Hydrogen Bonding in Ternary Polymer Blend Systems: Determination of Association Parameters

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ABSTRACT: The polymer blend system consisting of poly(4-vinylphenol) (PVPh), poly(vinyl acetate) (PVAc), and poly(ethylene oxide) (PEO) represents a rare case of a ternary system in which each binary pair is miscible in the amorphous state at 150 °C. Using the concept of competing equilibria, we show that the equilibrium constant describing hydrogen bonding between the OH group of PVPh and the ether oxygen of PEO can be determined from quantitative infrared spectroscopic analysis of the fraction of hydrogen-bonded PVAc carbonyl groups in single-phase ternary compositions rich in PVPh.

Introduction

The infrared carbonyl stretching vibration occupies a special place in studies of polymer blends that hydrogen bond. It is sensitive to the strength and, more importantly for our purposes, the fraction of hydrogen bonded carbonyl groups that are present in the blend sample but is beset by none of the absorptivity problems that occur in the O–H and N–H stretching regions of the infrared spectrum. This is a consequence of the carbonyl group's greater mass, bond stiffness, and smaller displacement during vibration.[1] In work in this laboratory we have relied exclusively on the carbonyl stretching vibration and its facility to separate into two well-resolved bands attributable to "free" and hydrogen bonded carbonyl groups, respectively, to quantitatively determine the fraction of such groups, which, in turn, permits us to calculate values for equilibrium constants describing the "interassociation" between different polymers in binary polymer blend systems. These parameters have allowed us to calculate the phase behavior of a wide range of mixtures, most frequently blends where one component is a polymer or copolymer containing phenolic or aliphatic hydroxyl groups, while the second component is a polymer or copolymer containing (meth)acrylate, ester, or acetoxy groups. Furthermore, carbonyl stretching modes can also be used to measure both self-association and interassociation in blends where one component contains urethane, amide, or acid groups while the second contains ether or pyridine groups.[1-3] Note that in all cases only one of the polymers in the binary blend contains a carbonyl group, and although this represents a large category of blends, it is nonetheless a select one.

Polymers containing ether oxygens such as polyethers also form strong hydrogen bonds with (co)polymers containing hydroxyl groups.[4-6] In these systems, however, we have no carbonyl group that can be used as a measure of the number of hydrogen bonded groups and it is practically impossible to quantitatively determine the fraction of hydrogen bonded hydroxyl or ether groups directly from mid-infrared studies of these binary blends. Complications involving the absorptivity coefficient values in the O–H stretching region have been alluded to above.[7] For a different reason, the C–O–C ether stretching mode, which is a relatively intense band that occurs near 1200 cm^{-1}, is also not appropriate for quantitative analysis of the fraction of hydrogen bonded ether groups. It is a highly coupled mode that is conformationally sensitive and does not separate conveniently into bands that can be unambiguously attributed to "free" and hydrogen-bonded ether groups.

How then can we experimentally determine interassociation equilibrium constants describing the hydroxyl–ether oxygen interaction and the like, where there is no convenient spectroscopic probe? One approach considered previously[5] was to employ values for the dimensionless interassociation equilibrium constant (K_A) and enthalpy of hydrogen bond formation (h_A), derived from near-infrared studies of low molecular weight analogs by Powell and West.[8] Is this approach valid? Can we transfer equilibrium constant values obtained from low molecular weight model compounds to polymers with analogous specific repeat units and expect to be within the bounds of acceptable error? For now this is an open question, one requiring further extensive experimental scrutiny, but initial studies performed in our laboratories suggest that transferring *all* the equilibrium constants from low molecular weight analogs, i.e. those describing *both* self- and interassociation, can lead to a significant reduction in the predictive capacity of the association model we employ to calculate the free energy of mixing and subsequent phase diagrams and miscibility windows or maps.

Nonetheless, we have demonstrated that we can successfully predict, with surprising accuracy, miscibility windows and maps for binary blends of (co)polymers containing hydroxyl groups with those containing (meth)acrylate, ester or acetoxy groups,[1] where we transferred the equilibrium constants describing *self-association* of the OH groups (K_2 and K_B) from appropriate model compounds. It is important to recognize that in these systems the parameter K_A was experimentally determined from a least-squares fit of infrared data acquired from a *miscible polymer blend* to equations describing the stoichiometry of the system, using constant values of K_2 and K_B. The experimentally determined equilibrium constants describing self- and interassociation are thus not independent. In addition, factors such as polymer chain stiffness are adsorbed into these experimentally determined parameters and, to a significant degree, errors

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in the absolute values of the self-association equilibrium constants tend to be compensated by the method used to obtain the complementary interassociation equilibrium constants.

It is important that we devise procedures to extend our measurements to the determination of parameters describing hydrogen bonds to functional groups other than those containing carbonyls, and in this communication we explore the possibility of using a ternary polymer blend system to obtain the equilibrium constant value describing the interassociation of poly(4-vinylphenol) (PVPh) with poly(ethylene oxide) (PEO). PVPh forms single-phase materials with poly(vinyl acetate) (PVAc)[9] and PEO[4-6] in the amorphous state across the entire composition range, the main driving force toward molecular mixing being the favorable hydrogen bonding contribution from the phenolic hydroxyl to carbonyl or ether oxygen specific interactions. Similarly, PEO and PVAc are also reported to be miscible,[10] which we have attributed to their closely matched non-hydrogen-bonded solubility parameters, (9.4 and 9.6 (cal cm^{-3})$^{0.5}$, respectively) and the presence of weak, but favorable, polar forces.[1] Accordingly, the three polymers considered here, PVPh, PVAc, and PEO, all form miscible binary blends with one another. While this does not assure that all ternary compositions are homogeneous in the amorphous phase (see below), it does significantly reduce the complexity of ternary systems in general. Thus we postulate that if we can find a systematic set of ternary compositions rich in PVPh that form single phase materials, we can use the concept of competing equilibria and determine the equilibrium constant describing the interassociation of PVPh and PEO from a quantitative infrared spectroscopic analysis of the fraction of hydrogen bonded PVAc carbonyl groups. Lest it go unnoticed, we are thus once again relying on our old friend the carbonyl band!

Experimental Section

Poly(4-vinylphenol) (PVPh) and poly(vinyl acetate) (PVAc) having reported molecular weights of 1500–7000 and 60 000 g mol^{-1}, respectively, were purchased from Polysciences. Both polymers are amorphous with glass transition temperatures (T_g) of 140 and 28 °C, respectively. Poly(ethylene oxide) (PEO) and atactic poly(methyl methacrylate) (PMMA) were purchased from Aldrich. The former, a semicrystalline polymer at ambient temperature with a T_g of −65 °C and an approximate crystalline melting point (T_m) of 70 °C, has a reported molecular weight of 100 000. PMMA, an amorphous polymer with a T_g of 105 °C, was designated to be of medium molecular weight. Blends were prepared by codissolving the polymers in appropriate proportions in a 70:30 mixture of tetrahydrofuran (THF) and chloroform. This mixed solvent was used to facilitate the dissolution of PEO.

Samples for FT-IR analysis were prepared by casting films, from a 1% (w/v) polymer solution, onto potassium bromide (KBr) windows. After evaporation of the majority of the solvent at room temperature, the samples were placed in a vacuum oven at 70 °C for 24 h. Infrared spectra were recorded on a Digilab FTS-60 Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. A minimum of 64 scans were signal averaged, and the spectra were stored on a magnetic disk system. All spectra were recorded at 150 °C, above the T_g's of the component polymers, using a SPECAC high temperature cell mounted in the spectrometer and a Micristar heat controller. Spectra were compared at room temperature before and after examination at 150 °C and found to be identical within experimental error. This indicates that thermal and oxidative degradation was minimal.

Samples for thermal analysis were prepared by casting films onto aluminum foil from a 10% (w/v) polymer solution. After evaporation of the majority of the solvent at room temperature, the samples were placed in a vacuum desiccator for a minimum of 48 h, and then in a vacuum oven at 70 °C for 24 h. Samples, approximately 15 mg in weight, were then prepared by stripping the polymer from the aluminum foil. Thermal analysis was conducted on a du Pont 2000 differential scanning calorimeter (DSC) coupled to a computerized data station. All sample were annealed at 150 °C for 5 min, then quenched in liquid nitrogen to −120 °C. A heating rate of 40 °C/min was used in all experiments.

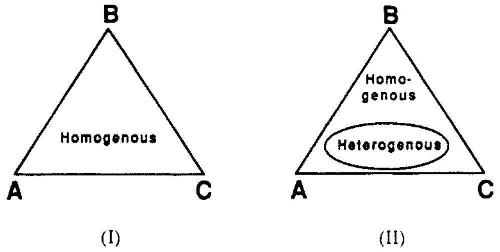

Figure 1. Schematic representation of the two possible ternary phase diagrams.

Results and Discussion

Ternary Blend Systems. With the addition of another degree of difficulty into an already complex field, ternary polymer mixtures have received scant attention since the early works of Scott[11] and Tompa.[12] In recent years however, several groups[13-15] have attempted to experimentally map ternary polymer phase diagrams, primarily relying on DSC and optical clarity techniques. Su and Fried[16] have also mathematically computed spinodal curves and critical points using the Flory–Huggins lattice theory for different combinations of the binary interaction parameters to provide guidelines for miscibility in ternary polymer mixtures.

The polymers used in the present work possess sites for strong hydrogen bonding interactions. Extending our previously employed nomenclature[1] to these systems, the self-associating polymer is denoted as polymer B, and the polymers which themselves do not self-associate, but have a site available for inter-association with polymer B, are denoted as polymers A and C. In this study we deliberately chose a system in which polymer B is completely miscible in the amorphous state with two interassociating polymers (A and C). Additionally, polymers A and C, which do not self-associate to any significant degree, are themselves miscible. Miscibility in the binary systems B–A and B–C is primarily a consequence of a favorable free energy contribution from the hydrogen bonds formed in the mixtures.[1,4] In contrast, strong specific interactions (hydrogen bonds) do not occur between polymers A and C, and miscibility of these two polymers is attributed to their closely matched non-hydrogen-bonded solubility parameters (measuring "physical interactions") and the presence of relatively weak, but favorable, polar forces.[1] In this case one can envision two types of possible ternary phase diagrams[16-18] shown schematically in Figure 1.

With all three binary pairs being miscible, a completely homogeneous phase diagram is possible (I). However, disparities in the interaction parameters of the binary systems B–A and B–C, the so-called "$\Delta\chi$" effect, can lead to closed loops which represent the boundary between homogeneous and heterogeneous phases. From an experimental (infrared spectroscopic) point of view, our experiments are necessarily confined to the region of the phase diagram that is rich in the self-associating polymer (PVPh). This is because at high concentrations of PVPh a larger proportion of the carbonyl groups are hydrogen-bonded and quantitative analysis of the fraction of these groups is consequently much more accurate (see later). Fortunately, it is in this region of the phase diagram that we expect the greatest possibility of homogeneous ternary mixtures and we next present evidence that shows this is indeed the case.

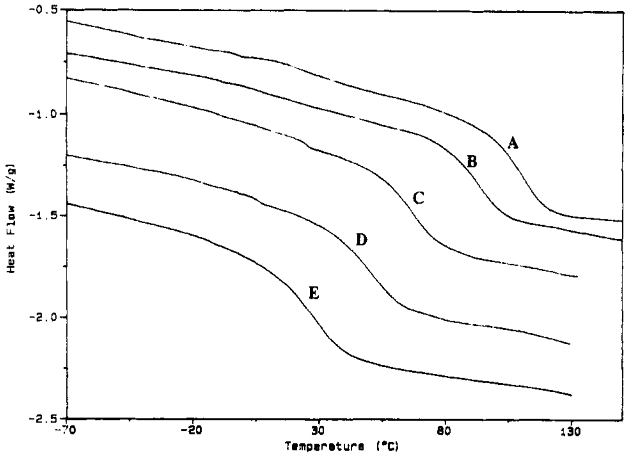

Figure 2. DSC thermograms of PVPh–PVAc–PEO blends: (A) 60:40:0; (B) 60:30:10; (C) 60:20:20; (D) 60:10:30; (E) 60:0:40 vol %.

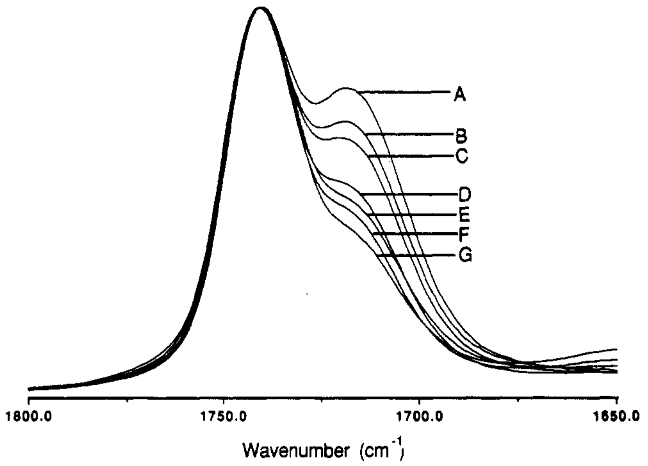

Figure 3. Infrared spectra of PVPh–PVAc–PEO blends in the carbonyl stretching region recorded at 150 °C: (A) 60:40:0; (B) 60:35:5; (C) 60:30:10; (D) 60:25:15; (E) 60:20:20; (F) 60:15:25; (G) 60:10:30 vol %.

Thermal Analysis. The glass transition temperatures (T_g) of the three pure polymers employed in this study, PVPh, PVAc and PEO, are 140, 28, and −65 °C, respectively. We must also recognize that under favorable conditions PEO may crystallize ($T_m \approx 70$ °C). However, we have determined that for the blend compositions considered in this study (i.e. those containing >60% PVPh), crystallization of PEO can be essentially eliminated by rapidly quenching the blend sample from 150 °C in the DSC instrument before recording the thermogram. Figure 2 shows representative thermograms recorded for a series of blends containing a constant concentration (60%) of PVPh with varying proportions of PVAc (0–40%) and PEO (0–40%) making up the remainder. Single, broad T_g's, varying systematically with the relative concentrations of PVAc to PEO are observed, which is strong evidence for the presence of homogeneous (single phase) mixtures. Increasing the amount of PVPh in the mixtures leads to a similar conclusion. Confident that we are dealing with homogeneous mixtures in the ternary blends containing >60% PVPh, we can now proceed to infrared spectroscopic studies of these blends.

Infrared Spectroscopic Analysis. Figure 3 shows representative infrared spectra recorded at 150 °C in the carbonyl stretching region for a series of blends containing a constant concentration (60%) of PVPh. (A temperature of 150 °C was chosen for these studies to assure that all bend compositions were amorphous and above the T_g's of the blend and individual components, thus facilitating the achievement of equilibrium conditions.) We have previously described in detail[1,9] the separation of the infrared acetoxy carbonyl band into two components, attributed to "free" and hydrogen bonded carbonyl groups, at approximately 1742 and 1717 cm^{-1}, respectively. Furthermore, the curve fitting methodology and choice of an appropriate absorptivity ratio[9] (in this case; $a_R = a_{HB}/a_F = 1.5$) have also been discussed; these factors are important in the quantitative determination of the fraction of hydrogen bonded groups.[1] Spectrum A represents the 60:40 binary blend of PVPh–PVAc, while spectra B through G are those recorded for ternary PVPh–PVAc–PEO blends of the following respective composition: 60:35:5, 60:30:10, 60:25:15, 60:20:20, 60:15:25, and 60:10:30. Qualitatively, it is evident that as the relative ratio of PEO to PVAc increases, the fraction of hydrogen bonded carbonyl groups decreases, a result of the competition between PVAc carbonyls and PEO ether oxygens for formation of hydrogen bonds with PVPh phenolic hydroxyl groups. The rapidity of this decrease with composition implies that the interassociation equilibrium constant describing PVPh–PEO blends has a larger value than that corresponding to PVPh–PVAc blends. To put this on a quantitative basis we require the fraction of hydrogen-bonded carbonyl groups for a series of blends containing a constant PVPh concentration as a function of PEO/PVAc ratio, and these results of are summarized in Table I.

Stoichiometric Equations. Hydrogen bonds are strong specific interactions, and their formation can be described using appropriate equilibrium constants. Because we employ these with a lattice model to describe the free energy, it is convenient to define these equilibrium constants as dimensionless quantities, specific to a particular pair of functional groups.[1] The equilibrium constants can be transferred between molecules containing the same functional groups but different amounts of non-hydrogen-bonding or "inert" segments, by accounting for the differences in the molar volumes of the repeat units.

The stoichiometry of hydrogen bonding and its relationship to infrared spectroscopic measurements in binary blends has been discussed at length[1] and only a brief summary is presented here, since extension of the PVPh–PVAc–PEO ternary blend system is quite straightforward. In common with our previous nomenclature[1] we utilize two self-association equilibrium constants, K_2 and K_B, to describe the formation of PVPh hydroxyl–hydroxyl dimers and hydroxyl–hydroxyl "chainlike" multimers, respectively, i.e.

$$B_1 + B_1 \overset{K_2}{\rightleftharpoons} B_2$$

$$B_h + B_1 \overset{K_B}{\rightleftharpoons} B_{h+1} \ (h \geq 2) \tag{1}$$

The interassociation equilibrium constants describing the specific interaction between the PVPh hydroxyl and the PVAc carbonyl group is represented by

$$B_h + A_1 \overset{K_A}{\rightleftharpoons} B_hA \tag{2}$$

Similarly, for hydrogen bonds between the PVPh hydroxyl and the PEO ether oxygen group

$$B_h + C_1 \overset{K_C}{\rightleftharpoons} B_hC \tag{3}$$

Of course, there are no hydrogen bonds between the segments of PVAc and PEO.

The equations relating the four equilibrium constants to the volume fractions of the species present are very similar to those derived previously (ref 1, pages 191–196)

Table I
Curve Fitting Results for PVPh–PVAc–PEO Blends

PVPh:PVAc:PEO blend composition (vol %)	free C=O band			hydrogen bonded C=O band			
	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	area	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	area	$f_{HB}{}^{C=O}$
60:40:0	1742	19.2	7.22	1717	34.0	12.40	0.53
60:35:5	1742	19.5	12.26	1717	33.5	17.44	0.49
60:30:10	1742	20.1	4.57	1718	33.0	5.70	0.45
60:25:15	1742	20.1	8.89	1718	31.9	8.34	0.39
60:20:20	1742	21.6	5.14	1717	32.6	4.10	0.35
60:15:25	1742	21.2	7.16	1718	31.0	5.13	0.32
60:10:30	1742	22.3	4.30	1716	31.2	2.53	0.28
70:30:0	1743	18.8	4.48	1717	34.0	9.72	0.59
70:25:5	1743	18.5	10.71	1718	33.0	19.86	0.55
70:20:10	1743	18.7	3.081	1717	32.9	5.25	0.53
70:15:15	1742	19.3	5.19	1717	33.1	7.90	0.50
70:10:20	1742	19.9	2.10	1718	32.9	2.52	0.44
75:25:0	1743	18.4	5.76	1717	32.9	13.11	0.61
75:19:6	1742	18.6	2.79	1717	33.0	5.70	0.58
75:15:10	1743	18.9	6.69	1717	34.2	13.73	0.58
75:13:12	1742	18.9	2.60	1717	33.7	5.13	0.57
75:10:15	1743	19.4	3.89	1717	34.2	6.74	0.54
75:7:18	1742	19.6	2.65	1717	34.2	4.40	0.53
75:5:20	1743	19.9	3.58	1717	34.3	5.75	0.52
80:20:0	1743	18.3	5.58	1717	33.5	14.18	0.63
80:15:5	1742	18.4	2.94	1717	33.3	7.03	0.61
80:10:10	1743	18.7	2.63	1717	34.0	6.24	0.61
80:7.5:12.5	1743	18.9	5.24	1717	34.1	11.88	0.60
80:5:15	1743	19.8	2.50	1717	34.8	4.83	0.56

and using the same nomenclature it can be readily shown that

$$\Phi_{B} = \Phi_{B_1}\Gamma_2\left[1 + \frac{K_A\Phi_{A_1}}{r_A} + \frac{K_C\Phi_{C_1}}{r_C}\right] \tag{4}$$

$$\Phi_A = \Phi_{A_1}[1 + K_A\Phi_{B_1}\Gamma_1] \tag{5}$$

$$\Phi_C = \Phi_{C_1}[1 + K_C\Phi_{B_1}\Gamma_1] \tag{6}$$

where

$$\Gamma_1 = \left(1 + \frac{K_2}{K_B}\right) = \frac{K_2}{K_B}\left(\frac{1}{(1 + K_B\Phi_{B_1})}\right) \tag{7}$$

$$\Gamma_2 = \left(1 + \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{(1 + K_B\Phi_{B_1})^2}\right) \tag{8}$$

Φ_B, Φ_A, and Φ_C are the volume fractions of PVPh, PVAc, and PEO in the blend, while Φ_{B_1}, Φ_{A_1}, and Φ_{C_1} are the corresponding volume fractions of isolated (non-hydrogen-bonded) PVPh, PVAc, and PEO segments, respectively. $r_A = V_A/V_B$ and $r_C = V_C/V_B$ are the ratios of the segment molar volumes of PVAc to PVPh and PEO to PVPh, respectively.

If values of the equilibrium constants (K_2, K_B, K_A, and K_C) and segment molar volumes (V_B, V_A, and V_C) are known, the fraction of hydrogen bonded carbonyl groups, f_{HB}, can be calculated from eqs 4–6, for a given blend composition (Φ_B, Φ_A, Φ_C), using[1]

$$f_{HB} = 1 - \frac{\Phi_{A_1}}{\Phi_A} \tag{9}$$

For our purposes, however, we will reverse the procedure and determine K_C from a least-squares fitting procedure of the experimental infrared f_{HB} data.

Determination of the PVPh–PEO Interassociation Equilibrium Constant K_C. Values of PVPh self-association (K_2 = 21.0 and K_B = 66.8) and PVPh–PVAc interassociation (K_A = 58.7) equilibrium constants at 25 °C have been previously determined from binary blend systems, as have the corresponding enthalpies of hydrogen bond formation (5.6, 5.2, and 3.8 kcal mol^{-1}, respectively, for h_2, h_B, and h_A).[1] Accordingly, assuming a van't Hoff relationship, values of K_2 = 1.27, K_B = 4.94, and K_A = 8.75 are appropriate at 150 °C (Table II). Holding these values constant, we performed a least-squares fit of *all* the experimental f_{HB} data given in Table I to the stoichiometric equations (eqs 4–6), using a modified version of the computer program that we have recently described.[1] We obtained a value for K_C = 33.0 at 150 °C. This value gives a fine agreement between the experimental and theoretical fraction of hydrogen bonded carbonyl groups for the four sets of results corresponding to fixed volume fractions of PVPh (Φ_B = 0.6, 0.7, 0.75, and 0.8, respectively) as illustrated in Figure 4.

Table II
Parameter Values for Ternary Blends

polymer	solubility parameter (cal/cm^3)$^{0.5}$	molar volume (cm^3/mol)	equilibrium constants at 150 °C: self-association K_2	K_B	interassociation K_A	K_C
PVPh	10.6	100.0	1.27	4.94		
PEO	9.4	38.1				33.0[a]
PVAc	9.6	69.8			8.75	
PMMA	9.1	84.9			5.67	

[a] Determined in the present study.

Note that at 150 °C the value of K_C is 4 times larger than that of K_A. This reflects the fact that phenolic hydroxyl groups hydrogen bond more strongly to PEO ether oxygens than to PVAc acetoxy carbonyl groups. (At 25 °C this corresponds to a value of K_C = 490, assuming an enthalpy of hydrogen bond formation h_C = 5.4 kcal·mol^{-1}, as reported by Powell and West.[8]) The experimental value of K_C = 33.0 at 150 °C, derived from the ternary PVPh–PVAc–PEO blend system, is some 5 times larger than that reported[8] (K_C = 5.9 at 150 °C) from dilute solution studies of phenol/diethyl ether mixtures in carbon tetrachloride.

Although the OH stretching region is difficult to use for quantitative work, we can nevertheless use the trends observed in this region of the infrared spectra of PVPh–PEO *binary* blends of varying compositions recorded at 150 °C (Figure 5) to substantiate that the higher value more accurately describes the interassociation of PVPh and PEO. Note that the relative intensity of the free hydroxyl band at approximately 3550 cm^{-1} increases very gradually up to a blend composition of approximately 60

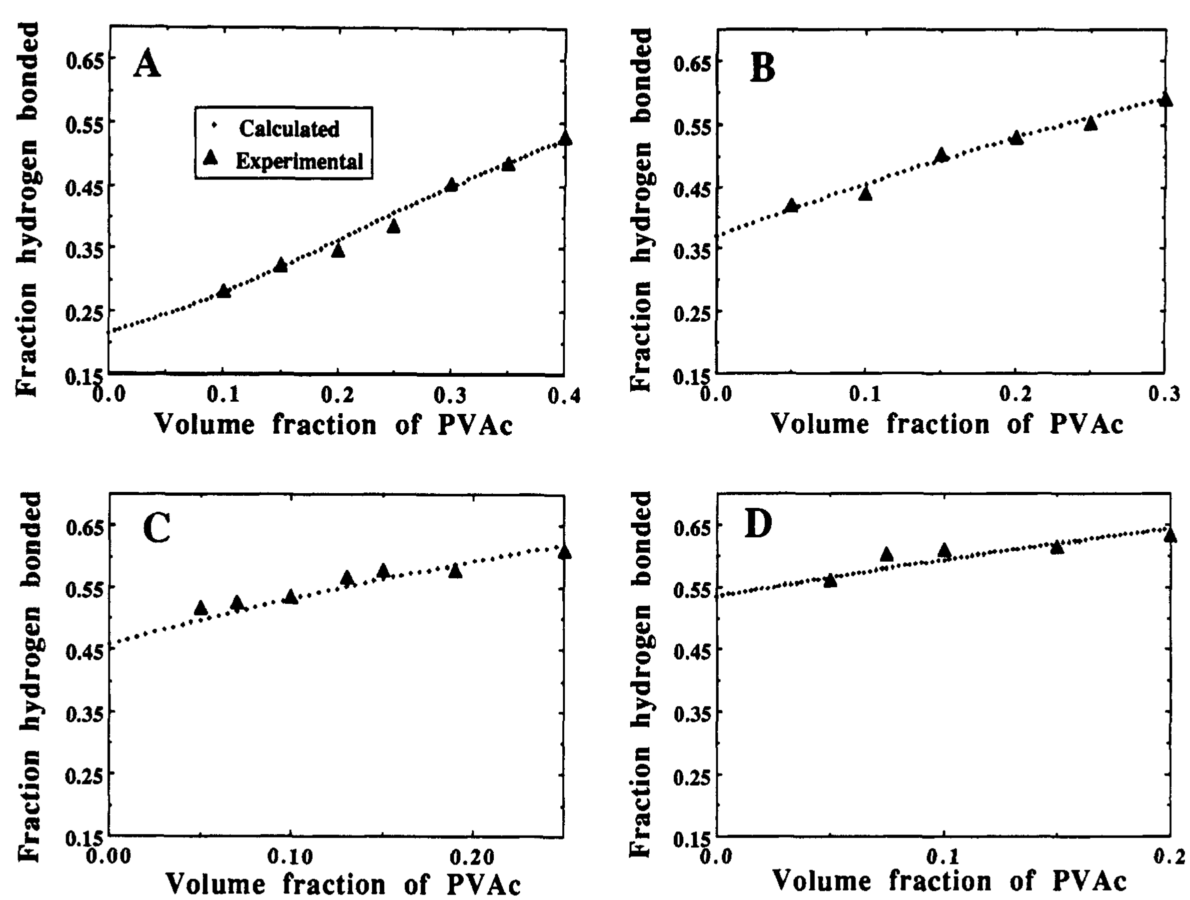

Figure 4. Comparison of experimental data to the theoretical curve calculated from the stoichiometric equations employing the value of K_C = 33.0 at 150 °C for PVPh–PVAc–PEO blends where (A) Φ_{PVPh} = 0.6; (B) Φ_{PVPh} = 0.7; (C) Φ_{PVPh} = 0.75; (D) Φ_{PVPh} = 0.8.

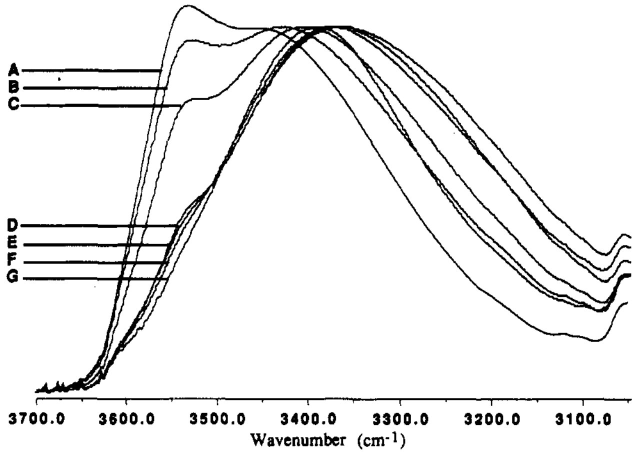

Figure 5. Infrared spectra of PVPh–PEO blends in the hydroxyl stretching region recorded at 150 °C: (A) pure PVPh; (B) 90:10; (C) 80:20; (D) 60:40; (E) 50:50; (F) 40:60; (G) 20:80 vol %.

vol % PVPh and then abruptly increases. This is characteristic for systems in which the magnitude of the interassociation equilibrium constant is significantly greater than that of the corresponding self-association equilibrium constant(s) and parallels the shape of the theoretical curve of the fraction of free hydroxyl groups (i.e. those hydroxyl groups that are not hydrogen bonded to either other hydroxyl groups or ether oxygens), calculated using a value of K_C = 33.0. The results of these calculations are shown in Figure 6 and were performed using the stoichiometric equations previously derived,[1] in conjunction with the parameters (K_2, K_B, V_C, and V_B) listed in Table II. On the other hand, substituting the value of K_C = 5.9 obtained from low molecular weight materials in CCl_4 produces a smooth theoretical curve of the fraction of free hydroxyl groups as a function of blend composition at 150 °C (Figure 6). This type of curve is typically obtained when the magnitude of the interassociation and self-association equilibrium constants are roughly comparable. This is not consistent with our infrared spectroscopic observations (Figure 5) and thus we conclude that the value of K_C = 33.0 is more appropriate.

We should caution, however, that we consider PEO, and presumably poly(methylene oxide), to be special cases. The infrared frequency shift at 25 °C between the "free" hydroxyl stretching band in PVPh and that corresponding to the PVPh–PEO specific interaction is approximately 325 cm^{-1}.[4] Conversely, the analogous shifts observed in PVPh blends with poly(vinyl methyl ether) (PVME) and poly(vinyl ethyl ether)[4,5] are in the range of 200–205 cm^{-1}. This implies that the PVPh–PEO specific interaction is considerably stronger than those of PVPh–poly(vinyl alkyl ethers). Accordingly, we do not believe it is entirely appropriate to transfer the value of K_C obtained here for PVPh–PEO blends to other PVPh–polyether blends. We intend to determine, in the near future, approximate K_C values by studying ternary blends such as PVPh–PVAc–PVME, PVPh–PBMA–PVME, etc. But in these cases we will have the added complexity that polymers A and C are not necessarily miscible. It remains to be seen if we can find composition ranges that are homogeneous and appropriate to quantitative infrared analysis.

The PVPh–PMMA–PEO Ternary System. PMMA is also miscible with both PVPh[1] and PEO.[19] Thus we have a ternary system similar to that of the PVPh–PVAc–PEO in which all binary blends form miscible systems. The interassociation equilibrium constant corresponding to the specific interaction between PVPh hydroxyls and methacrylate carbonyl groups has been determined previously[1] (K_A = 5.67 at 150 °C). Using this value in conjunction with values of the segment molar volumes and equilibrium constants, K_2, K_B, and K_C (Table II), we can test whether or not the theoretical fraction of hydrogen-

Table III
Curve Fitting Results for PVPh-PMMA-PEO Blends

PVPh:PMMA:PEO blend composition (vol %)	free C=O band ν (cm^{-1})	free C=O band $W_{1/2}$ (cm^{-1})	free C=O band area	hydrogen bonded C=O band ν (cm^{-1})	hydrogen bonded C=O band $W_{1/2}$ (cm^{-1})	hydrogen bonded C=O band area	$f_{HB}^{C=O}$
70:30:0	1734	21.0	3.26	1711	31.5	4.77	0.50
70:20:10	1734	21.6	2.32	1711	32.2	2.81	0.45
70:15:15	1734	22.1	1.97	1711	33.0	2.01	0.41
70:10:20	1734	22.9	1.88	1711	33.7	1.68	0.37
70:5:25	1734	24.6	2.91	1710	33.9	2.16	0.33

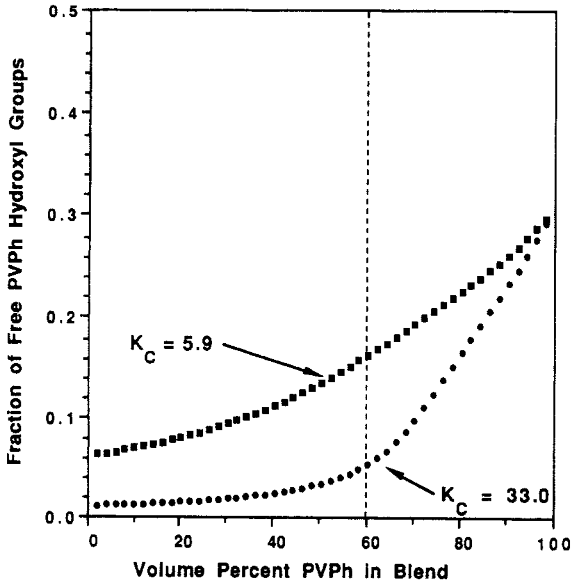

Figure 6. Calculated fraction of free hydroxyl groups at 150 °C in binary PVPh-PEO blends as a function of blend composition using two different values of the interassociation constant.

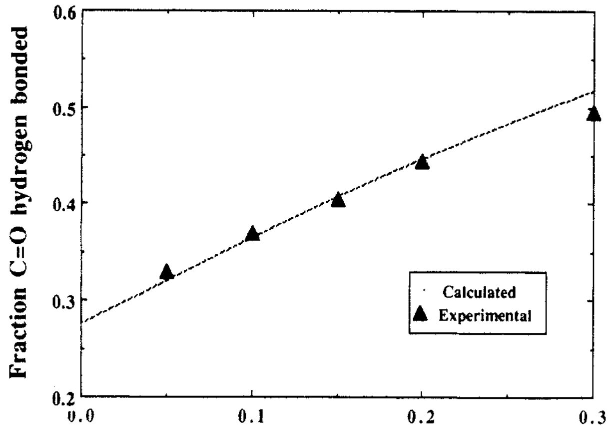

Figure 7. Comparison of experimental data to the theoretical curve calculated from the stoichiometric equations employing the value of K_C = 33.0 at 150 °C for PVPh-PMMA-PEO blends where Φ_{PMMA} is fixed at 0.7.

bonded methacrylate carbonyl groups agrees with the experimentally determined infrared analysis. Quantitative results for blends containing a constant volume fraction of PVPh (Φ_B = 0.7) are reported in Table III and compared to the theoretical curve, which we emphasize was calculated from eqs 4–6 with no adjustable parameters, in Figure 7. It can be seen that the agreement between the theoretical curve and experimental results is excellent, which implies that these blends are homogeneous and increases our confidence in the experimentally determined value of K_C.

Miscibility Windows for PEO with Vinylphenol Copolymers. With the methodology described previously,[1] it is a simple task to employ the new PVPh-PEO interassociation equilibrium constant to calculate miscibility windows and ask the question, "how much vinylphenol must one introduce (copolymerize) into, for example, polystyrene (PS), polybutadiene (PBD), or polyethylene (PE), in order to produce a miscible polymer blend with PEO in the amorphous state at 150 °C?" Such a calculation leads to a *prediction* that <1 wt % VPh is necessary in the case of PS and between 10 and 12 wt % for PBD and PE.

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