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Compositional Heterogeneities in Hydrogen-Bonded Polymer Blends: Infrared Spectroscopic Results

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ABSTRACT: The equilibrium constants describing phenolic OH/ester carbonyl hydrogen bonds are experimentally determined for polymer blends, mixtures of low molecular weight analogues of the polymer repeat units, solutions of the polymers in the low molecular weight analogues, and random copolymers of the original blend segments. These equilibrium constants are determined by infrared spectroscopy, and it is demonstrated that the interactions in the low molecular weight analogues and polymer solutions are (within error) described by the same equilibrium constant. The blend equilibrium constant has a value that is much smaller (about 25% of the solution value), while the copolymer value is intermediate between these two extremes. We propose that this large difference is due to compositional heterogeneities in the blend.

Introduction

We have known for some time, and in fact have emphasized in recent publications,[1-6] that it is necessary to determine a *set* of equilibrium constants describing self-association and interassociation from an appropriate *single-phase polymer blend* to successfully employ the equations and methodology we have developed to predict phase diagrams, miscibility windows, and maps of polymer blend systems involving the same type of specific interactions.[1] In other words, we have known that the values of the equilibrium constants determined from the fraction of hydrogen-bonded groups in mixtures of low molecular weight model analogues, e.g., 4-ethylphenol (EPh) and ethyl isobutyrate (EIB), were significantly different from those determined in the comparable miscible polymer blend, i.e., poly(4-vinylphenol) (PVPh) and poly(ethyl methacrylate) (PEMA). It was simply not possible to transfer a set of equilibrium constants derived from low molecular weight analogues to the polymer blends and obtain accurate calculations of phase behavior. Even a cursory comparison of the infrared spectra of mixtures of EPh–EIB and PVPh–PEMA (Figure 1) in the carbonyl stretching region will convince the reader that the equilibrium fraction of hydrogen-bonded groups is far greater in the former, for equivalent compositions at the same temperature.

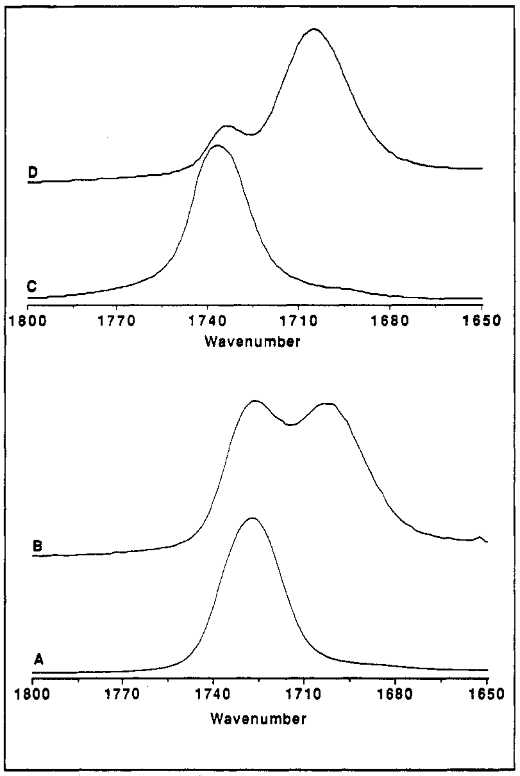

Figure 1. Infrared spectra recorded at room temperature in the carbonyl stretching region (1650–1800 cm^{-1}): (A) PEMA; (B) 71:29 wt % PVPh/PEMA blend; (C) EIB; (D) 70:30 wt % EPh/EIB mixture.

We found these results to be surprising, but when we employed equilibrium constants derived from single-phase polymer blend systems in our equations for the free energy of mixing,[1] the predicted miscibility windows and maps for a wide variety of polymer blends[1-7] were found to be in truly excellent agreement with experimental observations. This success convinced us that our approach was valid and that the nontransferability of the low molecular weight equilibrium constants was most probably attributed to factors such as chain stiffness, connectivity, etc. We reasoned that by determining the equilibrium constants from a single-phase mixture of two polymers we had incorporated these aforementioned factors and this was why our methodology worked so well. While this may still be essentially true, new experimental infrared data obtained from *copolymers* containing two specific interacting sites, one a hydrogen bond donor and the other an acceptor, such as poly(4-vinylphenol-*co*-ethyl methacrylate), reveal that the fraction of hydrogen-bonded carbonyl groups for comparable compositions lies between those of the low molecular materials and polymer blends (i.e., the EPh–EIB and PVPh–PEMA systems). Accordingly, this leads to the *apparent* conclusion that equilibrium constants determined from such copolymers also cannot be directly transferred to polymer blends.

Having different sets of equilibrium constants for low molecular weight molecules, copolymers, and polymer blends is not only unfortunate, in that it complicates the application of spectroscopy to the determination of parameters for the calculation of phase behavior, but it is also troubling on fundamental grounds. Some differences would be expected, due to the factors mentioned above, but as we will show in this paper, the variations are very

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Table 1. Polymers Employed

polymer	composition (wt %) EMA	VPh	M_n	T_g (°C)
PVPh	0	100	17000	170
PEMA	100	0	19000	67
EMAVPh[27]	73	27	16000	108
EMAVPh[39]	61	39	15000	127
EMAVPh[55]	45	55	13000	147
EMAVPh[71]	29	71	10000	156

large. For example, the equilibrium constant describing phenolic hydroxyl/ester carbonyl hydrogen bonds in random copolymers if of the order of twice the value found in miscible blends of homopolymers of the same chemical units. We would not have anticipated such major differences between what are very similar systems, and the result, although unequivocal, appears disconcerting. This suggests that there is some fundamental factor that we have neglected in our treatment so far. Coincidentally, at the same time that we were obtaining these experimental results, we discovered an inconsistency in the reference state chosen for our model—a model which paradoxically predicts the observed phase behavior of hydrogen-bonded polymer blends uncommonly well. Ironically, correcting the reference state yields calculated free energies that are very different, and the prediction of the phase behavior is totally at odds with experimental observation. What we believe has occurred is that our initial choice of reference state, originally made on semiempirical grounds (as discussed in 1), is compensating for the effect of compositional heterogeneities. The presence of compositional heterogeneities leads to a decrease in the fraction of hydrogen bonds formed between phenolic hydroxyl and ester carbonyl groups which, in turn, leads to calculated values of equilibrium constants that are very different for the various systems.

We have formulated a theory to account for compositional heterogeneities and long-range correlations in hydrogen-bonded polymer blends, and this is presented in a separate paper.[8] Here we will present the experimental results that serves as the primary driving force for this work. We will show that equilibrium constants determined for low molecular weight analogues and their mixtures with polymers are the same within experimental error, indicating that for these types of mixtures (phenol/ester polymer solutions) the effect of chain connectivity and stiffness is minimal. However, the corresponding equilibrium constants determined for random copolymers of equivalent units and analogous homopolymer blends are significantly different.

Experimental Section

4-Ethylphenol (EPh) and ethyl isobutyrate (EIB) were purchased from Aldrich and used without further purification. The former is a crystalline solid at ambient temperature and pressure with a melting point of 44 °C, while the latter is a liquid with a boiling point of 112 °C. Poly(4-vinylphenol) (PVPh) and four poly(ethyl methacrylate-*co*-4-vinylphenol) (EMAVPh) copolymers containing 27, 39, 55, and 71 wt% VPh (denoted EMAVPh[27], EMAVPh[39], etc.) were synthesized by solution free radical polymerization of, respectively, pure 4-(*tert*-butyldimethylsilyl)oxy)styrene (tBSOS) or appropriate mixtures of tBSOS and ethyl methacrylate, followed by selective removal of the *tert*-butyldimethylsilyl protective group. Details of the synthesis and the characterization of the copolymers have been reported elsewhere.[9] Poly(ethyl methacrylate) (PEMA) was synthesized by group transfer polymerization.[7b] A summary of the important physical characteristics of the above polymers is given in Table 1.

The PVPh/PEMA blends of various compositions were prepared by codissolving appropriate amounts of the components in methyl ethyl ketone (MEK) to yield a 1% (w/v) solution. Similarly, the EMAVPh copolymers were dissolved in MEK to yield a 1% (w/v) solution. Thin films for FTIR studies were obtained by casting the solutions onto potassium bromide (KBr) windows at room temperature. The solvent was allowed to evaporate slowly under ambient temperature for 24 h. These samples were then dried in a vacuum oven at 110 °C for *ca.* 4 h to completely remove the residual solvent. To minimize water absorption, samples were stored in a vacuum desiccator.

Polymer solutions of PVPh and EIB with low concentration of PVPh were prepared by directly mixing appropriate amounts of PVPh and EIB. FTIR samples were obtained by "sandwiching" the mixtures between two KBr windows, which were sealed around the edges with Teflon tape to minimize evaporation. It was quickly determined that conventional vertical mounting of the KBr "sandwich" in the FTIR spectrometer was unsuitable. Preliminary experiments with the PVPh/EIB mixtures revealed that the sample flowed significantly with time and temperature, precluding accurate quantitative measurements. Accordingly, we purchased a custom-designed transmission accessory (Harrick Scientific Corp.) that permits the sample to be mounted horizontally in the FTIR spectrometer. This accessory works admirably and in preparatory tests we determined from different liquid samples that there were no measurable changes in the amount of sample in the infrared beam and no compositional changes for periods of up to at least 30 min. PVPh/EIB blends with higher PVPh concentrations (>35% by weight) resemble plasticized gels and were prepared as follows. In a covered vial, a mixture of PVPh/EIB with an initial composition of 35 wt% was stirred for 24 h to ensure complete mixing. After a precalculated amount of EIB was removed by evaporation, the remaining PVPh/EIB mixture of known composition was sampled and placed between two KBr windows as described above. This procedure was then repeated to give mixtures of varying composition. After an initial learning period, the reproducibility of this method was found to be remarkably good.

EPh/EIB mixtures ov varying composition were prepared by directly mixing appropriate amounts of EPh and EIB. Conventional liquid cells could not be employed for quantitative analysis, however, because they are not manufactured with sufficiently narrow path lengths to produce infrared spectra in the carbonyl stretching region that have absorbance values in a range where the Beer–Lambert law is obeyed (≈0.2–0.6 absorbance units). Thus samples were prepared in a similar manner to the dilute PVPh/EIB polymer solutions described above.

Infrared spectroscopic measurements were recorded on Digilab Model FTS-45 and FTS-60 Fourier transforma infrared (FTIR) spectrometers at a resolution of 2 cm^{-1}. Spectra recorded at elevated temperature were obtained using a heating cell mounted inside the sample chamber. Temperature was regulated by a Micristar 828D digital process controller, which has a reported accuracy of ±0.1 °C. Special attention was paid to ensure that all FTIR samples were sufficiently thin to be within the absorption range where the Beer–Lambert law is obeyed. 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 was used, and the glass transition temperature were recorded as the midpoint of the heat capacity change.

Results and Discussion

Before we become embroiled in the details of our results, it is worthwhile reiterating the main objective of the experiments described in this work. As mentioned in the Introduction, we have known qualitatively that the equilibrium fraction of hydrogen-bonded carbonyl groups formed in (say) a single-phase PVPh and PEMA blend of a particular composition and termperature is considerably less than that of two very similar low molecular analogues, in this case, EPh and EIB. As one can see from Figure 2, EPh and EIB are almost ideal models for PVPh and PEMA.[10,11] Furthermore, we have recently synthesized EMAVPh copolymers[9] and noticed that the equilibrium fraction of hydrogen bonds formed appears to be inter-

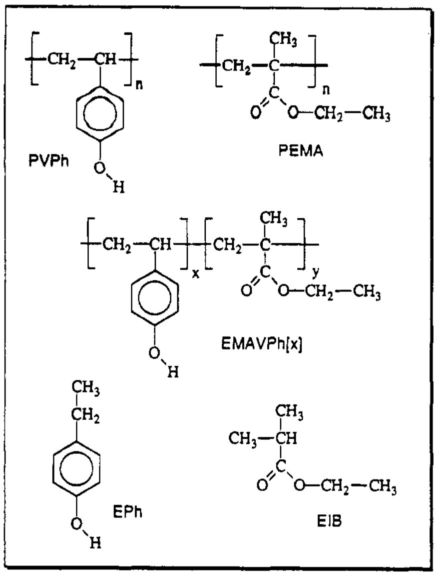

Figure 2. Chemical structures.

mediate between those of PVPh/PEMA blends and EPh/EIB mixtures of comparable composition. This we had not anticipated. While we had previously rationalized that there should be differences in the fraction of hydrogen-bonded carbonyl groups (or the corresponding values of the equilibrium constants describing the distribution of hydrogen-bonded species) between the high molecular weight polymer blend and two low molecular weight analogs, we did not expect the copolymer result.[12] This brings up another question. What would one expect in the case of concentrated mixtures of a strongly self-associated polymer and low molecular weight solvent, for example, PVPh and EIB? We had not studied such systems, primarily because we had not recognized the implications of our results but also because sample preparation for quantitative infrared analysis is far from trivial. Necessity is the mother of invention, however, and using the experimental infrared methodology described above, we obtained reproducible quantitative data on all four systems, and these can be used to test various theoretical hypotheses. This is what we will now describe, starting first with the PVPh/PEMA blends, followed by the EMAVPh copolymers, the PVPh/EIB polymer solutions, and finally the EPh/EIB mixtures.

In previous work[1,7a-c] we have described in detail the infrared spectra that are obtained from PVPh-poly(*n*-alkyl methacrylate) blends and the methodology used to calculate the fraction of free ($f_F^{C=O}$) or hydrogen-bonded ($f_{HB}^{C=O} = (1 - f_F^{C=O})$ carbonyl groups in a blend at any particular concentration and temperature. We will assume that the reader is familiar with this work and only briefly mention the salient points in passing. PVPh-PEMA blends were first examined in detail by Serman et al.,[7a] who determined the equilibrium fraction of hydrogen-bonded carbonyl groups as a function of composition and temperature.[7a,13] Using these results, values of the equilibrium constant describing the interassociation of phenolic hydroxyls to methacrylate carbonyl groups, K_A, were calculated at different temperatures from a least squares fit of the stoichiometric equations.[1] The enthalpy of hydrogen bond formation was determined to be $h_A = 3.8$ kcal/mol, and assuming adherence to the van't Hoff relationship, $K_A = 37.1$ at 25 °C. [Note that in this methodology we employed values of the equilibrium constants describing the self-association of PVPh at 25 °C, $K_2 = 21.0$ and $K_B = 66.8$, together with the enthalpies of hydrogen bond formation, $h_2 = 5.6$ and $h_B = 5.2$ kcal/mol, which were obtained from studies of phenol mixtures and were held constant in the least squares fit.[1]]

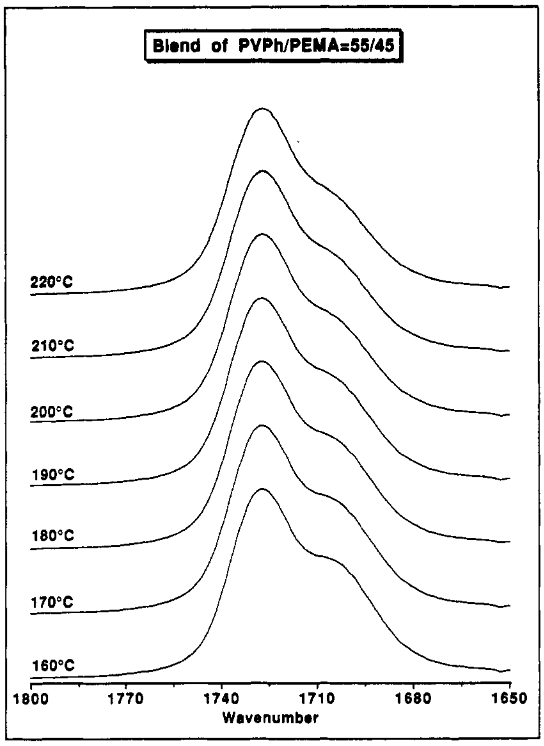

Figure 3. Infrared spectra of a 55:45 wt % PVPh/PEMA blend film recorded between 160 and 220 °C in the carbonyl stretching region.

Given the nature of this present study, it was deemed important to independently test the reliability and precision of our measurements by repeating the above experiments using completely different polymer samples (Table 1). Figure 3 shows representative examples of infrared spectra in the carbonyl stretching region obtained from a 55:45 mol % PVPh-PEMA blend sample and recorded at temperatures from 160 to 220 °C (above the T_g of the blend). Briefly, the band at ≈1729 cm^{-1} corresponds to "free" (non-hydrogen-bonded) carbonyl groups, while that at ≈1705 cm^{-1} is attributed to hydrogen-bonded carbonyl groups. Table 2 summarizes the curve-fitting results for four different blend compositions (the reason for the choice of these particular blend compositions will become clear later when we discuss the analogous EMAVPh copolymer). Using these data, values of $K_A = 38.4$ and $h_A = 4.1$ kcal/mol were obtained, which are in good agreement with results of Serman. From this and other studies, we estimate that under favorable conditions, i.e., when the bands attributed to "free" and hydrogen-bonded carbonyl groups are separated into two well-resolved bands, the error in K_A and h_A is less than 5 and 10%, respectively.

Similar studies were performed on films of the EMAVPh copolymers containing the same mole ratio of EMA:VPh as the polymer blends discussed above. Figure 4 shows representative spectra obtained from the EMAVPh[55] copolymer recorded at temperatures from 160 to 220 °C, and these can be directly compared to the blend spectra shown in Figure 3. It is immediately apparent that the fraction of hydrogen-bonded carbonyl groups is greater in the copolymer case at any particular temperature. Quantitative results are presented in Table 3, from which K_A was determined as a function of temperature, yielding values of $h_A = 4.2$ kcal/mol and $K_A = 67.4$ at 25 °C. Thus, all other things being equal, the interassociation equilibrium for the copolymer is some 1.8 times that of the blend

Table 2. Curve-Fitting Results for PVPh/PEMA Blends

temp	free C=O band			hydrogen-bonded C=O band			
(°C)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	area	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	area	$f_F^{C=O}$
PVPh/PEMA = 27/73							
150	1729	21.8	17.9	1705	30.0	9.33	0.742
160	1729	21.9	17.8	1705	30.4	9.23	0.742
170	1729	21.9	17.6	1705	30.6	9.12	0.743
180	1729	22.1	17.7	1705	30.5	8.96	0.748
190	1729	22.2	17.8	1705	30.3	8.71	0.753
200	1729	22.4	17.8	1706	30.6	8.66	0.755
210	1729	22.4	17.8	1706	30.6	8.66	0.755
220	1729	22.5	17.6	1706	30.8	8.40	0.761
PVPh/PEMA = 39/61							
150	1729	22.0	14.6	1705	29.8	8.03	0.721
160	1729	22.2	14.4	1705	29.7	8.31	0.723
170	1729	22.3	14.4	1705	29.7	8.06	0.728
180	1729	22.4	14.4	1705	29.9	7.93	0.732
190	1729	22.6	14.6	1705	29.5	7.57	0.743
200	1729	22.6	14.6	1706	29.8	7.45	0.745
210	1729	22.7	14.6	1706	29.9	7.12	0.752
220	1729	22.8	14.7	1706	30.3	7.06	0.757
PVPh/PEMA = 55/45							
150	1729	21.5	9.54	1705	30.0	8.91	0.616
160	1729	21.6	9.54	1705	30.1	8.75	0.621
170	1729	21.7	9.56	1705	30.3	8.61	0.625
180	1729	21.9	9.63	1705	30.4	8.45	0.631
190	1729	21.9	9.56	1705	30.7	8.33	0.632
200	1729	22.1	9.62	1706	31.0	8.21	0.637
210	1729	22.2	9.67	1706	31.3	8.09	0.641
220	1729	22.3	9.69	1706	31.4	7.86	0.649
PVPh/PEMA = 71/29							
150	1728	20.1	1.93	1704	30.8	3.08	0.482
160	1728	20.4	2.00	1704	31.5	3.19	0.483
170	1728	20.1	1.90	1704	31.0	3.03	0.484
180	1728	20.3	1.95	1704	31.6	2.96	0.496
190	1728	20.6	1.97	1704	31.9	2.92	0.503
200	1728	20.8	2.02	1705	31.4	2.81	0.518
210	1728	21.2	2.10	1705	31.6	2.76	0.533
220	1728	21.3	2.13	1705	31.6	2.69	0.543

at 25 °C. Note that the enthalpy of hydrogen bond formation is within error the same, which is consistent with the comparable differences in the frequency of the free and hydrogen-bonded carbonyl bands ($\Delta\nu \approx 24$ cm^{-1}). This means that although the "strength" (enthalpy) of the phenolic OH/methacrylate carbonyl hydrogen bond is the same, the *number* of hydrogen bonds formed in a mixture of identical composition is very different.

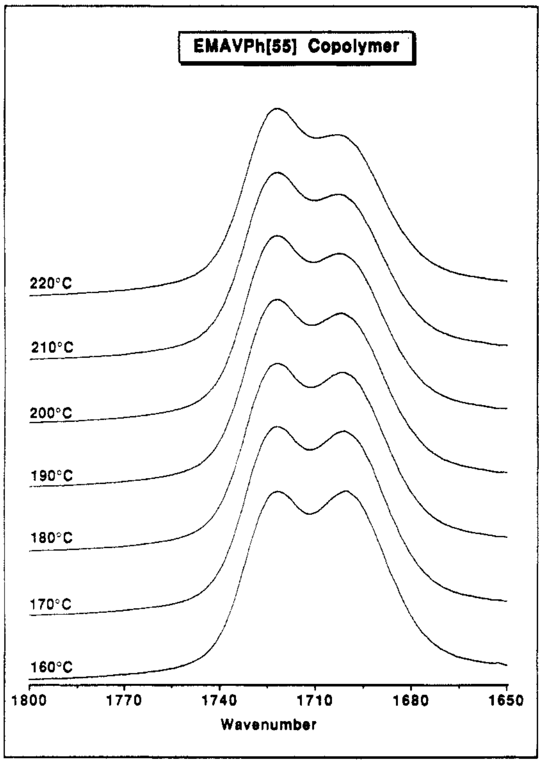

Figure 4. Infrared spectra of EMAVPh[55] copolymer film recorded between 160 and 220 °C in the carbonyl stretching region.

Table 3. Curve-Fitting Results for EMAVPh Copolymers

temp	free C=O band			hydrogen-bonded C=O band			
(°C)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	area	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	area	$f_F^{C=O}$
EMAVPh[27]							
160	1727	21.2	5.52	1703	28.0	2.79	0.748
170	1727	20.4	5.04	1703	28.0	2.47	0.753
180	1727	20.4	4.98	1704	28.0	2.42	0.755
190	1727	20.1	4.74	1704	28.0	2.27	0.758
200	1727	20.1	4.72	1705	28.0	2.23	0.761
210	1727	20.0	4.63	1705	28.0	2.16	0.763
220	1727	20.5	4.85	1705	28.0	2.20	0.768
EMAVPh[39]							
160	1726	20.5	7.31	1702	29.8	6.58	0.625
170	1726	20.5	7.31	1702	29.8	6.41	0.630
180	1726	20.8	7.34	1703	29.4	6.26	0.641
190	1726	20.8	7.37	1703	29.6	6.11	0.644
200	1726	20.9	7.41	1703	29.6	6.11	0.646
210	1726	21.0	7.48	1703	29.7	6.04	0.650
220	1726	21.1	7.53	1703	29.7	5.92	0.656
EMAVPh[55]							
160	1725	20.7	5.86	1700	29.2	9.60	0.478
170	1725	20.6	5.86	1700	29.2	9.45	0.482
180	1725	20.6	5.88	1700	29.6	9.39	0.484
190	1725	20.8	5.96	1700	29.5	9.08	0.496
200	1725	20.9	6.03	1700	29.7	9.01	0.501
210	1725	21.0	6.08	1701	29.9	8.82	0.508
220	1725	21.1	6.13	1701	29.9	8.59	0.517
EMAVPh[71]							
160	1724	20.0	2.43	1699	28.7	5.71	0.390
170	1724	20.4	5.49	1699	28.2	5.49	0.410
180	1724	20.3	2.53	1699	28.5	5.40	0.413
190	1724	20.3	2.57	1699	28.7	5.35	0.419
200	1724	20.4	2.61	1700	28.7	5.19	0.430
210	1724	20.6	2.70	1700	28.9	5.14	0.438
220	1724	20.5	2.73	1700	29.1	5.05	0.448

The next set of infrared spectra (Figure 5) are of PVPh/EIB mixtures of varying composition recorded at room temperature. The top two spectra are of mixtures containing 50 and 60% PVPh and are thus roughly equivalent in composition to the 55:45 PVPh/PEMA blend and EMAVPh[55] copolymer samples shown, respectively, in Figures 3 and 4. Again, it is immediately clear that the fraction of hydrogen-bonded carbonyl groups has apparently increased significantly over that of the analogous copolymer and blend of the same composition. [Unfortunately, we cannot obtain reproducible spectra of the polymer/solvent mixtures at 150 °C and above with which to compare directly to the spectra of the blend and copolymer. Conversely, spectra recorded at room temperature of the copolymer or blend will not reflect the true equilibrium fraction of hydrogen-bonded carbonyl groups because the T_g's of these materials are above room temperature. However, knowing that $h_A \approx 4.1$ kcal/mol, we can extrapolate from 150 °C to room temperature and calculate the equilibrium fraction of hydrogen-bonded carbonyls for the case of the blend or copolymer. This adjustment is minimal compared to the large difference noted in the spectra of the PVPh/EIB mixtures.] Quantitative results are presented in Table 4. A values of K_A = 168 at 25 °C was determined using the least squares methodology described above. This is approximately 4.4 times the magnitude determined for the PVPh/PEMA

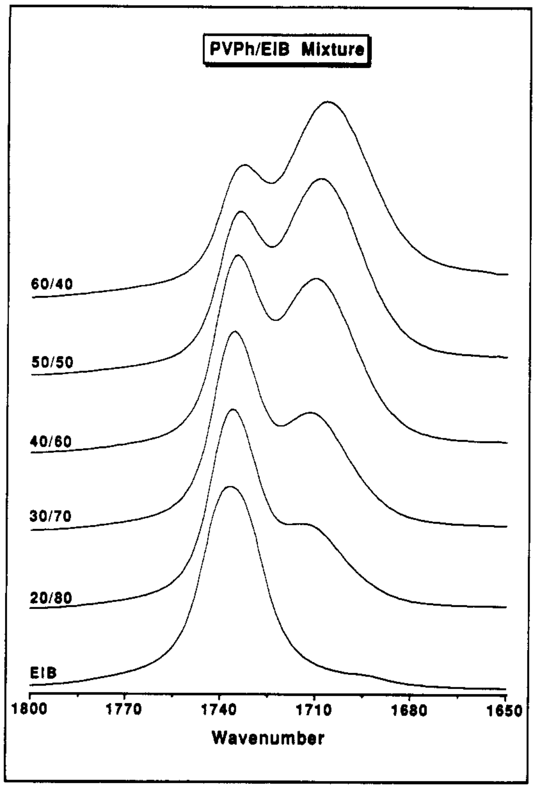

Figure 5. Infrared spectra of PVPh/EIB mixtures of different compositions recorded at room temperature in the carbonyl stretching region.

Table 4. Curve-Fitting Results for PVPh/EIB Mixtures at Room Temperature

	free C=O band			hydrogen-bonded C=O band			
comp (by weight)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	area	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	area	$f_F^{C=O}$
20/80	1737	17	15.95	1713	28	11.98	0.666
30/70	1737	17	13.21	1712	29	14.70	0.574
35/65	1737	17	14.47	1712	29	17.07	0.560
40/60	1736	17	10.33	1710	29	17.66	0.468
50/50	1736	17	5.23	1708	30	13.13	0.374
60/40	1735	16	8.89	1707	31	29.96	0.308
65/35	1735	16	3.99	1706	30	17.51	0.255

blend and about 2.5 times that of the copolymer. [Note that there are some subtleties in curve resolving the spectra of the free EIB band, as its band shape is closer to that of a Lorentzian rather than the Gaussian found in the polymer spectra. However, the integrated absorption coefficient also changes in almost direct proportion to the change in overall band area, so that by fitting to a Gaussian we can use our previously determined ratio of the integrated absorption coefficients,[1] a_R. We will present a more complete account of these subtleties and how they can be dealt with in a future publication.]

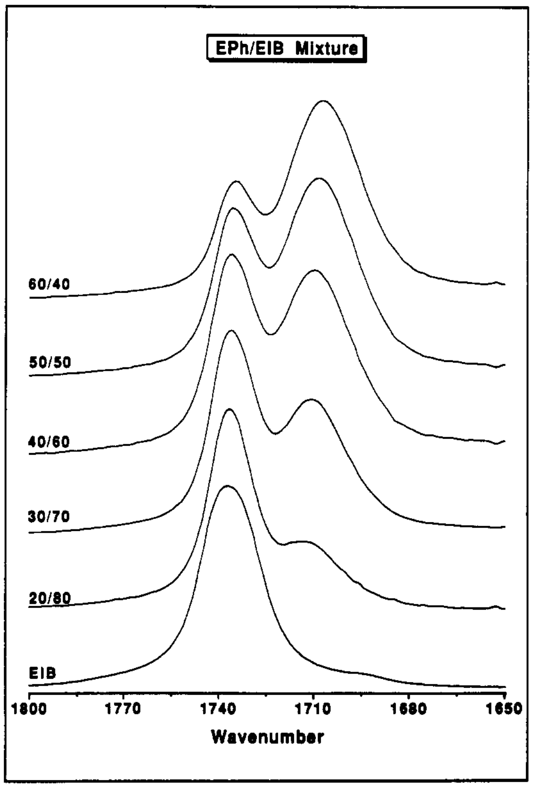

Figure 6. Infrared spectra of EPh/EIB mixtures of different compositions recorded at room temperature in the carbonyl stretching region.

Table 5. Curve-Fitting Results for EPh/EIB Solutions at Room Temperature

	free C=O band			hydrogen-bonded C=O band			
comp (by weight)	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	area	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	area	$f_F^{C=O}$
90/10	1734	17[a]	1.140	1703[a]	25	12.15	0.123
80/20	1735	16	1.955	1704	26	13.38	0.180
70/30	1735	16	1.877	1705	27	9.829	0.223
60/40	1736	15	3.380	1707	27	11.68	0.303
50/50	1736	16	5.346	1708	27	11.97	0.398
40/60	1737	16	3.526	1710	27	5.899	0.473
30/70	1737	16	9.283	1712	26	9.216	0.602
20/80	1737	16	10.91	1712[a]	26[a]	7.588	0.731

[a] Fixed parameters.

Finally, representative room temperature infrared spectra of the EPh/EIB low molecular weight mixtures as a function of composition are shown in Figure 6, and quantitative results are presented in Table 5. We must be careful, however, not to make simple direct comparisons of these spectra to those of the blends, copolymers, and polymer solutions of comparable concentrations (Figures 3–5), as this can be rather misleading. The molar volume of the VPh segment (100 cm^3/mol) that we employ for PVPh homopolymer and the EMAVPh copolymers is significantly different from that of the EPh molecule (130 cm^3/mol), and this we must take into account when calculating equilibrium constants and the fraction of hydrogen-bonded carbonyl groups. The dimensionless equilibrium constants describing the self-association of EPh at 25 °C (K_2 = 16.2 and K_B = 51.4) are readily calculated from[1]

$$K^{\mathrm{EPh}} = K^{\mathrm{VPh}}\left[\frac{V^{\mathrm{VPh}}}{V^{\mathrm{EPh}}}\right] \tag{1}$$

Holding these values constant and using the least squares procedure to obtain the best fit of the stoichiometric equations to the fraction of "free" carbonyl groups (Table 5), we obtain a value for K_A = 132 at 25 °C (see Figure 7). Now, in order to directly compare the magnitude of K_A to those we have determined for the PVPh/PEMA blend, the EMAVPh copolymer, and the PVPh/EIB polymer solution, we need to again employ eq 1 and scale to the common reference volume, V_B = 100 cm^3/mol. The yields a value of K_A = 172 at 25 °C, which is remarkably close, and certainly within error, of the value obtained for the PVPh/EIB mixtures (K_A = 168). Accordingly, connecting vinylphenol units into a polymer chain has a minimal effect on the ability of the hydroxyl group to hydrogen bond to the carbonyl group of a low molecular weight ester.

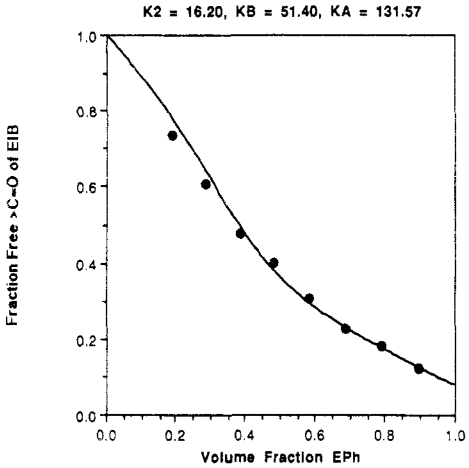

Figure 7. Graph showing the least squares fitting of the stoichiometric equations to experimental results for the determination of K_A for EPh/EIB mixtures.

Table 6. Summary of the Values of K_A at 25 °C[a]

system	description	K_A (dimensionless)
polymer blend	PVPh/PEMA	38.4
copolymer	EMAVPh	67.4
polymer solution	PVPh/EIB	168
solvent/solvent	EPh/EIB	172

[a] K_2 = 21.0, K_B = 66.8, and V_B = 100 cm^3/mol.

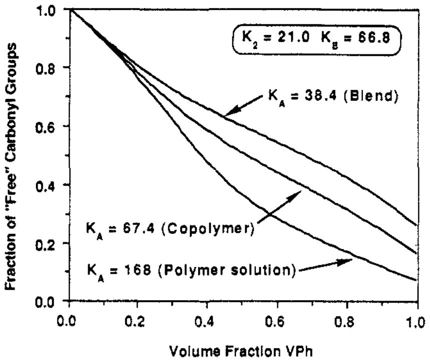

Figure 8. Calculated theoretical fraction of free carbonyl groups at 25 °C as a function of volume fraction of VPh for PVPh/PEMA blends, EMAVPh copolymers, and PVPh/EIB polymer solutions.

Table 6 summarizes the values of K_A (all based upon the common reference volume of V_B = 100 cm^3/mol), which correspond to the interassociation equilibrium constants of phenolic hydroxyl to methacrylate carbonyl groups for PVPh/PEMA polymer blends, EMAVPh copolymers, PVPh/EIB polymer solutions, and EPh/EIB solvent mixtures. Using these values of K_A together with the PVPh self-association equilibrium constants (K_2 and K_B), we can readily calculate the theoretical fraction of hydrogen-bonded carbonyl groups at 25 °C as a function of the volume fraction of VPh segments[1,7] (Φ_B) for all the different systems, and this is illustrated in Figure 8. At 50 vol %, for example, the fraction of hydrogen-bonded carbonyl groups in the PVPh/PEMA blend is calculated to be ≈40%, in the EMAVPh[50] copolymer ≈50%, and in the PVPh/EIB polymer solution ≈63%. As we will discuss elsewhere, we believe that these differences are a manifestation of compositional heterogeneities in hydrogen-bonding polymer systems.[8]

Table 7. Glass Transition Temperatures for EMAVPH Copolymers and PVPh/PEMA Blends

composition (weight ratio)	T_g (DSC, °C) exptl	T_g (DSC, °C) theor[a]
Copolymers		
EMAVPh[27]	108	111
EMAVPh[39]	127	127
EMAVPh[55]	147	145
EMAVPh[71]	156	155
Blends		
27:73 PVPh/PEMA	100	104
39:61 PVPh/PEMA	117	120
55:45 PVPh/PEMA	133	135
71:29 PVPh/PEMA	153	153

[a] Calculated from eq 2.

Comparison of the Glass Transition Temperatures of PVPh/PEMA Blends to the Analogous EMAVPh Copolymers. In two recent publications we have described an equation for the compositional dependence of the T_g for miscible polymer blends and copolymers that involve hydrogen bonds:[14,15]

$$T_{g_m} = \frac{X_A T_{g_A} + k X_B T_{g_B}}{X_A + k X_B} + X_A X_B (q_m'(X) + q_B'(T)) \qquad (2)$$

where T_{g_m}, T_{g_A}, and T_{g_B} are the glass transition temperatures of the mixture and the pure A and B components, respectively. X_A and X_B are the mole fractions, k is the ratio of the specific heat increments ($\Delta C_{p_B}/\Delta C_{p_A}$), $q_m'(X)$ is a composition-dependent term that depends on the contribution of hydrogen-bonding interactions to the liquid-state heat of mixing, and q_B' (T) represents the contribution from the change in liquid-state specific heat of the self-associating polymer (B) on going from T_{g_B} to T_{g_m}. This last term is significant in polymers that self-associate. To use this equation we require the T_g's and the difference in heat capacity (ΔC_p), liquid minus glass[14], of the pure polymers, PVPh and PEMA; the molar volumes of the "specific repeats" of the two segments; the two equilibrium constants that describe self-association of VPh, K_2 and K_B; the equilibrium constant that describes interassociation between phenolic hydroxyl and methacrylate carbonyl groups (K_A); and corresponding enthalpies of hydrogen bond formation (h_2, h_B, and h_A).[1]

This leads to a rather interesting prediction. If K_A has the same value for the PVPh/PEMA blends as the EMAVPh copolymer, then the T_g of a copolymer of a specific composition should be identical to that of the polymer blend of the same composition. But we have demonstrated above that the value of K_A for the PVPh/PEMA blends (K_A = 38.4) is significantly different from that of the EMAVPh copolymer (K_A = 67.4), which implies that the experimentally observed T_g's for PVPh/PEMA blends and EMAVPh copolymers of the same VPh:EMA composition should be different. This can be readily tested, since we have already prepared PVPh/PEMA blend samples of the same composition as the EMAVPh copolymers that were synthesized. Table 7 lists the results obtained from thermal analysis together with the predicted T_g's calculated using 2. First, note that there is a significant difference in the T_g's of the blend and copolymer at comparable compositions, especially in the intermediate composition range. For example, the experimentally observed T_g of the 55:45 PVPh/PEMA blend is some 14 °C lower than that of the comparable EMAVPh[55] copolymer, which is outside the bounds of experimental error. Second, the theoretically calculated values of T_g, using eq 2 with the appropriate values of K_A for the blend and copolymer, are in very good agreement with experiment (the maximum difference being only 4 °C). Finally, we present in Figure 9 the experimental results superimposed upon the theoretical curves showing the calculated compositional dependence of the T_g for the PVPh/PEMA

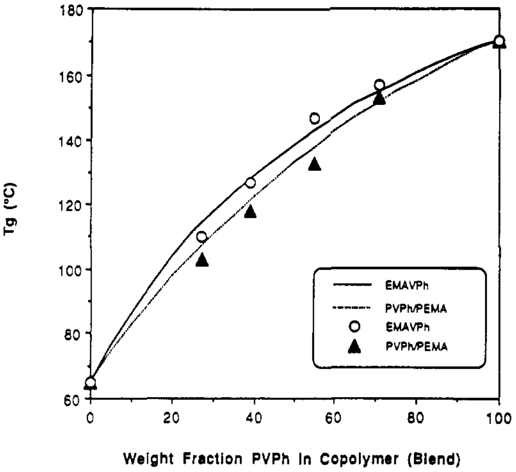

Figure 9. Comparison of the experimentally determined T_g's for (▲) PVPh/PEMA blends and (○) EMAVPh copolymers to the theoretical curves calculated using K_A values of 38.4 and 67.4, respectively.

blends and EMAVPh copolymers. We stress that these curves are calculated without using any adjustable parameters.

Conclusions and Ramifications

The results presented here suggest that the nature of hydrogen bonding in polymeric materials involves additional complexities. One would expect some differences between polymers and their low molecular weight analogues as a result of various factors. There are three obvious ones, the first of which is steric. Chain connectivity might limit the accessibility of a functional group in a polymer relative to its low molecular weight analogue. The second factor introduced by connectivity involves rotational freedom. If the two immediate same chain neighbors of a particular segment are hydrogen bonded to other units, then this central segment may not have the freedom to orient itself to form hydrogen bonds to any of its neighbors that happen to have appropriate functional groups. The third factor is a consequence of the entropy changes that occur upon hydrogen bond formation. In low molecular weight materials the formation of hydrogen bonds leads to a loss of rotational freedom of the molecule as a whole, while in polymers there is a loss of internal degrees of rotational freedom (i.e., rotations around backbone bonds). All of these factors would lead to a difference in the number of hydrogen bonds formed between polymers and equivalent concentrations of low molecular weight species (note that the hydrogen bonds that do form might have the same enthalpy or "strength"). These effects appear to be minimal, however, when only one of the components is a polymer (at least in PVPh systems). The results presented in this paper show that the equilibrium constants describing the distribution of hydrogen bonds in PVPh/EIB solutions are within error identical to those describing EPh/EIB mixtures. We do assume that self-association of both PVPh and EPh is governed by the equilibrium constants taken originally from phenol, but it is a relatively easy matter to show that in reproducing the observed infrared spectroscopic results it is the *ratio* of equilibrium constants that is important (i.e., K_A/K_B).

In polymer blends, the situation appears to be completely different. Self-association in pure PVPh (B units) must remain the same, but once we connect the A units into chains we see a significant decrease in the number of B- - -A hydrogen bonds formed, which is reflected in a dramatic change in the calculated value of K_A. Essentially, we absorb all changes into this parameter, calculated by fitting the equations for the stoichiometry of hydrogen bonding to the observed infrared results. The fact that K_A (or, more precisely, K_A/K_B) is so different for the polymer blends relative to the analogous polymer solutions demonstrates that there is some major effect (or effects) that reduces the number of B- - -A hydrogen bonds in the blend. Certainly part of this effect may be related to the steric and rotational freedom factors mentioned at the start of this discussion. We would expect that there would be only minor differences between the polymer blends and corresponding random copolymers, however, but the calculated values of K_A differ by a factor of almost 2. Accordingly, we suggest that at least in part the observed differences are due to compositional heterogeneities.

In polymer blends, compositional heterogeneities can arise in two ways, from intramolecular or intermolecular factors. The former is a consequence of chain connectivity (in *both* components of the mixture) and would result in a chosen B unit "seeing" a higher than average number of other B units because of enhanced contacts with like units in the same chain.[16] We have called the latter effect, enhanced intermolecular contacts, clustering, and a theoretical description of this phenomenon is described elsewhere.[8] It is linked to long-range correlations that are a result of the combined effect of covalent and hydrogen bond connectivity. In many of the hydrogen-bonded blends we have studied, the value of χ, which we use to describe physical interactions (e.g., dispersive forces) only, is fairly large and positive. Accordingly, if we were to focus our attention on a specific B segment, then a tendency to favor non-hydrogen-bonded or covalently bonded contacts with another B segment directly affects other B- - -B physical contacts in the neighborhood, as each of the two B segments in question are hydrogen bonded to up to four other B units (two covalent, excluding end groups, and up to two hydrogen-bonded B units). The tendency of B units to "cluster" should therefore be cooperative, and the extent of this effect should depend upon χ. Whether we have intermolecular or intramolecular effects, or both, the local composition of B units will be higher than the nominal or overall concentration of B units; *hence the number of B- - -A hydrogen bonds will be lower than in a "random" copolymer or low molecular weight mixture* (obviously there must also be local regions where the composition of A units is higher than average).

There is one final factor that leads us to believe that there are compositional heterogeneities in hydrogen-bonded polymer blends. The model we have employed to calculate the free energy of mixing uses a reference state that was chosen on semiempirical grounds.[1] However, if a more conventional reference state is chosen, then free energies that are totally at odds with observed phase behavior are calculated (positive free energies for miscible systems). In effect, if we use equilibrium constants determined directly from studies of the blend, then the reference state we have chosen in our work compensates for the effect of compositional heterogeneities. A preliminary discussion of this is presented elsewhere[17] and will be explored more completely in future work.

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