Macromolecules 1994, *27*, 245–251

Hydrogen Bonding in Polymer Systems Involving Poly(*p*-vinylphenol). 1. Binary Blends with Poly(ethyl methacrylate-*co*-methyl methacrylate)

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Received March 15, 1993; Revised Manuscript Received July 12, 1993®

ABSTRACT: An association model for describing the thermodynamics of polymer blends with strong directionally specific interactions has been applied to poly(ethyl methacrylate-*co*-methyl methacrylate) (EMA-*co*-MMA)/poly(*p*-vinylphenol) (PVPh) blends. Parameters describing interassociation such as the equilibrium interassociation constant (K_A) and the enthalpy of hydrogen bond formation (h_A) have been obtained from Fourier transform infrared (FTIR) measurements at 165 and 200 °C. Both the temperature range of miscibility and the glass transition–composition curve predicted by the model were found to be in good agreement with experimental results. Also, the magnitude of the enthalpic interaction energy derived in the liquid state for this system is similar to that found for analogue liquid mixtures of the corresponding polymers. Model results suggest that entropic contributions are also very important in determining the miscibility of these systems. Thus, entropic contributions unfavorable to mixing were predicted for the EMA-*co*-MMA/PVPh system, unlike the favorable contributions for the corresponding analogue mixtures.

I. Introduction

The miscibility of polymer blends has been widely interpreted using mean-field treatments such as the Flory–Huggins theory[1,2] or the equation-of-state theories.[3-9] These approaches employ the assumption of a mean field to account for contacts between polymer interacting groups. However, in these treatments, no provision is made for directional-specific interactions, such as hydrogen bonds. Recently, Painter, Coleman, and co-workers have extended the association (physical–chemical) theory of hydrogen-bonding solutions[10,11] to describe the thermodynamics of polymer blends when strong specific interactions are present.[12] The association model employed by these authors is able to reproduce a great variety of phenomena related to blend miscibility. The model allows one to calculate the free energy of mixing as a function of composition and temperature, so phase diagrams, miscibility windows, and maps can be constructed.[13] Also, the composition dependence of the glass transition temperature in the blends as well as the melting point depression of a crystalline polymer caused by the addition of a miscible diluent can be predicted.[14,15] Moreover, this simple model has been applied successfully to obtain the phase diagrams of some rigid-rod/random-coil polymer blends when hydrogen-bonding interactions are present.[16] The general validity of the association model is now supported by the good agreement between theoretical predictions and experimental results in several systems.[13] In particular, PVPh-related blends have been found to be very useful in testing the predictive capabilities of this model.

In this paper, the association model is applied to the EMA-*co*-MMA/PVPh system. Although poly(ethyl methacrylate) (PEMA)/poly(methyl methacrylate) (PMMA) blends are immiscible,[17,18] the molecular constraint imposed by copolymerization prevents macroscopic phase separation (of the random copolymer) when it is blended with PVPh.[19] Conversely, ternary PEMA/PMMA/PVPh blends show phase separation if the PVPh content is lower than 60 wt %.[20] In this work, FTIR spectroscopy is employed to determine several parameters required in the association model such as the equilibrium interassociation constant and the corresponding enthalpy of hydrogen bond formation. A comparison is, then, made between model predictions and experimental observations of phase behavior and glass transition trends. Heat of mixing information from analogue mixtures[20,21] of EMA-*co*-MMA/PVPh blends is also compared to the model predictions for this system. Finally, an estimate of the entropic contributions to the free energy of mixing is also reported for both the analogue mixtures and the polymer blends.

In a second paper, the association model will be extended to ternary polymer blends and applied to the PEMA/PMMA/PVPh system. Hence, an attempt to rationalize the different miscibility behavior of binary EMA-*co*-MMA/PVPh and ternary PEMA/PMMA/PVPh systems will be made in terms of this theoretical approach.

Summary of the Association Model for Binary Systems. In terms of this model, the free energy of mixing two polymers with specific interactions between them is described by the following equation:[13]

$$\frac{\Delta G_m}{RT} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \chi \phi_A \phi_B + \frac{\Delta G_H}{RT} \qquad (1)$$

The first three terms correspond to the well-known Flory–Huggins relationship, but in the association model the interaction parameter χ reflects only the contribution from dispersive and weak polar forces opposing miscibility.[22] The number and the strength of the favorable specific interactions, usually hydrogen bonds, are taken into account by the last term of eq 1. This contribution, for blends containing a self-associating component B and a second component A, which does not but may associate with B, is given explicitly by[13]

$$\frac{\Delta G_H}{RT} = \phi_B \ln\left[\frac{\phi_{B1}}{\phi_{B1}{}^{\circ}\phi_B{}^{1/n_H{}^{\circ}}}\right] + \frac{\phi_A}{r} \ln\left[\frac{\phi_{A1}}{\phi_A}\right] + \phi_B\left[\frac{\Gamma_1{}^{\circ}}{\Gamma_2{}^{\circ}} - \frac{\Gamma_1}{\Gamma_2}\right] + \phi_B\left(\frac{\Gamma_1}{\Gamma_2}\right)\left[\frac{K_A\phi_{A1}/r}{1 + K_A\phi_{A1}/r}\right] \qquad (2)$$

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® Abstract published in *Advance ACS Abstracts*, November 15, 1993.

0024-9297/94/2227-0245$04.50/0

Table I. Description of Polymers and Random Copolymers Used

polymer	weight-average mol wt	source
poly(methyl methacrylate) (PMMA)	108 000[a]	ICI, Diacom Acrylic
poly(ethyl methacrylate-*co*-methyl methacrylate, 40:60) (EMA-*co*-MMA(60))	435 000[a]	Polysciences Inc.
poly(ethyl methacrylate-*co*-methyl methacrylate, 70:30) (EMA-*co*-MMA(30))	370 000[a]	Polysciences Inc.
poly(ethyl methacrylate) (PEMA)	310 000[b]	Du Pont (Elvacite 2042)
poly(*p*-vinylphenol) (PVPh)	30 000[c]	Polysciences Inc.

[a] Determined by GPC. [b] Reference 24. [c] Provided by supplier.

where

$$\Gamma_1 = \left(1 - \frac{K_2}{K_B}\right) + \left(\frac{K_2}{K_B}\right)\left[\frac{1}{1 - K_B\phi_{B1}}\right] \qquad (3)$$

$$\Gamma_2 = \left(1 - \frac{K_2}{K_B}\right) + \left(\frac{K_2}{K_B}\right)\left[\frac{1}{(1 - K_B\phi_{B1})^2}\right] \qquad (4)$$

and

$$n_H^\circ = \Gamma_2^\circ/\Gamma_1^\circ \qquad (5)$$

In addition, the stoichiometry of the system requires

$$\phi_A = \phi_{A1}(1 + K_A\phi_{B1}\Gamma_1) \qquad (6)$$

$$\phi_B = \phi_{B1}\Gamma_2(1 + K_A\phi_{A1}/r) \qquad (7)$$

In the preceding equations, ϕ_A and ϕ_B are the volume fractions of polymers A and B, respectively, ϕ_{A1} and ϕ_{B1} are the volume fractions of the respective repeat units that are not hydrogen bonded, and r is the ratio of molar volumes, V_A/V_B. Parameters corresponding to pure component B are denoted by the superscript 0. K_2 and K_B are the self-association equilibrium constants describing the formation of dimers and n-mers, respectively, and K_A is the interassociation equilibrium constant describing the formation of B_nA complexes.

The entropic (ΔS_m) and enthalpic (ΔH_m) contributions to the free energy of mixing can be calculated in a direct way following fundamental thermodynamic relationships:

$$\Delta S_m = -(\partial \Delta G_m/\partial T) \qquad (8)$$

$$\Delta H_m = \Delta G_m + T\Delta S_m \qquad (9)$$

Taking the enthalpy as the thermodynamic variable, Painter et al.[14] have recently derived an expression for the compositional dependence of the glass transition temperature (T_g) for miscible polymer blends involving strong specific interactions. The final expression is similar to the Couchman–Karasz equation[23] but with an additional term that takes into account the presence of strong specific interactions:

$$T_g = \frac{X_A\Delta C_{pA}T_{gA} + X_B\Delta C_{pB}T_{gB}}{X_A\Delta C_{pA} + X_B\Delta C_{pB}} + X_AX_B[q_m'(X) + q_B'(T)] \qquad (10)$$

In eq 10, T_g is the glass transition temperature of the blend; T_{gi}, X_i, and ΔC_{pi} are the glass transition, the mole fraction, and the specific heat increment (at T_{gi}) of pure component i, and $q_m'(X)$ and $q_B'(T)$ are two factors accounting for the presence of specific interactions. The first is proportional to the heat of mixing contribution arising from specific interactions, whereas the second is related to that part of the temperature dependence of the specific heat that is due to self-association.[14]

II. Experimental Section

The polymers and copolymers used in this study, and the sources from which they were obtained, are described in Table I. Throughout the text, PEMA has been considered the EMA-*co*-MMA copolymer having 0 wt % of MMA (i.e., EMA-*co*-MMA(0)) and PMMA that having 100 wt % of MMA (i.e., EMA-*co*-MMA(100)).

Table II. Parameters Used for the EMA-*co*-MMA/PVPh System[a]

polymer	molar vol (cm^3 mol^{-1})	deg of polymerization	solubility param (cal cm^{-3})$^{0.5}$	χ
PMMA	84.9	915	9.06	0.38
EMA-*co*-MMA(60)	91.5	3760	9.02	0.42
EMA-*co*-MMA(30)	96.5	3245	8.96	0.45
PEMA	101.4	2750	8.89	0.49
PVPh	100.0	250	10.6	

[a] Parameters for PVPh, PMMA, and PEMA were taken from ref 26.

Thin films of the blends prepared for the FTIR measurements were cast from 1% (w/v) methyl ethyl ketone solutions onto potassium bromide windows at room temperature. After the samples were dried under ambient conditions, they were heated in a vacuum oven at 423 K for 3 h and then slowly cooled to room temperature. This thermal treatment ensured a complete removal of residual solvent.

Infrared spectra were recorded with a Nicolet 5DXC spectrometer. A minimum of 64 scans were signal averaged at a resolution of 2 cm^{-1}. Spectra at elevated temperatures (200 and 165 °C) were obtained by using a SPECAC high-temperature cell, mounted in the spectrometer, with an accuracy of ±2 °C. All the films studied were sufficiently thin to be within the range where the Beer–Lambert law is obeyed.[13]

III. Results and Discussion

A. Determination of the Model Parameters. The association model requires the determination, or at least estimates, of several parameters related to the presence of specific interactions as well as unfavorable forces in the polymer blend. As in the simpler Flory–Huggins theory, the degree of polymerization of both components and an interaction parameter χ are used to determine the contribution to the free energy of mixing from nonspecific (weak) interactions. According to Coleman et al.,[13] the χ parameter can be estimated from the equation

$$\chi = \frac{V_B}{RT}(\delta_A - \delta_B)^2 \qquad (11)$$

and the solubility parameter δ_i from group molar attraction and molar volume constants.[22] The solubility parameter of copolymers is related to the values of the pure homopolymers by means of the Scott relationship:[25]

$$\delta_A = \phi_1\delta_1 + \phi_2\delta_2 \qquad (12)$$

Table II shows the values of the parameters employed for the EMA-*co*-MMA/PVPh system.

Specific interactions are considered in the model by means of association equilibria and their related equilibrium constants. In the case of pure PVPh, the constants K_2 and K_B describing self-association through dimers or higher multimers, respectively, cannot be extracted directly from infrared spectroscopic measurements in the stretching region of the hydroxyl groups because of the lack of reliable absorptivity coefficients and the presence

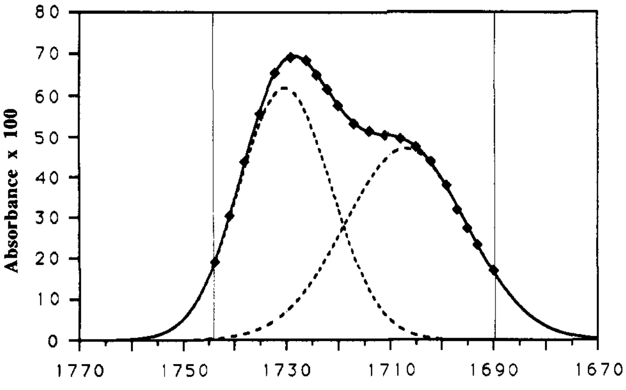

Figure 1. Illustration of the least-squares deconvolution of the carbonyl stretching region of the FTIR spectrum of an EMA-*co*-MMA(30)/PVPh 40:60 blend at 165 °C. The points represent the experimental data, the solid line represents the fitted curve, and the dashed lines represent the theoretical peaks.

of satellite bands and overtones. However, following Coleman et al.,[13] a reasonable estimate can be obtained from the self-association constants of phenol[27] after correcting for differences in molar volumes between the model compound and the polymer. Thus, the values obtained for PVPh are $K_2 = 21.0$ and $K_B = 66.8$ at 25 °C. To determine the temperature dependence of the equilibrium constants a van't Hoff relationship is usually employed, in terms of the enthalpy of hydrogen bond formation. Hence, the enthalpies corresponding to phenol self-association[27] will also be used in this work for pure PVPh ($h_2 = -5.63$ kcal/mol and $h_B = -5.22$ kcal/mol).

Conversely, the interassociation equilibrium constant K_A can be unambiguously determined for EMA-*co*-MMA/PVPh blends by FTIR measurements and equations describing the stoichiometry of hydrogen bonding. An analysis of the carbonyl stretching region of the infrared spectrum of the blends allows one to quantify the fraction of carbonyl groups involved in hydrogen bonding with PVPh (f_B) as a function of composition at fixed temperature.[28] In the model, this quantity is given by[13]

$$f_B = 1 - \frac{\phi_{A1}}{\phi_A} = 1 - \frac{1}{1 + K_A \phi_{B1} \Gamma_1} \tag{13}$$

Therefore, it is possible to determine K_A from a least-squares fit of f_B to the experimental fraction of hydrogen-bonded carbonyl groups at each composition using eqs 6, 7, and 13. To be consistent with this equilibrium approach, spectroscopic measurements must be made in the liquid state above the glass transition temperature of the blend. For the EMA-*co*-MMA/PVPh system, we have found 165 and 200 °C as appropriate temperatures to obtain representative and reliable data. Figure 1 shows, as an example, the FTIR spectrum of an EMA-*co*-MMA(30)/PVPh 40:60 blend at 165 °C in the region of 1770–1670 cm^{-1}. The carbonyl band of EMA-*co*-MMA(30) splits into a doublet in the presence of PVPh as a consequence of hydrogen-bonding interactions in the blend. The area of each peak can be quantified by means of a least-squares curve-fitting procedure using Gaussian functions.[29] Then the fraction of carbonyl groups involved in hydrogen bonding with PVPh can be calculated by[28]

$$f_B = \frac{1}{1 + a_r(A_F/A_B)} \tag{14}$$

where A_B and A_F are the areas corresponding to hydrogen-bonded and free carbonyl groups, respectively, and a_r is the absorptivity ratio, which takes into account the difference between the absorptivities of the hydrogen-bonded and free carbonyl groups. Table III summarizes the best-fit parameters obtained from the curve-fitting analysis of EMA-*co*-MMA/PVPh blends as well as the experimental f_B data at 165 °C. A least-squares program was used to obtain K_A from the compositional variation of f_B at a given temperature. Figures 2–5 show a comparison between the experimental fractions of hydrogen-bonded carbonyl groups at 165 and 200 °C and the calculated ones by using the K_A values contained in Table IV. Also, an estimate of the enthalpy of hydrogen bond formation can be obtained by assuming the validity of a van't Hoff relationship over the temperature range between 165 and 200 °C. Although some error could be involved in this procedure, we would argue that nearly the same value was obtained for each blend system as was expected due to the similar chemical nature of the intermolecular interaction. In this sense, we have noted that the average value obtained in this work lies in the range of data previously reported in the literature.[26,30] Table V summarizes the K_A values of PEMA/PVPh blends determined by Coleman, Painter, and co-workers[26,31] as well as the

Table III. Curve-Fitting Results for the EMA-*co*-MMA/PVPh System at 165 °C

	free C═O band			H-bonded C═O band			
ϕ_B	ν (cm^{-1})	$W_{1/2}$ (cm^{-1}	A_F	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	A_B	f_B[a]
			PMMA/PVPh				
0.20	1732	19	5.32	1708	23	1.27	0.137
0.40	1733	19	5.26	1708	23	2.98	0.274
0.50	1733	19	5.31	1709	23	4.11	0.340
0.60	1733	19	2.53	1709	24	2.80	0.425
0.80	1732	18	2.37	1709	24	3.46	0.493
			EMA-*co*-MMA(60)/PVPh				
0.19	1731	20	9.63	1708	26	2.47	0.146
0.39	1732	19	4.36	1708	27	3.06	0.319
0.49	1732	19	5.05	1708	27	4.51	0.373
0.59	1732	20	3.37	1708	27	3.71	0.423
0.79	1732	19	1.92	1708	27	3.06	0.515
			EMA-*co*-MMA(30)/PVPh				
0.19	1731	20	11.05	1706	25	3.44	0.172
0.39	1731	19	10.11	1706	24	6.67	0.305
0.49	1730	19	7.52	1707	24	5.96	0.346
0.59	1730	18	1.37	1707	24	1.38	0.402
0.79	1730	19	1.03	1707	25	1.65	0.516
			PEMA/PVPh				
0.19	1729	19	5.66	1703	24	1.43	0.144
0.38	1729	19	3.45	1704	25	2.39	0.316
0.48	1729	18	3.53	1705	26	3.07	0.367
0.58	1728	18	3.08	1704	25	3.56	0.435
0.79	1729	18	1.65	1705	25	2.92	0.557

[a] An absorptivity ratio (a_r) of 1.5 was employed according to Coleman et al.[13]

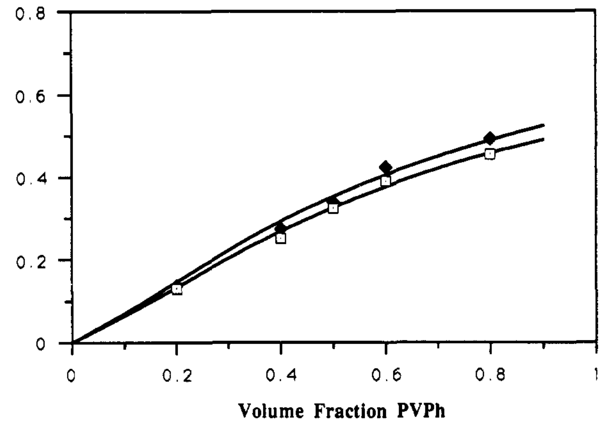

Figure 2. Comparison of the theoretical and experimental fractions of hydrogen-bonded carbonyl groups for PMMA/PVPh blends at 165 (◆) and 200 °C (□).

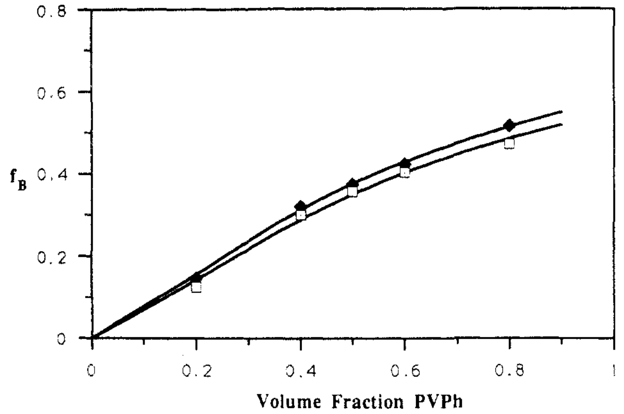

Figure 3. Comparison of the theoretical and experimental fractions of hydrogen-bonded carbonyl groups for EMA-*co*-MMA-(60)/PVPh blends at 165 (◆) and 200 °C (□).

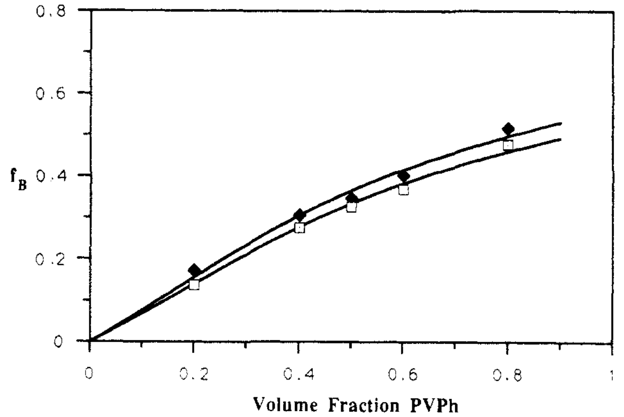

Figure 4. Comparison of the theoretical and experimental fractions of hydrogen-bonded carbonyl groups for EMA-*co*-MMA-(30)/PVPh blends at 165 (◆) and 200 °C (□).

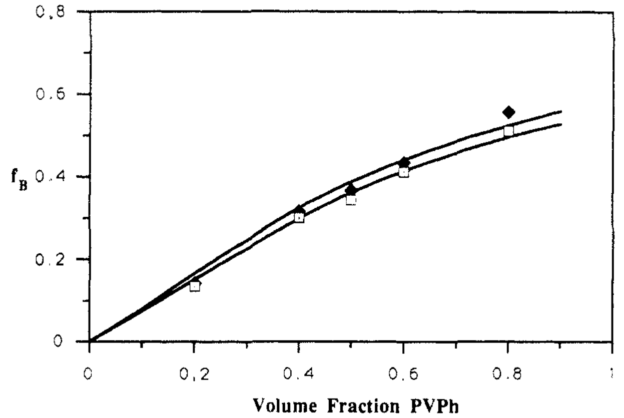

Figure 5. Comparison of the theoretical and experimental fractions of hydrogen-bonded carbonyl groups for PEMA/PVPh blends at 165 (◆) and 200 °C (□).

Table IV. Interassociation Equilibrium Constant (K_A) and Enthalpy of Hydrogen Bond Formation (h_A) for EMA-*co*-MMA/PVPh Blends

Interassociation Equilibrium Constant (K_A)

T (°C)	PMMA/ PVPh	EMA-*co*-MMA(60)/ PVPh	EMA-*co*-MMA(30)/ PVPh	PEMA/ PVPh	average
200	2.48	2.76	2.47	2.88	2.65 ± 0.21
165	3.66	4.03	3.72	4.19	3.90 ± 0.25

Enthalpy of Hydrogen Bond Formation (h_A (kcal/mol))

PMMA/ PVPh	EMA-*co*-MMA(60)/ PVPh	EMA-*co*-MMA(30)/ PVPh	PEMA/ PVPh	average
−4.58	−4.46	−4.82	−4.41	−4.57 ± 0.18

Table V. Interassociation Equilibrium Constant (K_A) for Poly(ethyl methacrylate)/PVPh Blends

	K_A	
source	T = 200 °C	T = 165 °C
Serman et al.[a]	3.47	4.79
Coleman et al.[b]	2.97	4.21
this work	2.88	4.19
model compounds[c]	3.76 (CT) 4.20 (H) 4.28 (N)	5.70 (CT) 6.59 (H) 6.98 (N)

[a] Reference 26. [b] Reference 31. [c] Estimated from data of methyl acetate/phenol mixtures in several solvents[30] (CT = carbon tetrachloride, H = n-heptane, N = naphtha), after correcting for molar volume differences between phenol and PVPh.

results of this work. The K_A values evaluated from model compounds in several solvents[30] (after scaling to a reference molar volume equal to that of the repeat unit of PVPh) are also included in Table V for comparison. Although an identical value of K_A should be found from diverse sources if the chains are sufficiently flexible,[13] significant differences are observed when low-molecular-weight mixtures and polymer blends are compared. Similar results have recently been obtained by Coleman, Painter, and coworkers, who point out that compositional heterogeneities in the polymer blend system[31] rather than chain stiffness effects[13] are responsible for this behavior.

The model parameters described above will subsequently be used to make predictions about phase behavior, glass transition trends, and the magnitude of the enthalpy of mixing for EMA-*co*-MMA/PVPh blends. In the second paper, several model parameters from this study will be used when the association model is applied to ternary PMMA/PVPh/PEMA blends.

B. Miscibility Predictions. It is well-known that polymer blend miscibility depends on temperature and blend composition. In general, a phase diagram can be constructed based on experimental results derived from glass transition behavior and cloud point measurements. The association model provides a way to calculate theoretical phase diagrams that can be compared to experimental ones. Thus, the free energy of mixing and the thermodynamic conditions for phase stability (binodal and spinodal curves) are used in the model to predict miscibility boundaries.[13]

Phase diagrams for PMMA/PVPh and PEMA/PVPh blends were calculated previously by Serman et al.,[26] showing no phase separation in the temperature range between 25 and 220 °C (onset of thermal degradation of polymethacrylates). For these blends, theoretical predictions compare very favorably to experimental results.

In this case, for EMA-*co*-MMA(60)/PVPh and EMA-*co*-MMA(30)/PVPh blends, the model again predicts miscibility across the full composition range between 25 and 220 °C, in agreement with previous DSC results showing no phase separation in this temperature range.[19]

On the other hand, the glass transition behavior of the blend is closely related to the homogeneity of the system and, therefore, to the blend miscibility. From a practical point of view, the location of the T_g–composition line in the phase diagram determines the limit of dimensional stability of amorphous polymer blends. Recently, a predictive T_g–composition equation has been derived by Painter et al.[14] in terms of the association model. For PMMA/PVPh blends a reasonable agreement was obtained between calculated T_g values and those determined experimentally by Gow and Siow.[24]

For the EMA-*co*-MMA/PVPh system, Figures 6–9 show a comparison between theoretical and experimental glass

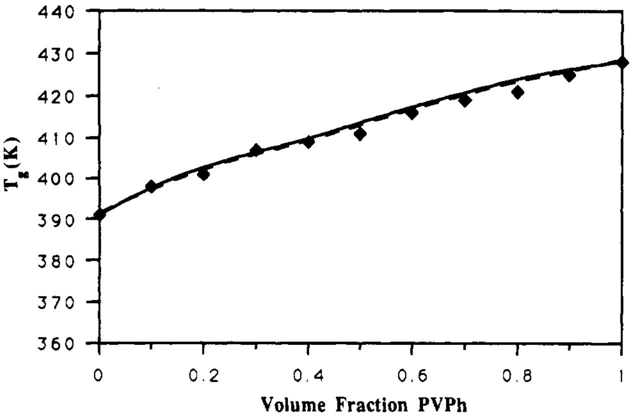

Figure 6. Comparison of the theoretical and experimental[19] T_g data for PMMA/PVPh blends. The dashed line was calculated using the interassociation parameters for this system (Table IV). The solid line was calculated with the average parameters of EMA-*co*-MMA/PVPh blends (Table IV).

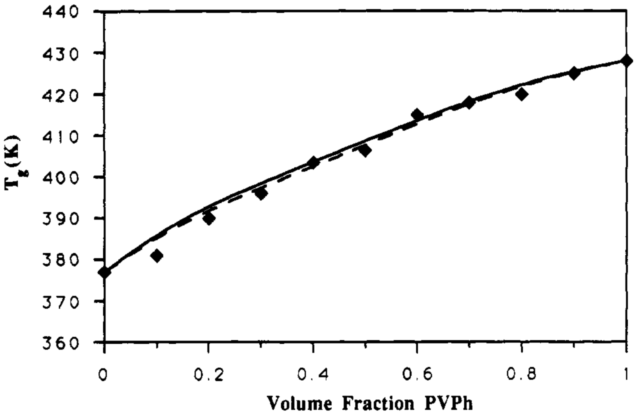

Figure 7. Comparison of the theoretical and experimental[19] T_g data for EMA-*co*-MMA(60)/PVPh blends. The dashed line was calculated using the interassociation parameters for this system (Table IV). The solid line was calculated with the average parameters of EMA-*co*-MMA/PVPh blends (Table IV).

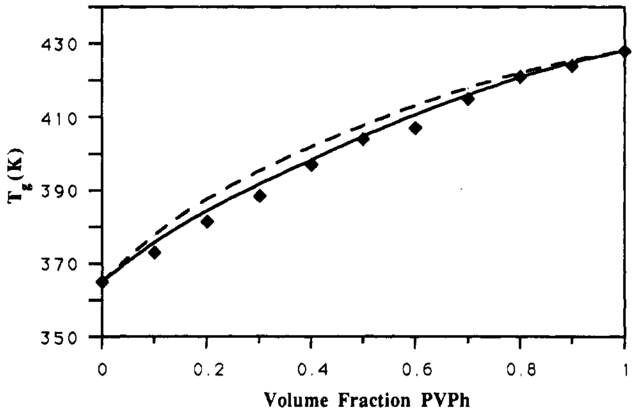

Figure 8. Comparison of the theoretical and experimental[19] T_g data for EMA-*co*-MMA(30)/PVPh blends. The dashed line was calculated using the interassociation parameters for this system (Table IV). The solid line was calculated with the average parameters of EMA-*co*-MMA/PVPh blends (Table IV).

transition behavior.[19] The calculated data compare favorably to experimental results in spite of the assumptions of the theory and the error inherent in the determination of the model parameters. For example, by changing the interassociation parameters for each system with the average ones, an estimate of the accuracy of the T_g predictions can be obtained. However, additional errors arising from both self-association parameters[27] and ΔC_{pi} values[32] could not be excluded. Nevertheless, the success of eq 10 points to an accurate estimation of the enthalpic contributions in the EMA-*co*-MMA/PVPh system. This feature will be discussed in more detail in the following section.

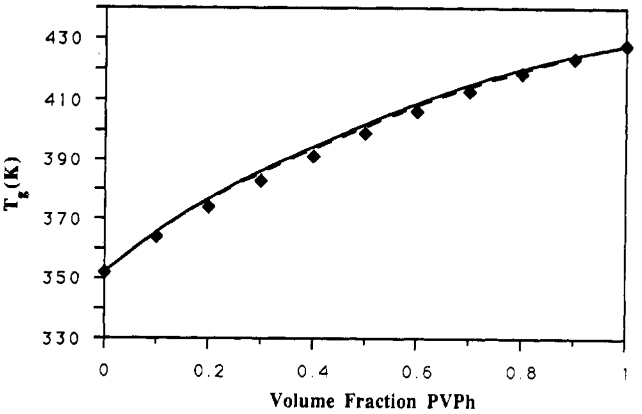

Figure 9. Comparison of the theoretical and experimental[19] T_g data for PEMA/PVPh blends. The dashed line was calculated using the interassociation parameters for this system (Table IV). The solid line was calculated with the average parameters of EMA-*co*-MMA/PVPh blends (Table IV).

C. Enthalpy of Mixing Predictions. When entropic contributions to the free energy of mixing are negligible, the magnitude and the sign of the enthalpy of mixing determine the thermodynamic miscibility of the polymer blend. The direct measurement of the enthalpy of mixing of two polymers is not possible given the high viscosities and low diffusion coefficients involved, so indirect methods have to be used. Thus, analogue calorimetry has been very useful to estimate the heat of mixing using low-molecular-weight model compounds of the corresponding polymers.[33,34] Originally, this approach was used with relative success for blends where interactions are not very strong, but it has been shown recently that for several systems the heats of mixing of strongly interacting model compounds (where entropic contributions are presumably not negligible) are also useful in predicting the miscibility of the corresponding polymers.[21,35–38] Therefore, a great insight into polymer blend miscibility predictions could be expected when both enthalpic and entropic changes upon mixing are taken into account. For this purpose, association models are very useful since they can be applied both to mixtures of hydrogen-bonded small molecules and to polymer blends. Experimental and predicted heats of mixing for mixtures of model compounds can then be compared using equilibrium constants and enthalpies of hydrogen bond formation determined from spectroscopic measurements. If reasonable agreement is found, information about the magnitude of the excess entropic effects in the mixture can be gained. Subsequently, both the heat and the entropy of mixing of the corresponding polymers can be predicted using the model parameters for the blend system. This procedure allows one to check the validity of the analogue calorimetry approach in terms of the association model and likewise to quantify the entropic contributions.

We have used the association model for hydrogen-bonded small molecules[10,12] and the model parameters given in Table VI to predict the heats of mixing of methyl pivalate (MPI)/4-ethylphenol (EPH) mixtures at 79 °C. MPI is a model compound of PMMA, and EPH is an analogue of PVPh. Equilibrium constants and enthalpies of hydrogen bond formation describing self-association of phenol in cyclohexane (K_2 and K_B) have been taken from the work of Whetsel and Lady,[27] scaled to the molar volume of EPH, and converted to the dimensionless constants required in the model. In the same way, the values of the interassociation constant (K_A) shown in Table VI were calculated from data reported by Nagakura[30] for ester/

Table VI. Model Parameters for MPI/EPH Mixtures at 25 °C

model compd	molar vol (cm^3 mol^{-1})	solubility param (cal cm^{-3})$^{0.5}$
MPI	132.0	8.13
EPH	112.2	9.78

Association Parameters

equilib constant	value	enthalpy of H-bond formation (kcal mol^{-1})	value
K_2	18.7	h_2	-5.63
K_B	59.5	h_B	-5.22
K_A[a]	71.8 (CT) 103.0 (H) 138.2 (N)	h_A[a]	-4.91 (CT) -5.31 (H) -5.75 (N)

[a] Determined in several solvents: CT = carbon tetrachloride, H = *n*-heptane, N = naphtha.

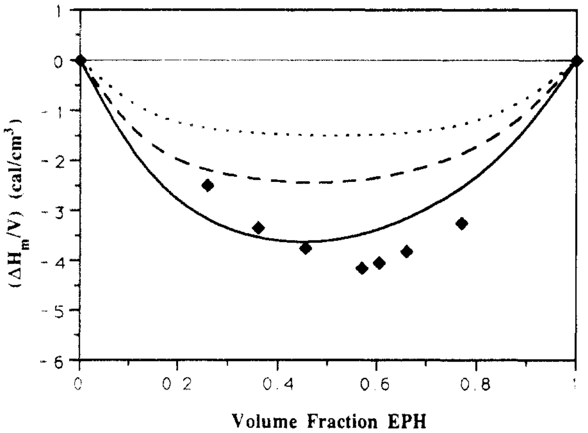

Figure 10. Comparison of the theoretical and experimental[20] heats of mixing for MPI/EPH mixtures at 79 °C: (···) K_A = 71.8, h_A = -4.91 kcal/mol; (- - -) K_A = 103.0, h_A = -5.31 kcal/mol; (—) K_A = 138.2, h_A = -5.75 kcal/mol.

phenol mixtures in several solvents. The corresponding enthalpies of hydrogen bond formation reported by this author are also shown in Table VI. Solubility parameters and molar volumes were calculated with the group contribution method reported in ref 22. Figure 10 shows a comparison between the heats of mixing predicted by the model and the experimental data.[20] As can be seen, the model predictions are very sensitive to the values of the interassociation parameters (K_A and h_A) employed and therefore to the *inert* solvent used to determine them. Better agreement was found when parameters were obtained from ester/phenol mixtures in hydrocarbon solvents rather than in chlorine-containing solvents. In particular, values of K_A and h_A calculated from mixtures of ethyl acetate and phenol in naphtha reproduce the experimental trend reasonably well. With these values, a sizeable entropic contribution to the free energy of mixing, favoring miscibility, is predicted by the association model, as shown in Figure 11. In this case, the free energy of mixing differs considerably from the enthalpy of mixing (see Figure 11), so we can conclude that, in addition to the exothermic enthalpic contribution, favorable entropic changes are also responsible for the miscibility of the MPI/EPH mixture. Very similar results were found when the association model for hydrogen-bonded small molecules was used to reproduce the experimental heats of mixing of ethyl isobutyrate (EIB)/EPH mixtures,[21] which can be considered as a model system of PEMA/PVPh blends.

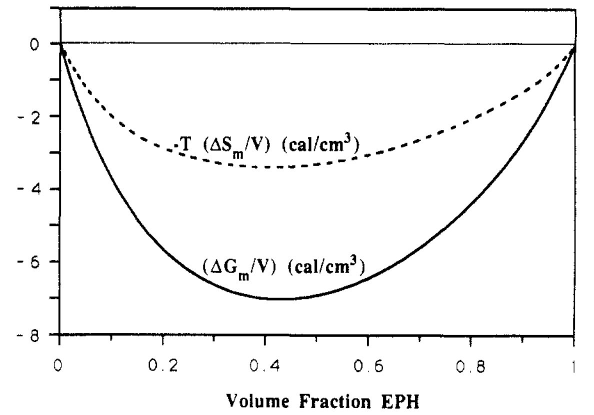

Figure 11. Free energy of mixing ($\Delta G_m/V$) and entropic contribution to the free energy of mixing ($-T\Delta S_m/V$) predicted by the association model for MPI/EPH mixtures at 79 °C using K_A = 138.2 and h_A = -5.75 kcal/mol.

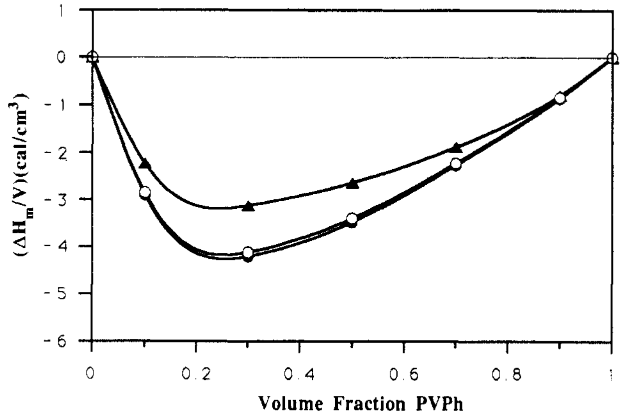

Figure 12. Heats of mixing predicted by the association model for PMMA/PVPh blends at 165 (◆) and 200 °C (●) using the average interassociation parameters of Table IV. Data at 200 °C (○) employing parameters of Table IV for this system are also shown for comparison.

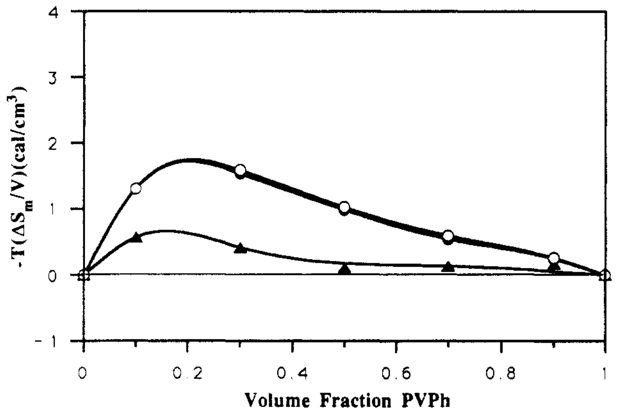

Figure 13. Entropic contribution to the free energy of mixing predicted by the association model for PMMA/PVPh blends at 165 (◆) and 200 °C (●) using the average interassociation parameters of Table IV. Data at 200 °C (○) employing parameters of Table IV for this system are also shown for comparison.

To compare the results of the analogue mixtures with those of the corresponding polymer blends, we now need to determine the enthalpic and entropic contributions using the association model. To do this, we have employed the model parameters given in Tables II and IV. Figure 12 shows the predicted heats of mixing for PMMA/PVPh blends at 165 and 200 °C. The entropic contribution to the free energy of mixing is represented in Figure 13. Again, a simple estimate of the errors involved has been obtained by changing the interassociation parameters within experimental error. Referring to Figure 12, the magnitude of the enthalpy of mixing is very similar to that of the mixture of model compounds and, although we recognize that data at different temperatures are used, we think that this comparison will be enough to derive qualitative but consistent conclusions. In relation to the entropic

Table VII. Excess Heat Capacity (C_p^E) Predicted by the Association Model for the EMA-*co*-MMA(60)/PVPh 50:50 Blend

T (°C)	C_p^E (cal K^{-1} cm^{-3})	T (°C)	C_p^E (cal K^{-1} cm^{-3})
165	−0.0221	185	−0.0230
170	−0.0223	190	−0.0234
175	−0.0227	195	−0.0236
180	−0.0228	200	−0.0238

contribution ($\Delta S_m/V$) the model predicts a negative value, unfavorable to mixing, opposite that of the model for the corresponding analogue mixture. This behavior may be due to the large difference of molecular weight between the polymers and their relative analogues. Similar conclusions were gained when EIB/EPH mixtures and PEMA/PVPh blends were compared in terms of the model. Both enthalpy and entropy of mixing predictions for EMA-*co*-MMA(30)/PVPh and EMA-*co*-MMA(60)/PVPh blends are comparable to those shown in Figures 12 and 13 for PMMA/PVPh blends.

Finally, Table VII gives the temperature dependency of the heat of mixing (e.g., the excess heat capacity) predicted by the association model for the EMA-*co*-MMA-(60)/PVPh 50:50 blend in the temperature range between 165 and 200 °C. A careful experimental determination of C_p^E has not been made for EMA-*co*-MMA/PVPh blends yet, so it could provide another test of the validity of the association model employed in this work.

IV. Summary and Conclusions

Blends of EMA-*co*-MMA and PVPh have been analyzed in terms of the association model developed by Painter, Coleman, and co-workers[12] to describe the free energy changes occurring in binary polymer mixtures containing strong directionally specific interactions. Parameters describing interassociation were determined from the composition dependence of the fraction of hydrogen-bonded carbonyl groups at 165 and 200 °C and were found to be similar to those reported by Serman et al.[26] On the other hand, K_A values determined from model compound mixtures[30] were generally higher than those corresponding to the polymer blend system.

A good agreement was found when the phase diagrams predicted by the association model for EMA-*co*-MMA/PVPh blends were compared to experimental results. Moreover, the predictive T_g–composition equation of Painter et al.[14] was able to reproduce with success the location of the glass transition zone in the phase diagram, pointing to a reasonable estimation of the enthalpic contributions by the model.

In this sense, heats of mixing calculated for analogue mixtures of PMMA/PVPh and PEMA/PVPh blends using the association model for hydrogen-bonded small molecules[10,12] compare reasonably with experimental data,[20,21] although the K_A values employed were affected by a *solvent effect*. For the polymer blends, the heats of mixing predicted by the model for equilibrium temperatures above the glass transition were similar to those of the corresponding model compounds. As expected, entropic contributions were far from negligible for both analogue mixtures and polymer blends. They were found to be unfavorable to mixing for the polymer system, opposite the predictions for the analogue mixtures. The large difference of molecular weight between the polymers and the corresponding model compounds could be responsible for this behavior.

Finally, negative excess heat capacities were calculated for EMA-*co*-MMA/PVPh blends in the liquid state. Although this latter prediction has not yet been confirmed experimentally, it appears that the association model provides a useful framework to describe the miscibility and phase behavior of the EMA-*co*-MMA/PVPh system.

Acknowledgment. We would like to thank Professors P. C. Painter and M. M. Coleman for useful discussions.

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