen bonds found in the mixture compared to the pure components. It is important to recognize that the separation of 'weak' and 'strong' forces is not just a matter of convenience—contributions to the free energy of mixing from 'weak' and 'strong' forces have very different temperature and compositional dependences, which markedly affect the shape and form of phase diagrams.

This separation of 'weak' and 'strong' forces has strategic implications for the design of miscible polymer mixtures[2]. It is obvious that the probability of obtaining a single phase binary polymer mixture increases if the unfavourable contribution from the χ term is reduced and the favourable contribution from the $\Delta G_H/RT$ term is increased. The former can be achieved by reducing the difference in the non-hydrogen bonded solubility parameters of the two co(polymers) in the blend (for example, by varying the chemical nature and composition of the copolymers and using the principle of cosolvency)[1,2]. On the other hand, the magnitude of the $\Delta G_H/RT$ term is determined by the nature and number of specific interaction sites per unit volume in the blend and the relative 'strength' of self-association and interassociation. Manipulating the balance in favour of interassociation over self-association favours miscibility and is the main focus of this paper.

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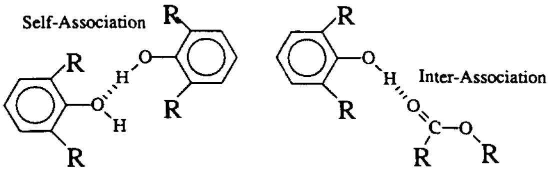
In our review article[2] and a recent paper concerned with the design of a miscible polymeric antioxidant for poly(tetrahydrofuran)[3], we introduced the concept of using 2,6-dialkyl substituted poly(4-vinyl phenol)s to maximize the relative 'strength' of interassociation over self-association by varying the degree of steric hindrance that is experienced by the phenolic hydroxyl group. To elaborate, the formation of a hydrogen bond between two phenolic hydroxyl groups (self-association) requires the close proximity of the 'interior' oxygen atom of one hydroxyl group to that of the 'exterior' hydrogen atom of another phenolic hydroxyl group in the same or another chain, as illustrated schematically in *Scheme 1*.



Scheme 1

On the other hand, the formation of a hydrogen bond between a phenolic hydroxyl group and an acceptor such as the oxygen atom of a carbonyl group (inter-association) is not quite as stringent, requiring the relatively easier approach of the carbonyl oxygen to the 'exterior' hydrogen atom of the phenolic hydroxyl group (also shown in *Scheme 1*). Viewed in simple terms, with increasing size of the R groups a point is reached where steric hindrance severely restricts the formation of a hydrogen bond, but the extent of this effect is greater for self-association than that of interassociation. Accordingly, by varying the size of the R groups it should be possible to optimize interassociation over self-association and enhance the probability of finding miscible polymer blend systems.

I.r. spectroscopy is particularly sensitive to the strength and number of hydrogen bonds formed and the affect of steric hindrance on self-association from 2,6-dialkyl substitution may be expressed both qualitatively (from the difference in frequency of the 'free' and hydrogen bonded O–H stretching vibrations) and quantitatively (from equilibrium constants determined from the fraction of hydrogen bonded hydroxyl groups as a function of concentration in inert solvents). We have previously reported such infrared spectroscopic studies of the low molecular weight model compounds, ethylphenol (EPh), 2,6-dimethylphenol (DMPh), 2,6-di-*iso*-propylphenol (DIPPh) and 2,6-di-t-butylphenol (DTBPh). Of particular relevance to the studies reported here are the equilibrium constants that describe self-association[3,4]. We employ two equilibrium constants describing the formation of hydrogen bonded hydroxyl–hydroxyl dimers (denoted K_2) and chain-like multimers (K_B)[1,2]. For EPh, DMPh and DIPPh values of K_2 and K_B from dilute cyclohexane solutions (dimensionless and all scaled to a common reference volume of 100 cm^3 mol^{-1}) were determined to be 21.0, 66.8, 6.7, 24.2 and 2.2, 5.6, respectively. Analogous equilibrium constants for DTBPh could not be determined, but, to all intent and purposes, DTBPh does not self-associate to any measurable extent and the values of the equilibrium constants are effectively zero. As expected, the above results, which we will employ later in this work, show that the self-association of the phenol model compounds decreases systematically in the order EPh > DMPh > DIPPh > DTBPh.

Corresponding equilibrium constants that describe the inter-association (K_A)of the above phenolic hydroxyls to ester carbonyl groups in *low molecular weight* model compounds have been determined from the fraction of hydrogen bonded carbonyl groups in ethyl isobutyrate (EIB) mixtures[3,5]. In a similar vein, heat of mixing studies of a number of low molecular weight substituted phenols with methyl isobutyrate have been recently reported by Teegarden and Landry[6]. For EPh, DMPh and DIPPh values of K_A (once more scaled to a common reference volume of 100 cm^3 mol^{-1}) were determined to be 172, 61.4 and 24.5, respectively. Again, we were not able to accurately measure K_A for the EIB/DTBPh mixtures, but judging from the frequency shift and the relatively small absorbance contribution from the hydrogen bonded carbonyl band in the DTBPh rich mixtures, the value of K_A is very small indeed. As we mentioned at the beginning of this Introduction, the main focus of this work is the balance between inter-association and self-association and a convenient measure of this is the ratio K_A/K_B. For EIB mixtures with EPh, DMPh and DIPPh this ratio is 2.5, 2.5 and 4.4, respectively. This is strong evidence that inter-association has been enhanced over self-association in the case of DIPPh compared to both EPh and DMPh.

It is important to emphasize that the set of equilibrium constants (K_2, K_B and K_A) obtained for the above model phenol/EIB mixtures is only applicable to low molecular weight compounds and not directly transferable to analogous polymer blends. Chain connectivity and screening effects are implicated and the interested reader is referred to refs 2 and 5 for further details. In any event, our present methodology used to calculate the 'chemical' free energy contribution from the mixing of hydrogen bonded polymer blends, $\Delta G_H/RT$, requires a set of equilibrium constants that are experimentally determined from an appropriate *miscible polymer blend.* These equilibrium constant values are then utilized in the free energy of mixing equation that we derived and is described in detail in our monograph[1]. As we now recognize[2], this free energy equation contains a semi-empirical term that corrects for chain connectivity and screening effects, etc. Notwithstanding, application of this equation has proved to be remarkably successful in predicting phase behaviour, miscibility windows and miscibility maps for hydrogen bonding polymer blends[1,2].

The major focus of the work presented in this paper is the determination of the equilibrium constants that describe the self-association of the partially hindered poly(2,6-dimethyl-4-vinyl phenol) (PDMVPh) and poly(2,6-diisopropyl-4-vinyl phenol) (PDIPVPh), and the inter-association of these phenolic polymers with complimentary (co)polymers that contain carbonyl moeities such as methacrylates and acetoxy groups. For this we will require miscible polymer blend systems. Blends of PDMVPh and PDIPVPh with poly(n-butyl methacrylate) (PBMA) and an ethylene-*co*-vinyl acetate (EVA) copolymer containing 70 wt% vinyl acetate EVA[70] are appropriate for these studies. The equilibrium constants obtained will then be compared to those previously determined for the analogous poly(4-vinyl phenol) (PVPh) blends to ascertain whether or not interassociation has been accentuated over self-association in the case of the partially hindered poly(2,6-dialkyl-4-vinyl phenol)s. In this communication we will discuss in some detail the spectroscopic methodology we have developed over the past few years, as this is crucial to obtaining accurate parameters. In the following paper we will apply these equilibrium constants to calculate miscibility windows for blends of the different phenolic polymers with a homologous series of poly(n-alkyl methacrylate)s and the entire copolymer composition range of EVA copolymers. These predicted miscibility windows are then compared to experimental data performed in our laboratories.

EXPERIMENTAL

Materials

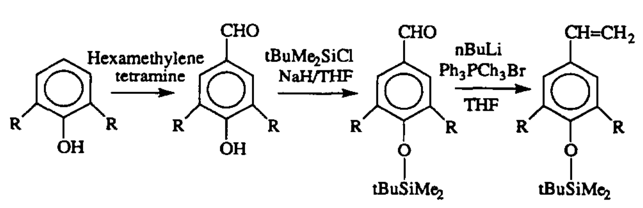
Tetrahydrofuran (THF), benzene, toluene, acetic acid, 2,2′-azoisobutyronitrile (AIBN), 2,6-dimethylphenol, 2,6-diisopropylphenol, hexamethylenetetramine, t-butyldimethylsilylchloride, methyltriphenylphosphonium bromide and tetrabutylammonium fluoride (TBAF) were all purchased from Aldrich Chemical Co. Inc., Milwaukee, WI. AIBN was recrystallized from acetone. THF and benzene were distilled, respectively, from sodium/benzophenone and calcium hydride immediately before use. All other reagents were used without further purification. All glassware was flame-dried under vacuum (0.01 mm) prior to use.

Poly(n-butyl methacrylate) (PBMA) and an ethylene-*co*-vinyl acetate copolymer containing 70 wt% vinyl acetate (EVA[70]) have been used extensively in prior blends studies with (co)polymers of 4-vinyl phenol[1,7] and were purchased from Scientific Polymer Products, Inc., Ontario These polymers are amorphous with glass transition temperatures (T_gs) of 21 and −21°C, respectively, and have reported weight average molecular weights of 100 000 and 285 000.

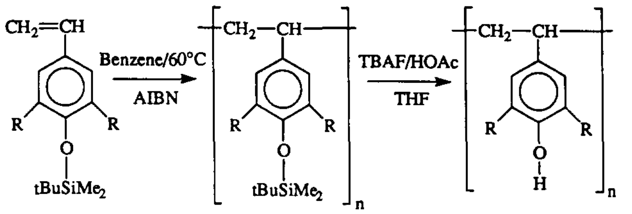
Synthesis of the phenolic monomers and polymers

The synthetic methodology used to prepare the monomers 2,6-dimethyl-4-(t-butyldimethylsilyloxy)styrene and 2,6-diisopropyl-4-(t-butyldimethylsilyloxy)styrene has been described previously[3] and only a brief summary is presented in *Scheme 2*.

Poly(2,6-dimethyl-4-(t-butyldimethylsilyloxy)styrene) and poly(2,6-diisopropyl-4-(t-butyldimethylsilyloxy)-styrene) were synthesized by free radical polymerization of the above monomers and the polymers deprotected to yield poly(2,6-dimethyl-4-vinyl phenol) (PDMVPh) and poly(2,6-diisopropyl-4-vinyl phenol) (PDIPVPh), respectively, in essentially the same manner as that described by Xu *et al.*[8] and illustrated schematically in *Scheme 3*.



Scheme 2



Scheme 3

Isolation of the PDMVPh and PDIPVPh polymers was performed by precipitation into a large excess of water followed by filtration and washing also with water. The polymers were then dissolved in THF and reprecipitated in water. This dissolution/reprecipitation cycle was repeated several more times to remove water soluble impurities formed during the deprotection step. Finally, the polymers were reprecipitated into hexane and then dried under vacuum at 80°C. G.p.c. analyses were performed on the two amorphous PDMVPh and PDIPVPh polymers before deprotection and were determined to have polystyrene equivalent weight average molecular weights of 11 800 and 12 300 g mol^{-1} with polydispersities in the range of 1.4–1.5. The T_gs of the two polymers were determined by thermal analysis to be 122 and 117°C, respectively.

Sample preparation and instrumentation

I.r. spectroscopic measurements were recorded on a Digilab model FTS60 Fourier transform infra-red (*FT*i.r.) spectrometer at a resolution of 2 cm^{-1}. Special attention was paid to ensure that all *FT*i.r. samples were sufficiently thin to be within the absorption range where the Beer–Lambert law is obeyed. Polymer blend films for transmission *FT*i.r. were cast on KBr windows from THF solution in the case of the EVA[70] blends and from 90/10 THF/toluene mixture for PBMA blends. After the majority of the solvent had evaporated, the films were placed under vacuum at room temperature for at least 24 h, followed by 2 h at 150°C, to completely remove residual solvent. ^{1}H and ^{13}C n.m.r. spectra were obtained on Bruker WP-200 and 300 MHz FT-NMR spectrometers using tetramethylsilane as an internal standard. Molecular weights and molecular weight distributions were determined using a Waters 150C gel permeation chromatograph equipped with a refractive index detector and four μStyragel columns (100 000; 10 000; 500 and 100) connected in series. Thermal analysis was conducted on a Perkin–Elmer differential scanning calorimeter (DSC-7) coupled to a computerized data station. A heating rate of 20°C min^{-1} was used and the glass transition temperatures recorded as the mid-point of the heat capacity change.

RESULTS AND DISCUSSION

A brief comparison of the infra-red spectra of PVPh, PDMVPh and PDIPVPh

Figure 1 compares the i.r. spectra of PVPh, PDMVPh and PDIPVPh recorded at room temperature in the range 500–4000 cm^{-1}. For the purposes of this study an in-depth interpretation and assignment of all the i.r. bands is not necessary and we will focus our attention on just a few salient features. Examining, in order, the spectra of PVPh, PDMVPh and PDIPVPh, we note that

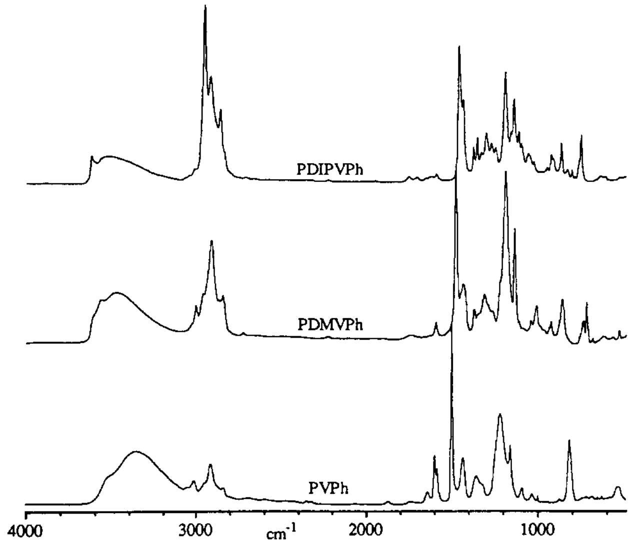


Figure 1 I.r. spectra of PVPh, PDMVPh and PDIPVPh recorded at room temperature in the region of 500–4000 cm^{-1}

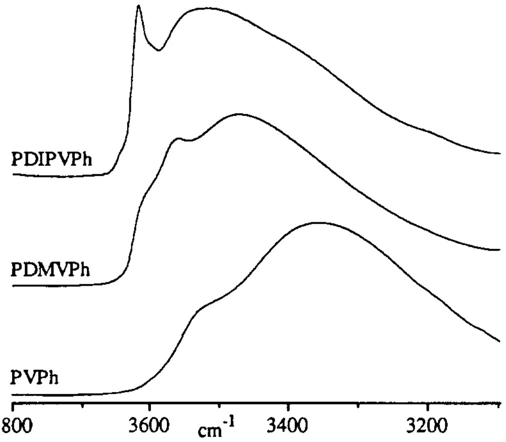


Figure 2 Scale expanded i.r. spectra of PVPh, PDMVPh and PDIPVPh recorded at room temperature in the O–H stretching region (3100–3800 cm^{-1})

the relative intensity (area) of the bands in the hydroxyl stretching region ($\approx$ 3200 – 3700 cm^{-1}) decreases significantly relative to the C–H stretching region ($\approx$ 2800 – 3100 cm^{-1}). This is, of course, consistent with the increasing number of C–H groups per repeat in the respective polymers, but it is only part of the story. The hydroxyl stretching region (3100–3800 cm^{-1}) of the three phenolic polymers is scale expanded and shown in *Figure 2*. There is a complex set of bands, composed of contributions from hydrogen bonded and 'free' (non hydrogen bonded) O–H stretching vibrations, where the individual absorptivity coefficient values can be very different depending upon the strength and geometry of the hydrogen bond[1]. Accordingly, the total area of the hydroxyl stretching region relative to that of an internal standard such as the C–H stretching region will also be seriously affected by the fraction, strength and geometry of hydrogen bonded hydroxyl groups present in the PVPh compared to PDMVPh and PDIPVPh.

The relatively sharp band observed prominently in the spectrum of PDIPVPh at $\approx$ 3610 cm^{-1} and as an obvious shoulder in the spectrum of PDMVPh, but which is barely detected in the spectrum of PVPh, is assigned to the O–H stretching vibration of non hydrogen bonded or 'free' hydroxyl groups. Qualitatively, as expected, this immediately suggests that self-association decreases in the order PVPh > PDMVPh > PDIPVPh. (We caution, however, that this can only be a qualitative observation at this stage, as the number of hydroxyl groups per unit volume is not constant for the three polymers—see below.)

The very broad band that spans the region of $\approx$ 3600 – 3100 cm^{-1} in the spectrum of PVPh and has maximum absorbance at $\approx$ 3340 cm^{-1} is assigned to O–H stretching vibrations of hydrogen bonded hydroxyl groups. The frequency difference ($\Delta\nu$) between the 'free' and hydrogen bonded bands is a rough measure of the enthalpy of formation of the hydrogen bond and qualitatively reflects the 'strength' of the specific interaction. More importantly, the breadth and complexity of this band reflects a wide distribution of hydrogen bonded hydroxyl–hydroxyl groups of different lengths and geometries that is characteristics of dimers ($\approx$ 3570 cm^{-1}) and higher multimers or 'chain-like' structures that are formed in the self-association of alcohols, phenols, and the like[1]. Turning now to the spectrum of PDMVPh, we observe that the broad hydrogen bonded band associated with 'chain-like' structures has shifted to a higher frequency, indicating that the average strength of the hydrogen bond has decreased *vis-a-vis* PVPh. Furthermore, the relative contributions from the bands attributed to hydrogen bonded dimers and 'free' hydroxyls have increased at the expense of the hydrogen bonded 'chain-like' structures. This is all qualitatively consistent with a decrease in the relative 'strength' of PDMVPh self-association compared to that of PVPh. This trend continues for PDIPVPh. Here we see a further shift to higher frequency and a much smaller contribution from hydrogen bonded bands due to 'chain-like' structures. Both the 'free' and hydrogen bonded hydroxy dimer bands are prominent. The relatively large contributions from the 'free' hydroxyl and hydrogen bonded dimer bands, coupled with the relatively small contribution from hydrogen bonded 'chain-like' structures, leads to the conclusion that in relative terms PDIPVPh is only weakly self-associated.

One final point before we leave the i.r. spectra of the three phenolic polymers; quantitative analyses of the fraction of hydrogen bonded carbonyl groups in the PDMVPh and PDIPVPh blends with PBMA and EVA[70] are performed in the carbonyl stretching region (1650–1800 cm^{-1}) and it would be ideal if there were no infra-red absorption in this region of the spectrum. Unfortunately, this is not the case, as is evident in *Figure 1*. There are weak infra-red active overtones that occur in the region of 1600–2000 cm^{-1}, often with distinctive patterns that are characteristic of the particular phenyl ring substitution[9]. In most of the quantitative blend studies reported in this and the following paper we can ignore these weak bands as the errors they introduce are minimal. However, there are cases where we cannot ignore contributions from these overtone bands; specifically, spectra of blends that are compositionally very rich in the phenolic polymer (i.e. >80%) and blends in which the concentration of total carbonyl groups is relatively small (e.g. in blends

Table 1 Dimensionless self-association equilibrium constants

Polymer	Molar volume ($cm^3 mol^{-1}$)	Dimer formation K_2	Multimer formation K_B
PVPh	100	21.0	66.8
PDMVPh	139	4.8	17.4
PDIPVPh	207	1.1	2.7

Table 2 Glass transition temperatures determined by thermal analysis

Blend composition (wt%)	T_g (°C)	Blend composition (wt%)	T_g (°C)
PDMVPh–PBMA		PDIPVPh–PBMA	
100/0	122	100/0	117
75/25	98	75/25	87
50/50	79	50/50	76
25/75	47	25/75	48
0/100	21	0/100	21
PDMVPh–EVA[70]		PDIPVPh–EVA[70]	
100/0	122	100/0	117
75/25	82	75/25	64
50/50	49	50/50	50
25/75	1	25/75	−3
0/100	−21	0/100	−21

with EVA copolymers containing < 20% vinyl acetate or poly(n-alkyl methacrylates) of > n-octyl). In these systems we employ i.r. spectral subtraction techniques to eliminate the contribution from the overtones using the spectrum of the pure phenolic polymer[10].

Self-association equilibrium constants for PVPh, PDMVPh and PDIPVPh

Self-association equilibrium constants of (co)polymers containing hydroxyl groups cannot be determined directly and are estimated from low molar mass analogues[1,2]. In essence, dimensionless equilibrium constants that describe the distribution of hydrogen bonded dimers (K_2) and higher multimers or 'chain-like' complexes (K_B) are determined from an interative least squares fitting procedure of the stoichiometric equation to infra-red spectroscopic data obtained from appropriate model compounds in dilute 'inert' solvents (e.g. cyclohexane) as a function of concentration. The methodology has been described in detail in our recent review to which the interested reader is referred[2]. We will simply note here that the values of the dimensionless self-association equilibrium constants (K_2 and K_B) obtained in our laboratories for the low molecular weight models DMPh and DIPPh in cyclohexane[3] are $K_2 = 6.7$; $K_B = 24.2$ and $K_2 = 2.2$; $K_B = 5.6$, respectively, *scaled to a common reference molar volume* ($100\,cm^3\,mol^{-1}$). For comparison purposes, values of $K_2 = 21.0$; $K_B = 66.8$, based on the same reference volume, have been previously determined by Whetsel and Lady for phenol in cyclohexane[11].

Self-association equilibrium constants for PDMVPh and PDIPVPh are now simply calculated by scaling the appropriate model compound values with respect to the molar volumes of the polymer repeat unit. For example, $K_B = 24.2$ for DMPh based upon a reference molar volume of $100\,cm^3\,mol^{-1}$. From group contributions the molar volume of the repeat unit of PDMVPh is $139\,cm^3\,mol^{-1}$. Hence, $K_B = 24.2(100/139) = 17.4$ for PDMVPh. A complete listing of the molar volumes and self-association equilibrium constants for PVPh, PDMVPh and PDIPVPh is given in *Table 1*.

Equilibrium constants describing the interassociation of PDMVPh and PDIPVPh hydroxyls with (co)polymers containing methacrylate and acetoxy carbonyl groups

Verification that the blends are single phase. As mentioned in the Introduction, our present methodology for calculating the free energy of mixing and predicting the phase behaviour of hydrogen bonded polymer blends requires a set of equilibrium constants, describing both self-association and interassociation, that have been obtained experimentally from an appropriate miscible polymer blend system. From a combination of previous experience with PVPh blends[1,2] and initial i.r. scouting experiments[3], we had reason to believe that it was most probable that the PDMVPh and PDIPVPh polymers form single phase blends over the entire composition range at ambient temperature with both PBMA and EVA[70]. This proved to be correct. All the blends prepared from solution casting were transparent and had single glass transition temperatures that occurred at intermediate temperatures between those of the pure components and varied systematically with composition. A summary of these results is presented in *Table 2*.

The carbonyl stretching region and least squares curve fitting. Having verified the miscibility of the PDMVPh and PDIPVPh blends with PBMA and EVA[70], we can now proceed to undertake i.r. spectroscopic studies to quantitatively determine the fraction of hydrogen bonded carbonyl groups present in the blends as a function of composition. These data will be employed to calculate the required equilibrium constants. *Figure 3* shows typical i.r. spectra of PDMVPh/PBMA blends as a function of composition in the carbonyl stretching region. Pure PBMA has a carbonyl stretching frequency at $\approx 1730\,cm^{-1}$, which is referred to as the 'free' (non hydrogen bonded) carbonyl band. The hydrogen bonded carbonyl band at $\approx 1710\,cm^{-1}$ is observed when a hydrogen bond is formed between the PBMA carbonyl and the PDMVPh hydroxyl group (interassociation).

To determine quantitatively the fraction of hydrogen bonded carbonyl groups present for any particular blend composition at a given temperature, one needs to carefully curve resolve the overlapping bands shown in *Figure 3* into their respective 'pure' components. In truth, least squares curve fitting is an exercise in applied common sense, and if employed in a cavalier manner can be a major source of experimental error.We strictly adhere to a set of principles for curve resolving each spectrum[1]. First, we spend the majority of our time on sample preparation and insist on infra-red spectra of superior quality, those with total absorbances of < 0.7 absorbance units and inherently straight baselines throughout the range of $500–4000\,cm^{-1}$, such as those shown in *Figure 1*. If this is not the case, we prepare a new sample. Second, a linear baseline is drawn from $500–4000\,cm^{-1}$ through points where there is minimal absorbance, such as the points near 3800 and $2100\,cm^{-1}$ in *Figure 1*. This baseline is now fixed and not permitted to vary in the least squares procedure. Third, the number of bands (two in our case) and the range over which the

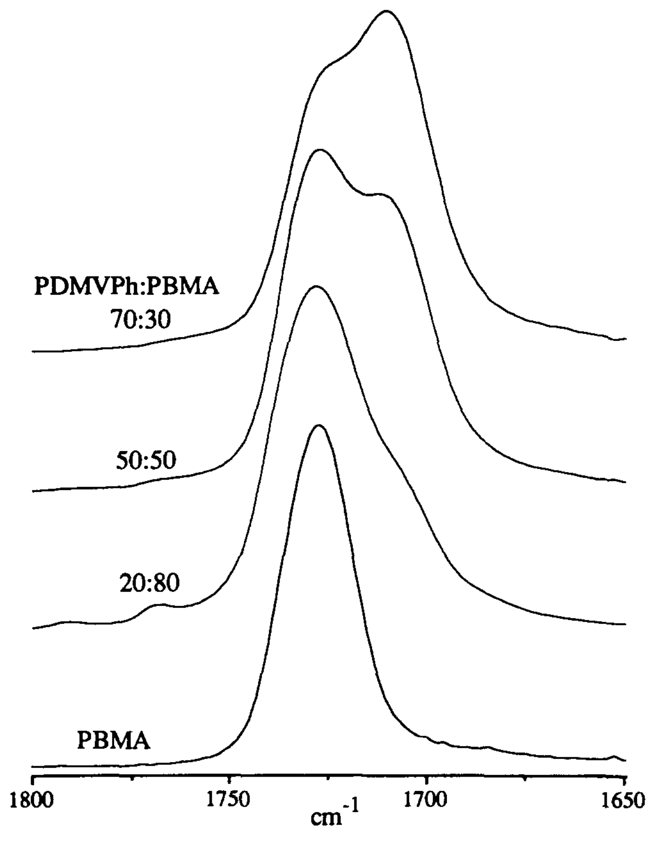


Figure 3 Infra-red spectra of films of pure PBMA and 70/30, 50/50 and 20/80 wt% PDMVPh–PBMA blends recorded at room temperature in the carbonyl stretching region (1650–1800 cm^{-1})

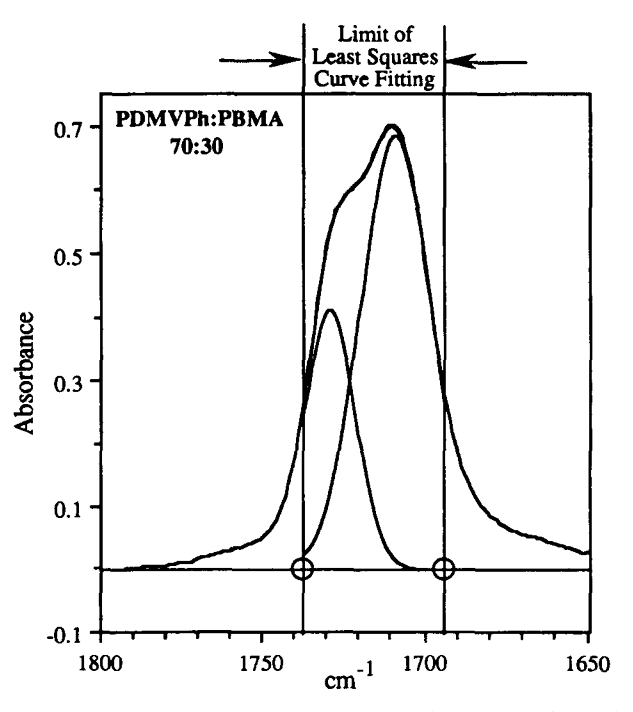


Figure 4 An example of curve fitting: the carbonyl stretching region (1650–1800 cm^{-1}) of a 70/30 PDMVPh–PBMA blend

least squares curve fitting will be performed is also fixed, as illustrated in *Figure 4*. It is invariably the case that one can obtain a superior fit to experimental data by including more bands, but without chemical and/or spectroscopic evidence to support the introduction of additional bands, doing so is illusory. To minimize the influence of neighbouring bands, which can affect the apparent band shape and breadth by distorting the wings of the bands to be resolved, a limited region is set for least squares curve fitting from approximately halfway up the high and low frequency sides of the envelope—see *Figure 4*. Fourth, from prior experience (1) and initial curve fitting studies of spectra of well resolved bands (such as the 70/30 and 50/50 PDMVPh/PBMA blend spectra, *Figure 3*) the shape of the bands is determined. For the studies presented in this and the subsequent paper both the 'free' and hydrogen bonded bands are fixed with a Gaussian bandshape and not varied in the least squares fitting procedure. (It should be emphasized in passing that the absorptivity ratios that we have determined from the respective areas of 'free' and hydrogen bonded carbonyl bands of model polymer blend systems[1] are significantly affected by band shape[4]. Proper use of these absorptivity ratios requires that identical band shapes be used for quantitative analysis). Fifth, the frequency and width at half height of the two bands is approximately determined, again from curve fitting studies of spectra with well resolved bands such as those mentioned above. In the least squares fitting program these initial values of band frequencies and width and half-heights are permitted to vary only within very strict limits; typically ± 2 cm^{-1}. In this manner, the number of variables is kept at a minimum and the limits within which they are permitted to vary severely restricted.

Simulation: optimum experimental conditions to determine K_A. Using the equations describing the stoichiometry of hydrogen bonding of the system, we have demonstrated previously[1,2] that the fraction of hydrogen bonded carbonyl groups $f_{HB}^{C=O}$ is related to the equilibrium constants, K_2, K_B (self-association) and K_A (interassociation) through equation (2):

$$f_{HB}^{C=O} = 1 - \left(\frac{1}{\{1 + K_A \Phi_{B_1}[(1 - K_2/K_B) + (K_2/K_B)(1/(1 - K_B \Phi_{B_1})]\}} \right) \tag{2}$$

where Φ_B is the volume fraction of isolated (non-hydrogen bonded) B species in the mixture. In practice, the value of K_A is usually determined from a least squares fit of equation (2) to experimental $f_{HB}^{C=O}$ data acquired from mixtures of varying composition, while holding the values of K_2 and K_B constant—see below. Reversing the procedure, if the values of the three equilibrium constants (K_2, K_B and K_A) are known or assumed, the calculation of $f_{HB}^{C=O}$ as a function of the composition of the blend is straightforward and is included in the computer program that accompanies our monograph[1]. We recommend such simulations before embarking on the quantitative determination of $f_{HB}^{C=O}$ from i.r. spectroscopic studies, because there is an optimum range of blend compositions from which K_A can be determined where experimental errors are minimized.

Figure 5 shows an example of a simulation of the $f_{HB}^{C=O}$ *versus* blend composition for the PDMVPh–PBMA system using constant values of $K_2 = 4.8$ and $K_B = 17.4$ (the self-association equilibrium constants

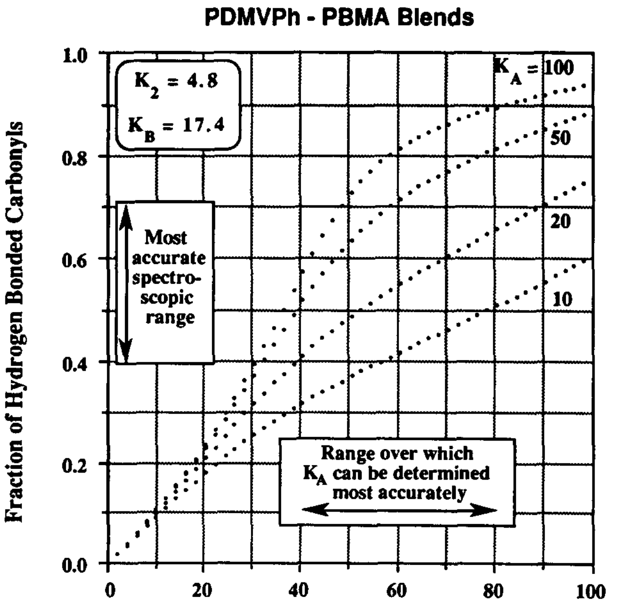


Figure 5 Simulation of the fraction of hydrogen bonded carbonyl groups as a function of composition for PDMVPh blends with PBMA at 25°C. The self-association equilibrium constants were kept constant at $K_2 = 4.8$ and $K_B = 17.4$, and calculations were performed using equation (2) (see text) with K_A values of 10, 20, 50 and 100

determined independently—see above) with various values of K_A ranging from 10 to 100 (the most probable range in which the value of K_A might be anticipated to lie). The most accurate range for determining $f_{HB}^{C=O}$ spectroscopically is from ≈ 0.4 to 0.7, because this is where both the 'free' and hydrogen bonded carbonyl bands have significant absorbances. Outside this range, one or other of the bands is buried under the other and is observed as a rather ill defined shoulder. Curve fitting in this case is subject to the greatest error. On the other hand, it can be seen from *Figure 5* that the value of $f_{HB}^{C=O}$ is most sensitive to the magnitude of K_A at PDMVPh blend compositions of > 50%. Below this composition, and especially below 40% PDMVPh, the variation of $f_{HB}^{C=O}$ with K_A is quite insensitive and below our ability to experimentally measure differences. Hence, for the PDMVPh–PBMA system the optimum blend composition for the quantitative analysis of the $f_{HB}^{C=O}$ is between 40 and 80 wt% PDMVPh.

The determination of K_A. The curve fitting results from the carbonyl stretching region of the i.r. spectra of five PDMVPh blends with both PBMA and EVA[70] from 40 to 80 wt% PDMVPh, (the optimum composition range for the determination of K_A), are listed in *Table 3*. The experimental $f_{HB}^{C=O}$ data, also presented in *Table 3*, were calculated using an absorptivity ratio of 1.4, and this warrants a brief digression.

Table 3 Curve fitting results for PDMVPh blends with PBMA and EVA[70]

Blend composition (wt%)	'Free' C=O band ν (cm^{-1})	$w_{1/2}$ (cm^{-1})	Area	Hydrogen bonded C=O band ν (cm^{-1})	$w_{1/2}$ (cm^{-1})	Area	$f_{HB}^{C=O\,a}$
PBMA							
40/60	1730	21	16.9	1709	26	17.2	0.42
50/50	1730	19	13.6	1709	26	18.6	0.49
60/40	1730	19	10.9	1709	28	22.5	0.60
70/30	1729	18	7.04	1709	26	18.5	0.65
80/20	1731	19	0.35	1711	29	1.08	0.68
EVA[70]							
40/60	1739	21	10.5	1716	29	12.7	0.46
50/50	1738	19	10.1	1716	28	14.9	0.51
60/40	1739	19	8.16	1716	30	15.7	0.58
70/30	1739	18	2.18	1716	30	6.09	0.67
80/20	1739	17	4.10	1717	30	14.1	0.71

[a] Absorptivity ratio = 1.4; see text

Table 4 Curve fitting results for PDIPVPh blends with PBMA and EVA[70]

Blend composition (wt%)	'Free' C=O band ν (cm^{-1})	$w_{1/2}$ (cm^{-1})	Area	Hydrogen bonded C=O band ν (cm^{-1})	$w_{1/2}$ (cm^{-1})	Area	$f_{HB}^{C=O\,a}$
PBMA							
40/60	1731	18	1.96	1713	23	1.79	0.41
50/50	1732	18	3.65	1714	22	2.29	0.47
60/40	1732	17	5.34	1714	23	7.95	0.53
70/30	1732	17	2.23	1714	23	4.56	0.61
80/20	1733	17	1.19	1714	24	3.14	0.67
EVA[70]							
40/60	1739	18	9.04	1722	26	7.00	0.37
50/50	1740	17	6.21	1722	26	6.73	0.45
60/40	1741	17	4.42	1721	26	7.75	0.57
70/30	1741	16	5.57	1722	29	14.9	0.67
80/20	1741	15	1.54	1722	28	6.35	0.76

[a] Absorptivity ratio = 1.3; see text

The absorptivity ratio, a_R, which is defined as:

$$a_R = \frac{\text{absorptivity of the hydrogen bonded carbonyl band}}{\text{absorptivity of the 'free' (non-hydrogen bonded) carbonyl band}}$$

has been determined experimentally for a number of different types of specific interactions from i.r. studies of hydrogen bonded polymer blends[1,12]. From our own studies of the interassociation of ester type carbonyl groups with the hydroxyl groups of PVPh and phenoxy blends, we have determined values of $a_R = 1.5$ and 1.3, respectively. This systematic decrease in the value of a_R for the different hydroxyl moieties is not unexpected and correlates well with the decrease in the average strength of the hydrogen bond formed between the hydroxyl and ester carbonyl groups, which is substantiated by the corresponding decrease in the frequency difference ($\Delta\nu$) between the 'free' and hydrogen bonded carbonyl bands; $\Delta\nu = 26$ and 19, respectively. From *Table 3*, it can be seen that the average value of $\Delta\nu$ for the PDMVPh blends with PBMA and EVA[70] is ≈ 22 cm^{-1}, which indicates that the average strength of the hydrogen bond formed is intermediate between that of the analogous PVPh and phenoxy blends. Accordingly, we have assumed a value of $a_R = 1.4$ for the PDMVPh blends. It should be emphasized that while this is a source of possible error in our quantitative measurements of $f_{HB}^{C=O}$, it is not a serious one. For example, the calculated $f_{HB}^{C=O}$ for the 50/50 blend of PDMVPh/EVA[70] is 0.51 if calculated using $a_R = 1.4$ (*Table 3*) and 0.49 for $a_R = 1.5$. To complete this section, the average value of

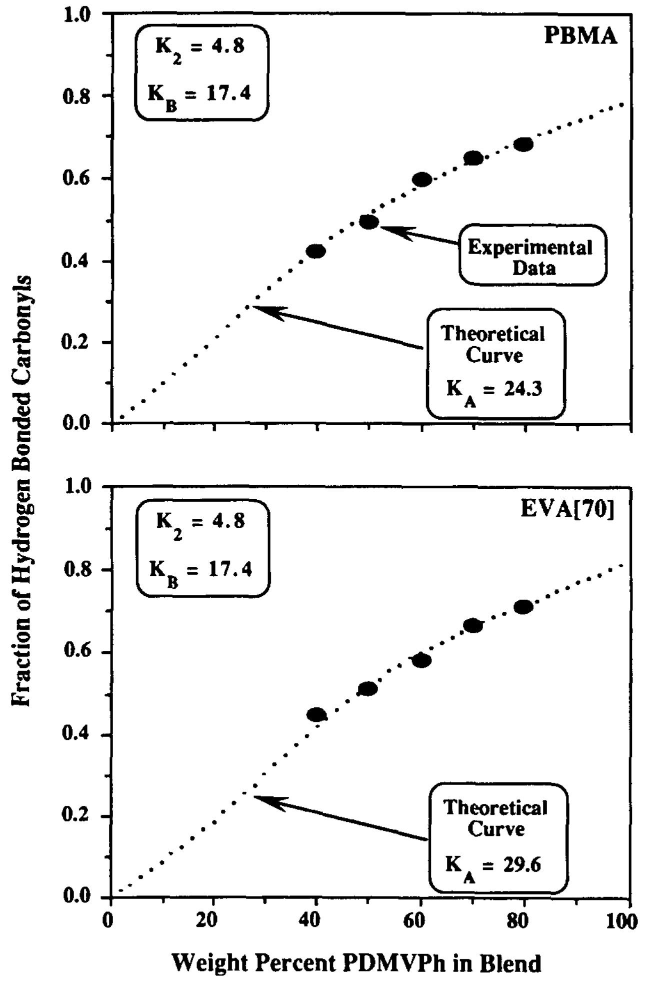


Figure 6 Least squares fitting of equation (2) to the experimental fraction of hydrogen bonded carbonyl groups for PDMVPh blends with (top) PBMA and (bottom) EVA[70]

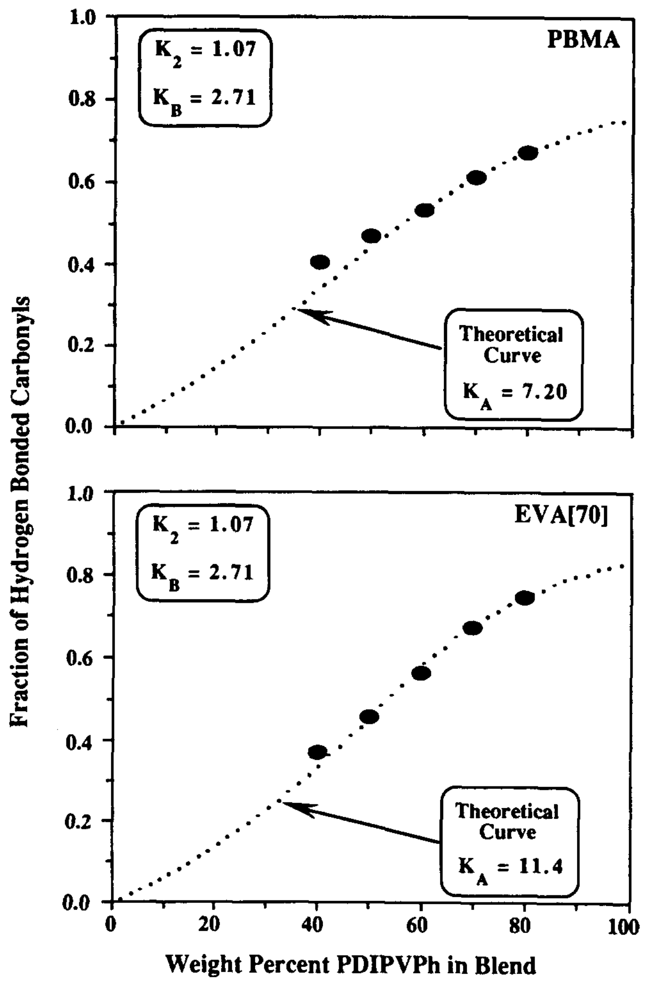


Figure 7 Least squares fitting of equation (2) to the experimental fraction of hydrogen bonded carbonyl groups for PDIPVPh blends with (top) PBMA and (bottom) EVA[70]

$\Delta\nu$ for the PDIPVPh blends with PBMA and EVA[70] is $\approx 18\,\text{cm}^{-1}$ (*Table 4*), again indicating a further weakening of the average strength of the hydrogen bond formed and more in line with that of the phenoxy blends. Correspondingly, we have assumed a value of $a_R = 1.3$ for the PDIPVPh blends.

Returning to the main topic of this section; the $f_{HB}^{C=O}$ data given in *Table 3* can now be used to determine equilibrium constants that describe the interassociation of (co)polymers containing hydroxyl groups of 2,6-dimethyl-4-phenols with (co)polymers containing acetoxy or methacrylate carbonyl groups. *Figure 6* illustrates the results of a least squares fit of the data to equation (2), with K_A values of 29.6 and 24.3 determined for acetoxy and methacrylate carbonyls, respectively. To reiterate, the values of the self-association equilibrium constants ($K_2 = 4.8$ and $K_B = 17.4$), which have been previously independently determined (*Table 1*), were held constant.

In a similar vein, the curve fitting results and experimental $f_{HB}^{C=O}$ data for the PDIPVPh blends with PBMA and EVA[70] are listed in *Table 4*. *Figure 7* illustrates the results of a least squares fit of the data to equation (2) (with constant $K_2 = 1.07$ and $K_B = 2.71$). K_A values of 11.4 and 7.20 were determined for acetoxy and methacrylate carbonyls, respectively.

Table 5 Dimensionless interassociation equilibrium constants

Polymer	Molar volume ($\text{cm}^3\,\text{mol}^{-1}$)	Acetoxy carbonyls K_A	Methacrylate carbonyls K_A
PVPh	100	58.0	37.8
PDMVPh	139	29.6	24.3
PDIPVPh	207	11.4	7.2

SUMMARY, CONCLUSIONS AND DIRECTION OF FUTURE WORK

Table 5 summarizes the interassociation equilibrium constant values determined for PVPh, PDMVPh and PDIPVPh blends with (co)polymers containing acetoxy and methacrylate carbonyls. Recall that these values are based upon the molar volumes of the particular hydroxyl containing polymer (*Table 1*) and if we are to directly compare these results we must scale them to the same reference volume ($100\,\text{cm}^3\,\text{mol}^{-1}$), which are presented in *Table 6*. In other words, equilibrium constants scaled to this common reference volume reflect the self- and interassociation of a segment containing a hydroxyl group having a molar volume of $100\,\text{cm}^3\,\text{mol}^{-1}$ in a specific chemical environment. We have previously mentioned that the magnitude of self-association decreases in the order PVPh > PDMVPh > PDIPVPh (i.e. $K_2 = 21.0$, 6.7, 2.3 and $K_B = 66.8$, 24.2, 5.6,

Table 6 Dimensionless self-association equilibrium constants scaled to a common reference volume of 100 cm^3 mol^{-1}

	Self-association		Interassociation	
Polymer	Dimer formation K_2	Multimer formation K_B	Acetoxy carbonyls K_A	Methacrylate carbonyls K_A
PVPh	21.0	66.8	58.0	37.8
PDMVPh	6.7	24.2	41.1	33.8
PDIPVPh	2.3	5.6	23.6	14.9

respectively). The same trend is seen for the interassociation with acetoxy ($K_A = 58.0$, 41.1, 23.6, respectively) and methacrylate carbonyls ($K_A = 37.8$, 33.8, 14.9). This decrease in the magnitude of both the self- and interassociation equilibrium constants was predictable because the bulky nature of the 2,6-dialkyl groups would be expected to partially block the approach of both another hydroxyl or carbonyl group. For our purposes, however, the more important question is 'have we evidence, similar to that described for the low molecular weight model compounds mentioned in the Introduction, that we have accentuated interassociation over self-association by introducing the 2,6-dialkyl groups onto PVPh?' Using the ratio of K_A/K_B as a measure the answer is affirmative. Values of $K_A/K_B \approx 0.9$, 1.7 and 4.2 are calculated for PVPh, PDMVPh and PDIPVPh blends with (co)polymers containing acetoxy carbonyl groups, while corresponding values of $K_A/K_B = 0.6$, 1.4 and 2.7 pertain to (co)polymers containing methacrylate carbonyl groups. This is encouraging because accentuating interassociation over self-association is a favourable direction for polymer blend miscibility.

Having obtained equilibrium constants that describe the stoichiometry of miscible hydrogen bonded PDMVPh and PDIPVPh blends with (co)polymers containing acetoxy and methacrylate carbonyl groups, we are now in a position to calculate the free energy of mixing (equation (1)) and predict miscibility windows for the entire range of EVA copolymers and the homologous series of poly(n-alkyl methacrylate)s. This and a comparison to experiment is presented in the next paper in this series.

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