Hydrogen Bonding in Polymer Systems Involving Poly(*p*-vinylphenol). 2. Ternary Blends with Poly(ethyl methacrylate) and Poly(methyl methacrylate)

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ABSTRACT: An association model extended to ternary systems has been applied to poly(ethyl methacrylate) (PEMA)/poly(methyl methacrylate) (PMMA)/poly(*p*-vinylphenol) (PVPh) blends. In this ternary blend, PVPh is miscible with PMMA and PEMA, while the last two polymers are immiscible with each other. Using model parameters previously determined for binary PMMA/PVPh and PEMA/PVPh blends, the spinodal curve of the ternary system at 165 °C has been predicted and found to be very sensitive to the values of the solubility parameters employed. Fourier transform infrared (FTIR) measurements were conducted in order to obtain an indication of the miscibility boundaries in the ternary diagram. By comparing the experimental fraction of hydrogen-bonded carbonyl groups corresponding exclusively to PMMA and that of PEMA to the theoretical ones from the model, ternary PEMA/PMMA/PVPh compositions where phase separation has taken place can be identified. Several limitations of this approach for the ternary system have been pointed out.

Introduction

The miscibility behavior of binary poly(methyl methacrylate)/poly(*p*-vinylphenol)(PMMA/PVPh) and poly(ethyl methacrylate)/poly(*p*-vinylphenol) (PEMA/PVPh) blends has been previously studied by means of differential scanning calorimetry (DSC).[1-3] For these systems, a single composition-dependent glass transition temperature (T_g) was found as a consequence of the blend homogeneity across the full composition range. In addition, Coleman et al.[4] claim these systems are miscible due to intermolecular hydrogen-bonding interactions which have been detected by Fourier transform infrared spectroscopy. On the other hand, although PMMA and PEMA have a similar chemical structure, it is well-known that the two methacrylate polymers are immiscible.[5,6]

Recently, we have determined the miscibility of ternary PMMA/PEMA/PVPh blends using DSC and scanning electron microscopy (SEM).[7] The phase behavior of this system is very different from that of binary poly(ethyl methacrylate-*co*-methyl methacrylate) (EMA-*co*-MMA)/PVPh blends, where miscibility is found across the entire range of copolymer composition.[3] In fact, since PEMA and PMMA are not covalently bonded in the ternary system, phase separation is found when the PVPh content is less than 60 wt %.

We have shown in a previous paper[8] that the results concerning EMA-*co*-MMA/PVPh blends can be described with success in terms of the association model developed by Painter, Coleman, and co-workers.[4] For this system, hydrogen-bonding interactions were found to play an important role in determining the temperature range where miscibility occurs, the change in enthalpy (and entropy) upon mixing, and the variation of the glass transition temperature with blend composition.

In a recent paper by Le Menestrel et al.,[9] the stoichiometry of hydrogen bonding and its relationship to infrared spectroscopy measurements have been extended to ternary PVPh/poly(ethylene oxide) (PEO)/poly(vinyl acetate) (PVAc) blends in which each binary pair is miscible. Hence, the interassociation constant between PVPh and PEO has been determined experimentally from a quantitative analysis of the fraction of hydrogen-bonded carbonyl groups in the ternary system. To our knowledge, the association model has not previously been applied to ternary polymer blends.

In the work presented here, the main goal was to check the applicability of the association model extended to ternary systems for PEMA/PMMA/PVPh blends, and determine the ability of the theory to predict the ternary miscibility diagram of this system. Also further indications about miscibility in this system have been obtained by comparing the fraction of hydrogen-bonded carbonyl groups predicted by the model to that found experimentally.

Theory

A two equilibrium constant self-association model has been developed previously by Coleman, Painter, and co-workers for binary systems.[10,11] In this work, we are concerned with ternary polymer blends containing a polymer (B) that self-associates and two polymers (A and C) that do not self-associate but are able to form hydrogen bonds with the first. The treatment employed in this case to obtain the free energy of mixing closely resembles that followed by Painter et al.[10] Stoichiometric equations for ternary blends have been reported recently by Le Menestrel et al.[9] The association model extended to ternary systems is undoubtedly subject to the same assumptions and limitations as that for binary blends. Specifically, free volume effects[12-14] that are neglected in this rigid lattice model could be important in several cases, especially when specific and dispersive forces are finely balanced.

A. Stoichiometric Relationships. The equilibria describing self-association of polymer B to form chains of hydrogen bonds when dimer formation is described by an equilibrium constant (K_2) different from that of subse-

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quent n-mer ($n \geq 2$) formation (K_B) can be represented as

$$B_1 + B_1 \overset{K_2}{\rightleftarrows} B_2 \tag{1}$$

$$B_n + B_1 \overset{K_B}{\rightleftarrows} B_{n+1} \tag{2}$$

where K_2 and K_B are dimensionless constants defined according to Flory[15] as

$$K_2 = \frac{\phi_{B_2}}{\phi_{B_1}{}^2}\left(\frac{1}{2}\right) \tag{3}$$

$$K_B = \frac{\phi_{B_{n+1}}}{\phi_{B_n}\phi_{B_1}}\left(\frac{n}{n+1}\right) \tag{4}$$

where ϕ_{B_n} is the volume fraction of n-mers and ϕ_{B_1} is the volume fraction of B units that are not hydrogen bonded to other groups. In this case, there are two competing equilibria given by

$$B_n + A_1 \overset{K_A}{\rightleftarrows} B_nA \tag{5}$$

$$B_n + C_1 \overset{K_C}{\rightleftarrows} B_nC \tag{6}$$

where both A and C units make no distinction between forming a hydrogen bond to a dimer or an n-mer. The corresponding equilibrium constants are

$$K_A = \frac{\phi_{B_nA}}{\phi_{B_n}\phi_{A_1}}\left(\frac{nr}{n+r}\right) \tag{7}$$

$$K_C = \frac{\phi_{B_nC}}{\phi_{B_n}\phi_{C_1}}\left(\frac{nq}{n+q}\right) \tag{8}$$

where ϕ_{B_nA} (or ϕ_{B_nC}) is the volume fraction of a hydrogen-bonded chain of n B units with one A (or C) unit at the end, ϕ_{A_1} (or ϕ_{C_1}) is the volume fraction of A (or C) units that are not hydrogen bonded to B groups, and the factors $r = V_A/V_B$ and $q = V_C/V_B$ account for the difference in size of the interacting units (where V_i is the molar volume per structural unit of component i).

The material balance allows one to obtain stoichiometric equations relating ϕ_{B_1}, ϕ_{A_1}, and ϕ_{C_1} to the overall volume fractions ϕ_B, ϕ_A, and ϕ_C and the equilibrium constants defined above. Following the algebraic procedures given in ref 10, the stoichiometric relationships can be expressed as

$$\phi_B = \left(1 + \frac{K_A\phi_{A_1}}{r} + \frac{K_C\phi_{C_1}}{q}\right)\phi_{B_1}\Gamma_2 \tag{9}$$

$$\phi_A = \phi_{A_1}(1 + K_A\phi_{B_1}\Gamma_1) \tag{10}$$

$$\phi_C = \phi_{C_1}(1 + K_C\phi_{B_1}\Gamma_1) \tag{11}$$

where

$$\Gamma_1 = \left(1 - \frac{K_2}{K_B}\right) + \left(\frac{K_2}{K_B}\right)\left[\frac{1}{1 - K_B\phi_{B_1}}\right] \tag{12}$$

and

$$\Gamma_2 = \left(1 - \frac{K_2}{K_B}\right) + \left(\frac{K_2}{K_B}\right)\left[\frac{1}{(1 - K_B\phi_{B_1})^2}\right] \tag{13}$$

However, the overall volume fractions are also related, and it is possible to express one (i.e., ϕ_C) in terms of the others:

$$\phi_C = 1 - \phi_A - \phi_B \tag{14}$$

Equations 9–11 allow one to determine ϕ_{B_1}, ϕ_{A_1}, and ϕ_{C_1} if equilibrium constants and molar volumes are known. Substitution of eqs 10, 11, and 14 in eq 9 leads to the following expression:

$$\phi_B - \phi_{B_1}\left[\left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\frac{1}{(1 - K_B\phi_{B_1})^2}\right] \times \left[1 + \frac{(K_A/r)\phi_A}{(1 + K_A\phi_{B_1}\Gamma_1)} + \frac{(K_C/q)(1 - \phi_A - \phi_B)}{(1 + K_C\phi_{B_1}\Gamma_1)}\right] = 0 \tag{15}$$

An iterative procedure (i.e., Newton's method) can be used to calculate ϕ_{B_1} from this equation and, then, ϕ_{A_1} and ϕ_{C_1} from eqs 10 and 11.

B. Free Energy of Mixing. The procedure employed in this work to obtain the free energy of mixing for the ternary system is similar to that used by Painter et al.[10,16] for binary polymer blends following Nagata's description.[17] The free energy of mixing is expressed as the sum of two contributions:

$$\frac{\Delta G_m}{RT} = \frac{\Delta G_m{}^H}{RT} + \frac{\Delta G_m{}^{FH}}{RT} \tag{16}$$

The component of the free energy of mixing associated with hydrogen bonding ($\Delta G_m{}^H$) is obtained from the ideal (athermal) free energy of mixing the n-mers present in the mixture (relative to the standard state where they are separate and oriented) after substraction of the combinatorial entropy term for mixing the components with no change in hydrogen bonding. On the other hand, the contribution to the free energy of mixing from nonspecific forces (i.e., dispersive and weak polar) involved in mixing ($\Delta G_m{}^{FH}$) is calculated by a Flory–Huggins-type relationship.[18] In this case

$$\frac{\Delta G_m{}^{FH}}{RT} = \frac{\phi_A}{N_A}\ln\phi_A + \frac{\phi_B}{N_B}\ln\phi_B + \frac{\phi_C}{N_C}\ln\phi_C + \phi_A\phi_B\chi_{AB} + \phi_A\phi_C\chi_{AC} + \phi_B\phi_C\chi_{BC} \tag{17}$$

A useful expression for the free energy of athermally mixing the hydrogen-bonded n-mers (ΔG_{ch}) can be obtained by considering that the chemical potentials of the stoichiometric components are equal to those of the respective monomers when the hydrogen-bonded chains are in chemical equilibrium with one another.[19] Then, using a procedure similar to that of ref 10, it can be shown that the chemical potentials of the components are given by

$$\frac{(\mu_B - \mu_B{}^\circ)_{ch}}{RT} = \ln\left(\frac{\phi_{B_1}}{\phi_{B_1{}^\circ}}\right) + \frac{V_B}{V^\circ} - \frac{V_B}{V} \tag{18}$$

$$\frac{(\mu_A - \mu_A{}^\circ)_{ch}}{RT} = \ln\phi_{A_1} + 1 - \frac{V_A}{V} \tag{19}$$

$$\frac{(\mu_C - \mu_C{}^\circ)_{ch}}{RT} = \ln\phi_{C_1} + 1 - \frac{V_C}{V} \tag{20}$$

where the standard state is defined as pure solutions of the individual components.[10,16] The ideal (athermal) free energy of mixing can be expressed in terms of the above potentials as

$$\frac{\Delta G_{\mathrm{ch}}}{RT} = \frac{(\mu_{\mathrm{B}} - \mu_{\mathrm{B}}{}^{\circ})_{\mathrm{ch}}}{RT} n_{\mathrm{B}} + \frac{(\mu_{\mathrm{A}} - \mu_{\mathrm{A}}{}^{\circ})_{\mathrm{ch}}}{RT} n_{\mathrm{A}} + \frac{(\mu_{\mathrm{C}} - \mu_{\mathrm{C}}{}^{\circ})_{\mathrm{ch}}}{RT} n_{\mathrm{C}} = n_{\mathrm{B}} \ln\left(\frac{\phi_{\mathrm{B}_1}}{\phi_{\mathrm{B}_1{}^{\circ}}}\right) + n_{\mathrm{A}} \ln \phi_{\mathrm{A}_1} + n_{\mathrm{C}} \ln \phi_{\mathrm{C}_1} + n_{\mathrm{B}}\left[\left(\frac{\Gamma_1{}^{\circ}}{\Gamma_2{}^{\circ}}\right) - \left(\frac{\Gamma_1}{\Gamma_2}\right)\right] + n_{\mathrm{B}}\left(\frac{\Gamma_1}{\Gamma_2}\right)\left[\frac{X+Y}{1+X+Y}\right] \quad (21)$$

where $X = K_{\mathrm{A}}\phi_{\mathrm{A}_1}/r$ and $Y = K_{\mathrm{C}}\phi_{\mathrm{C}_1}/q$. In order to obtain the change in free energy (per mole of lattice sites) associated with just the change in the distribution of hydrogen-bonded n-mers ($\Delta G_{\mathrm{m}}{}^{\mathrm{H}}$), the combinatorial entropy term for mixing the components with no change in hydrogen bonding must be substracted:[10,16]

$$(n_{\mathrm{B}}/n_{\mathrm{H}}{}^{\circ}) \ln \phi_{\mathrm{B}} + n_{\mathrm{A}} \ln \phi_{\mathrm{A}} + n_{\mathrm{C}} \ln \phi_{\mathrm{C}}$$

where

$$n_{\mathrm{H}}{}^{\circ} = \Gamma_2{}^{\circ}/\Gamma_1{}^{\circ} \quad (22)$$

Multiplying by V_{B}/V,

$$\frac{\Delta G_{\mathrm{m}}{}^{\mathrm{H}}}{RT} = \left[\phi_{\mathrm{B}} \ln\left(\frac{\phi_{\mathrm{B}_1}}{\phi_{\mathrm{B}_1{}^{\circ}}}\right) + \frac{\phi_{\mathrm{A}}}{r} \ln \phi_{\mathrm{A}_1} + \frac{\phi_{\mathrm{C}}}{q} \ln \phi_{\mathrm{C}_1} + \phi_{\mathrm{B}}\left[\left(\frac{\Gamma_1{}^{\circ}}{\Gamma_2{}^{\circ}}\right) - \left(\frac{\Gamma_1}{\Gamma_2}\right)\right] + \phi_{\mathrm{B}}\left(\frac{\Gamma_1}{\Gamma_2}\right)\left(\frac{X+Y}{1+X+Y}\right)\right] - \left[\frac{\phi_{\mathrm{B}}}{n_{\mathrm{H}}{}^{\circ}} \ln \phi_{\mathrm{B}} + \frac{\phi_{\mathrm{A}}}{r} \ln \phi_{\mathrm{A}} + \frac{\phi_{\mathrm{C}}}{q} \ln \phi_{\mathrm{C}}\right] \quad (23)$$

Note that eq 23 reduces to eq A41 in ref 10 when $\phi_{\mathrm{C}} = 0$, as it should.

C. Spinodal Equation. An analytical expression describing the spinodal curve can be determined in terms of eqs 16, 17, and 23 by considering that free volume effects in polymer blends are negligible to a first approximation when strong specific interactions are involved.[20] In the case of ternary systems, the spinodal condition is given by

$$\left(\frac{\partial^2(\Delta G_{\mathrm{m}}/RT)}{\partial \phi_{\mathrm{A}}{}^2}\right)\left(\frac{\partial^2(\Delta G_{\mathrm{m}}/RT)}{\partial \phi_{\mathrm{B}}{}^2}\right) - \left(\frac{\partial^2(\Delta G_{\mathrm{m}}/RT)}{\partial \phi_{\mathrm{A}}\partial \phi_{\mathrm{B}}}\right)\left(\frac{\partial^2(\Delta G_{\mathrm{m}}/RT)}{\partial \phi_{\mathrm{B}}\partial \phi_{\mathrm{A}}}\right) = 0 \quad (24)$$

Following an algebraic procedure similar to that of ref 21, it can be shown that the various terms in eq 24 are given by

$$\frac{\partial^2(\Delta G_{\mathrm{m}}/RT)}{\partial \phi_{\mathrm{A}}{}^2} = \left[\frac{1}{N_{\mathrm{A}}\phi_{\mathrm{A}}} + \frac{1}{N_{\mathrm{C}}\phi_{\mathrm{C}}} - 2\chi_{\mathrm{AC}}\right] + \left[\frac{1}{r\phi_{\mathrm{A}_1}}\frac{\partial \phi_{\mathrm{A}_1}}{\partial \phi_{\mathrm{A}}} - \frac{1}{q\phi_{\mathrm{C}_1}}\frac{\partial \phi_{\mathrm{C}_1}}{\partial \phi_{\mathrm{A}}}\right] - \left[\frac{1}{r\phi_{\mathrm{A}}} + \frac{1}{q\phi_{\mathrm{C}}}\right] \quad (25)$$

$$\frac{\partial^2(\Delta G_{\mathrm{m}}/RT)}{\partial \phi_{\mathrm{B}}{}^2} = \left[\frac{1}{N_{\mathrm{B}}\phi_{\mathrm{B}}} + \frac{1}{N_{\mathrm{C}}\phi_{\mathrm{C}}} - 2\chi_{\mathrm{BC}}\right] + \left[\frac{1}{\phi_{\mathrm{B}_1}}\frac{\partial \phi_{\mathrm{B}_1}}{\partial \phi_{\mathrm{B}}} - \frac{1}{q\phi_{\mathrm{C}_1}}\frac{\partial \phi_{\mathrm{C}_1}}{\partial \phi_{\mathrm{B}}}\right] - \left[\frac{1}{n_{\mathrm{H}}{}^{\circ}\phi_{\mathrm{B}}} + \frac{1}{q\phi_{\mathrm{C}}}\right] \quad (26)$$

$$\frac{\partial^2(\Delta G_{\mathrm{m}}/RT)}{\partial \phi_{\mathrm{A}}\partial \phi_{\mathrm{B}}} = \left[\frac{1}{N_{\mathrm{C}}\phi_{\mathrm{C}}} + \chi_{\mathrm{AB}} - (\chi_{\mathrm{AC}} + \chi_{\mathrm{BC}})\right] + \left[\frac{1}{r\phi_{\mathrm{A}_1}}\frac{\partial \phi_{\mathrm{A}_1}}{\partial \phi_{\mathrm{B}}} - \frac{1}{q\phi_{\mathrm{C}_1}}\frac{\partial \phi_{\mathrm{C}_1}}{\partial \phi_{\mathrm{B}}}\right] - \frac{1}{q\phi_{\mathrm{C}}} \quad (27)$$

$$\frac{\partial^2(\Delta G_{\mathrm{m}}/RT)}{\partial \phi_{\mathrm{B}}\partial \phi_{\mathrm{A}}} = \left[\frac{1}{N_{\mathrm{C}}\phi_{\mathrm{C}}} + \chi_{\mathrm{AB}} - (\chi_{\mathrm{AC}} + \chi_{\mathrm{BC}})\right] + \left[\frac{1}{\phi_{\mathrm{B}_1}}\frac{\partial \phi_{\mathrm{B}_1}}{\partial \phi_{\mathrm{A}}} - \frac{1}{q\phi_{\mathrm{C}_1}}\frac{\partial \phi_{\mathrm{C}_1}}{\partial \phi_{\mathrm{A}}}\right] - \frac{1}{q\phi_{\mathrm{C}}} \quad (28)$$

and the partial derivatives in eqs 25–28 are

$$\frac{\partial \phi_{\mathrm{A}_1}}{\partial \phi_{\mathrm{A}}} = \frac{\phi_{\mathrm{A}_1}}{\phi_{\mathrm{A}}}\left[1 - K_{\mathrm{A}}\phi_{\mathrm{A}_1}\Gamma_2\frac{\partial \phi_{\mathrm{B}_1}}{\partial \phi_{\mathrm{A}}}\right] \quad (29)$$

$$\frac{\partial \phi_{\mathrm{A}_1}}{\partial \phi_{\mathrm{B}}} = \frac{\phi_{\mathrm{A}_1}}{\phi_{\mathrm{A}}}\left[-K_{\mathrm{A}}\phi_{\mathrm{A}_1}\Gamma_2\frac{\partial \phi_{\mathrm{B}_1}}{\partial \phi_{\mathrm{B}}}\right] \quad (30)$$

$$\frac{\partial \phi_{\mathrm{C}_1}}{\partial \phi_{\mathrm{A}}} = -\frac{\phi_{\mathrm{C}_1}}{\phi_{\mathrm{C}}}\left[1 + K_{\mathrm{C}}\phi_{\mathrm{C}_1}\Gamma_2\frac{\partial \phi_{\mathrm{B}_1}}{\partial \phi_{\mathrm{A}}}\right] \quad (31)$$

$$\frac{\partial \phi_{\mathrm{C}_1}}{\partial \phi_{\mathrm{B}}} = -\frac{\phi_{\mathrm{C}_1}}{\phi_{\mathrm{C}}}\left[1 + K_{\mathrm{C}}\phi_{\mathrm{C}_1}\Gamma_2\frac{\partial \phi_{\mathrm{B}_1}}{\partial \phi_{\mathrm{B}}}\right] \quad (32)$$

$$\frac{\partial \phi_{\mathrm{B}_1}}{\partial \phi_{\mathrm{A}}} = -\left(\frac{\partial F}{\partial \phi_{\mathrm{A}}}\right)/\left(\frac{\partial F}{\partial \phi_{\mathrm{B}_1}}\right) \quad (33)$$

$$\frac{\partial \phi_{\mathrm{B}_1}}{\partial \phi_{\mathrm{B}}} = -\left(\frac{\partial F}{\partial \phi_{\mathrm{B}}}\right)/\left(\frac{\partial F}{\partial \phi_{\mathrm{B}_1}}\right) \quad (34)$$

where the implicit function $F = F(\phi_{\mathrm{B}}, \phi_{\mathrm{B}_1}, \phi_{\mathrm{A}}, \Gamma_1) = 0$ is given by eq 15. Hence, the derivatives are

$$\frac{\partial F}{\partial \phi_{\mathrm{A}}} = -\phi_{\mathrm{B}_1}\Gamma_2\left[\frac{X}{\phi_{\mathrm{A}}} - \frac{Y}{\phi_{\mathrm{C}}}\right] \quad (35)$$

$$\frac{\partial F}{\partial \phi_{\mathrm{B}}} = 1 + \phi_{\mathrm{B}_1}\Gamma_2\left[\frac{Y}{\phi_{\mathrm{C}}}\right] \quad (36)$$

and

$$\frac{\partial F}{\partial \phi_{\mathrm{B}_1}} = -\Gamma_3[1 + X + Y] + \phi_{\mathrm{B}_1}\Gamma_2{}^2\left[\frac{rX^2}{\phi_{\mathrm{A}}} + \frac{qY^2}{\phi_{\mathrm{C}}}\right] \quad (37)$$

where

$$\Gamma_3 = \Gamma_2 + \phi_{\mathrm{B}_1}\frac{\partial \Gamma_2}{\partial \phi_{\mathrm{B}}} = \Gamma_2 + \frac{2K_2\phi_{\mathrm{B}_1}}{(1 - K_{\mathrm{B}}\phi_{\mathrm{B}_1})^3} \quad (38)$$

Using the above expressions, it is relatively easy to show that eqs 27 and 28 are equal, as required by the condition for functions having continuous partial derivatives. Eqs 26, 32, and 34 reduce to eqs 15, 10, and 14 of ref 21, as they should when $\phi_{\mathrm{A}} = 0$ and $K_2 = K_{\mathrm{B}}$.

Experimental Section

The polymers used in this study, and the parameters necessary for the association model, are given in Table I.

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 complete removal of residual solvent.

Infrared spectra were recorded with a Nicolet 5DXC spectrometer. A minimum of 64 scans were signal averaged at a

Table I. Model Parameters of Ternary PMMA (A)/PVPh (B)/PEMA (C) Blends

polymer	molar vol[a] ($cm^3\ mol^{-1}$)	polymerizatn deg[b]	solubility param[a] ($cal\ cm^{-3})^{0.5}$	equilib const at 165 °C[b]
PMMA	84.9	915	9.06	$K_A = 3.66$
PVPh	100.0	250	10.6	$K_2 = 1.02$, $K_B = 4.04$
PEMA	101.4	2750	8.89	$K_C = 4.19$

[a] Reference 4. [b] Reference 8.

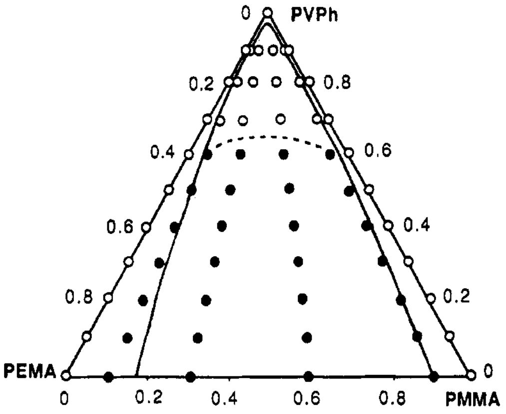

Figure 1. Miscibility diagram of ternary PMMA/PVPh/PEMA blends: (○) single-phase compositions, (●) phase-separated compositions, (- - -) experimental miscibility boundary. The continuous line is the spinodal curve predicted by the association model at 165 °C using the model parameters from Table I.

resolution of 2 cm^{-1}. Spectra at 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.[11]

Results and Discussion

A. Spinodal Calculations. In a previous paper,[8] we have shown that results concerning EMA-*co*-MMA/PVPh blends can be described with success in terms of the association model developed by Painter, Coleman, and co-workers.[11] An extension of this model to ternary blends containing a polymer that self-associates (i.e., PVPh) and two polymers that do not (i.e., PMMA and PEMA) but are able to form hydrogen bonds with the first has been reported in the theoretical section. Assuming that the model parameters determined for binary PMMA/PVPh and PEMA/PVPh blends can also be employed for ternary PMMA (A)/PVPh (B)/PEMA (C) blends (Table I), a comparison between the theoretical miscibility diagram predicted by the association model and experimental results[7] is valid. The requirements for ternary blend miscibility are given by

$$\Delta G_m/RT < 0 \tag{39}$$

and the stability criterion for phase separation is determined by eq 24. The spinodal curve is defined by equating the left-hand side of eq 24 to 0 (see Theory).

Figure 1 shows the spinodal curve predicted by the association model for PMMA/PVPh/PEMA blends at 165 °C using the parameters given in Table I. Ternary blend compositions having a single glass transition temperature T_g and two T_g's (phase-separated blends) are also indicated for comparison. As can be seen, the model does not reproduce adequately the experimental miscibility boundary of this system because a larger immiscibility region is predicted than that found by DSC and SEM.[7] No substantial changes were observed when the calculations were performed at several different temperatures (i.e., 25 and 200 °C). A change of the interassociation constants between the error limits previously stablished[8] has a negligible effect on the calculated miscibility diagram. In addition, no significant differences were found when the combinatorial entropy term in eq 23 was changed[22] to one of regular solution type. However, the results were found to be very sensitive to the values of the non-hydrogen-bonding solubility parameters employed. Indeed, if these parameters are assumed to be identical for every component, a totally miscible ternary system is predicted for the PMMA/PVPh/PEMA system. Therefore, in terms of this model the location of the miscibility boundary for the above system appears to be controlled by the contributions to the free energy of mixing arising from physical forces (i.e., weak polar and dispersive interactions) rather than from hydrogen bonding. In this case, accurate values of the χ_{ij} parameters corresponding to weak physical interactions will be required to reproduce quantitatively the experimental miscibility boundary. However, the group contribution scheme[11] used in this work to estimate the non-hydrogen-bonding solubility parameters, and hence χ_{ij}, is only approximate, and factors such as the temperature dependency of the solubility parameters[23] or the contributions from free volume[12–14] effects are not taken into account. Certainly, the error in calculating solubility parameters in this way has been estimated to be at least $\pm 0.4\ cal^{1/2}\ cm^{-3/2}$. The effect of this uncertainty over the calculated spinodal curve can be investigated following a reverse procedure to that employed to predict the miscibility diagram in Figure 1. Thus, by fitting the spinodal equation to the assumed miscibility boundary (Figure 1), we can for example determine the PEMA solubility parameter (δ_C) as a function of the PMMA solubility parameter (δ_A) employed (Figure 2A). In the calculation, we have retained both the value of the PVPh solubility parameter (δ_B) given in Table I and the condition $\delta_C < \delta_A$. As can be seen in Figure 2A, a progressive increase of δ_A leads to higher δ_C values, showing a slight composition dependence. This trend is better appreciated when the interaction parameter χ_{AC} corresponding to weak physical forces between PMMA and PEMA is plotted against composition, as represented in Figure 2B. We have also shown in this figure, as a reference value, the critical value of χ_{AC} estimated from only molecular weight consideration.[18] Since PMMA and PEMA are not miscible, only curves derived with χ_{AC} above the critical value have physical significance. It appears that a δ_A value at least above 9.66 $cal^{1/2}\ cm^{-3/2}$ is required to ensure that this condition is met. This procedure is, of course, only approximate as reflected by the fact that the composition dependence of χ_{AC} indicated above arises as a consequence of the change with composition of the fitted δ_C. Factors such as local chain packing[24] or free volume effects[12–14] that are not taken into account in the association model could actually make χ_{AC} composition dependent. In any case, the shape of the curves represented in Figure 2B is similar to that reported previously[7] using the classical Flory–Huggins theory and the miscibility diagrams of several ternaries involving the immiscible PMMA/PEMA pair. Nevertheless, in order to predict the precise miscibility boundary of ternary PMMA/PVPh/PEMA blends using the association model, accurately determined χ_{ij} parameters should be employed.

B. Model Predictions and FTIR Results. Although the miscibility boundary of ternary PMMA/PVPh/PEMA blends cannot be accurately determined in terms of the association model due to the lack of reliable χ_{ij} parameters

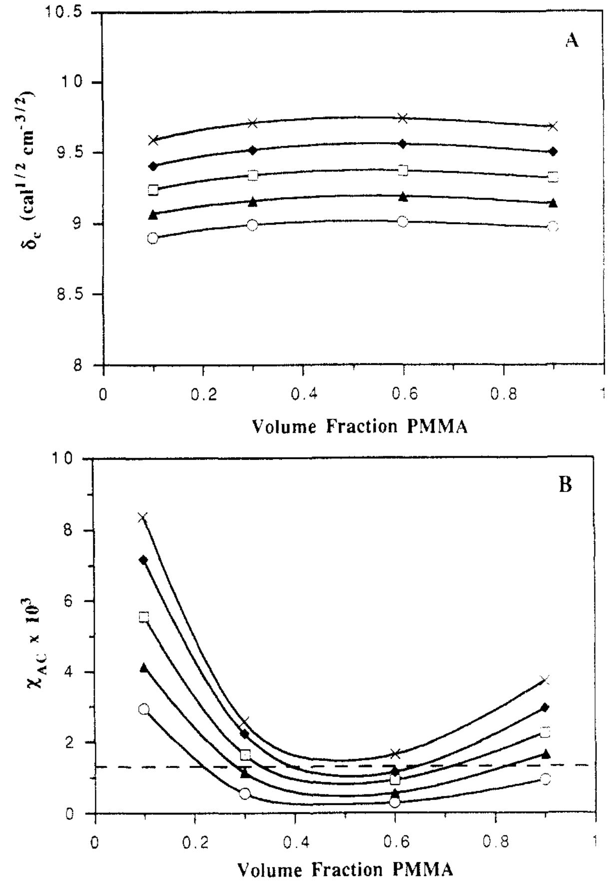

Figure 2. PEMA solubility parameter (δ_C) (A) and PMMA/PEMA interaction parameter (χ_{AC}) (B) determined by fitting the spinodal curve from the association model to the experimental miscibility boundary of Figure 1 using several values of the PMMA solubility parameter (δ_A): (×) δ_A = 9.86 cal$^{1/2}$ cm$^{3/2}$, (◆) δ_A = 9.66 cal$^{1/2}$ cm$^{3/2}$, (□) δ_A = 9.46 cal$^{1/2}$ cm$^{3/2}$, (▲) δ_A = 9.26 cal$^{1/2}$ cm$^{3/2}$, (○) δ_A = 9.06 cal$^{1/2}$ cm$^{3/2}$. The broken line represents the critical value of χ_{AC} estimated from molecular weight considerations.

corresponding to weak physical interactions, it is possible to check the model predictions related to the contributions from specific forces (hydrogen bonding). In this sense, the stoichiometric equations allow one to calculate the theoretical fraction of carbonyl groups hydrogen bonded (f_T^{theor}) as a function of composition that, in turn, can be compared to the experimental quantities (f_T^{exp}) determined by FTIR measurements. The parameters of the infrared carbonyl band corresponding to binary PMMA/PVPh and PEMA/PVPh blends are summarized in Table II. For ternary blends, the overall f_T^{exp} can be determined by curve-fitting the carbonyl stretching region (see Figure 3) using only two (Gaussian) bands:[25] the first band giving the overall contribution from free carbonyl (C=O) groups (both of PMMA and PEMA) and the second that from hydrogen-bonded C=O groups (both of PMMA and PEMA). Accordingly, the overall f_T^{exp} is

$$f_T^{\text{exp}} = \frac{1}{1 + a_r(A_T^{\text{f}}/A_T^{\text{b}})} \tag{40}$$

where A_T^{f} and A_T^{b} are the areas corresponding to the free and hydrogen-bonded C=O groups, respectively, and a_r

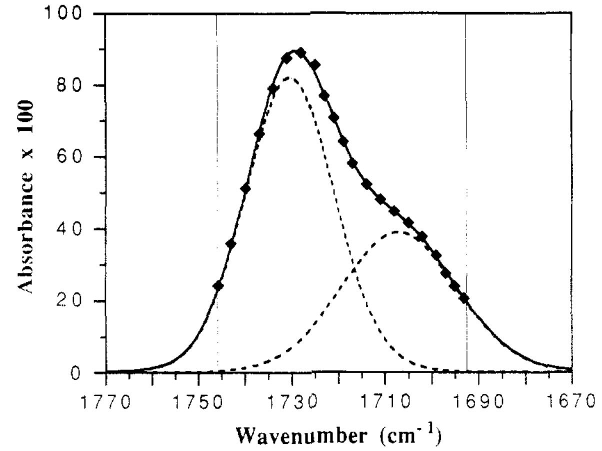

Figure 3. Example of least-squares deconvolution of the carbonyl stretching region for a PMMA/PVPh/PEMA (18/40/42) blend at 165 °C. The points represent the experimental data, the solid line represents the fitted curve, and the dashed lines represent the theoretical peaks.

is the absorptivity ratio that in this case amounts to 1.5.[4] On the other hand, the overall f_T^{theor} is given by

$$f_T^{\text{theor}} = 1 - \frac{\phi_{A_1} + \phi_{C_1}}{\phi_A + \phi_C} \tag{41}$$

The model parameters from Table I and the methodolgy described in the theoretical section can be used to determine ϕ_{A_1} and ϕ_{C_1} for each ternary composition and, hence, f_T^{theor}. Figure 4 shows a comparison of f_T^{theor} and f_T^{exp} for two selected cases of the ternary system. A striking feature in this figure is the good agreement between calculation and experiment even for immiscible ternary compositions. In general, for binary blends showing phase separation small f_T^{exp} values are usually found for the phase-separated compositions when compared to f_T^{theor} ones.[26,27] In fact, for these systems if phase splitting proceeds to nearly pure component phases, f_T^{exp} is expected to be negligible. However, for phase-separated ternary PMMA/PVPh/PEMA blends the picture cannot be so simple, since PVPh is miscible with both PMMA and PEMA. Although DSC indicates that there are two phases,[7] a considerable amount of hydrogen-bonded C=O groups can be present in each phase. Hence, it is possible that, within the experimental error of about ±0.03, f_T^{exp} equals the value for miscible systems, even though the blends are phase-separated.

The preceding analysis led us to consider separately the fraction of hydrogen-bonded C=O groups corresponding to PMMA (f_A) from that of PEMA (f_C). Therefore, a quantitative determination of four bands assigned to free and hydrogen-bonded C=O groups of PMMA and those of PEMA is required. However, given the increasing uncertainty in the results obtained by curve-fitting to a great number of overlapping bands, we have restricted the resolution of the C=O region into only three bands by considering the contribution from free C=O (both of PMMA and PEMA) as a single band due to their similar band widths (Table II). In the least-squares fitting procedure,[25] the limits for searching the position and width

Table II. Infrared Carbonyl Band Parameters of PMMA and PEMA in Binary Blends with PVPh[a]

	PMMA		PEMA	
	free C=O band	H-bonded C=O band	free C=O band	H-bonded C=O band
frequency ν (cm^{-1})	1732–1733	1708–1709	1728–1729	1703–1705
band width $W_{1/2}$ (cm^{-1})	18–19	23–24	18–19	24–26

[a] Reference 8.

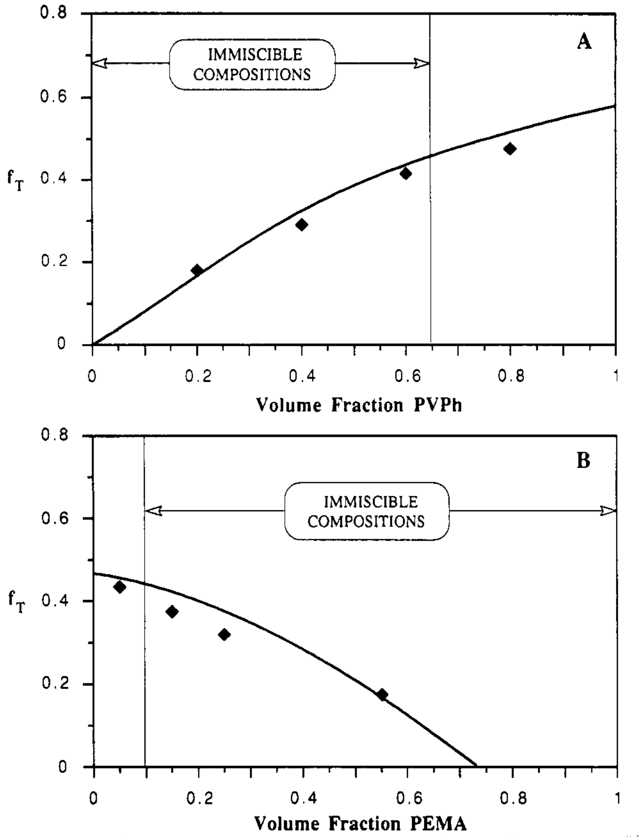

Figure 4. Comparison of the experimental overall fraction of hydrogen-bonded carbonyl groups (f_T^{exp}) and the theoretical quantity (f_T^{theor}) for two representative cases of the ternary PMMA/PVPh/PEMA system at 165 °C: (A) constant ϕ_A/ϕ_C ratio ($\phi_A/\phi_C = 3/7$), (B) constant ϕ_A ($\phi_A = 0.25$).

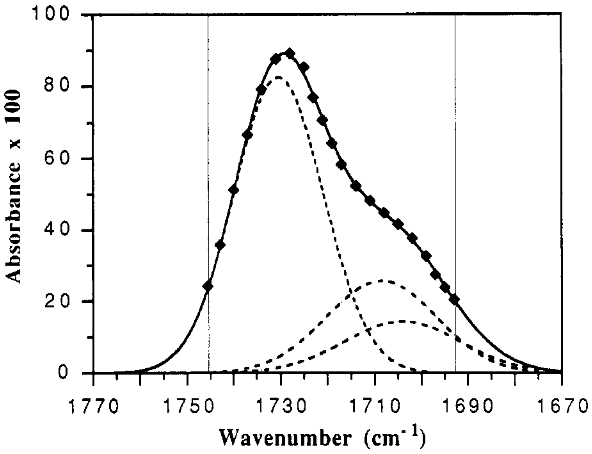

Figure 5. Illustration of the least-squares deconvolution of the carbonyl stretching region for a PMMA/PVPh/PEMA (18/40/42) blend at 165 °C employing three bands. The points represent the experimental data, the solid line represents the fitted curve, and the dashed lines represent the theoretical peaks.

of this band were restricted to the range of 1729–1732 and 18–19 cm^{-1}, respectively. The limits of the remaining band parameters employed corresponding to hydrogen-bonded C=O groups of PMMA and PEMA are summarized in Table II. The use of good prior estimates of band parameters is a necessary prerequisite in order to avoid meaningless results, but even so the error affecting the results is considerably higher than that previously indicated. Figure 5 shows the typical least-squares fitting result using the above methodology. From the areas corresponding to each peak it is possible to estimate the experimental fraction of hydrogen-bonded C=O groups corresponding to PMMA (f_A^{exp}) and PEMA (f_C^{exp}) that can be compared to the theoretical quantities (see Appendix). Figures 6 and 7 give a comparison between theoretical and experimental results concerning f_A and f_C for the same representative cases as in Figure 4. Although the error increases enormously for certain compositions where the contribution from the hydrogen-bonded C=O groups of PMMA and/or PEMA is relatively small, a certain trend becomes clear. A systematic deviation between experimental and theoretical values is found for the phase-separated compositions, as illustrated by the fact that f_A^{exp} remains above f_A^{theor} while f_C^{exp} is below f_C^{theor}. By increasing the PVPh content in the ternary system, a better agreement between experimental and theoretical predictions is progressively observed. Despite the uncertainty associated with the experimental data, the agreement for the miscible ternary compositions is almost quantitative. In this sense, we have also found for other different cases features similar to those represented in Figures 4, 6, and 7 (see Table III). Therefore, it appears that phase separation in this ternary system is better assessed using f_A and f_C than the overall f_T. Finally, from Figures 6 and 7 it could be inferred that a higher interaction degree exists between PMMA and PVPh than in the case of PEMA and PVPh for the immiscible compositions. However, this analysis can be perhaps too simplistic because we do not know if a true thermodynamic equilibrium exists between phases and also the presence of interfacial regions could complicate the matter. In any case, these observations would have interesting implications for other ternary systems where experimental limitations such as superimposed bands are not present.

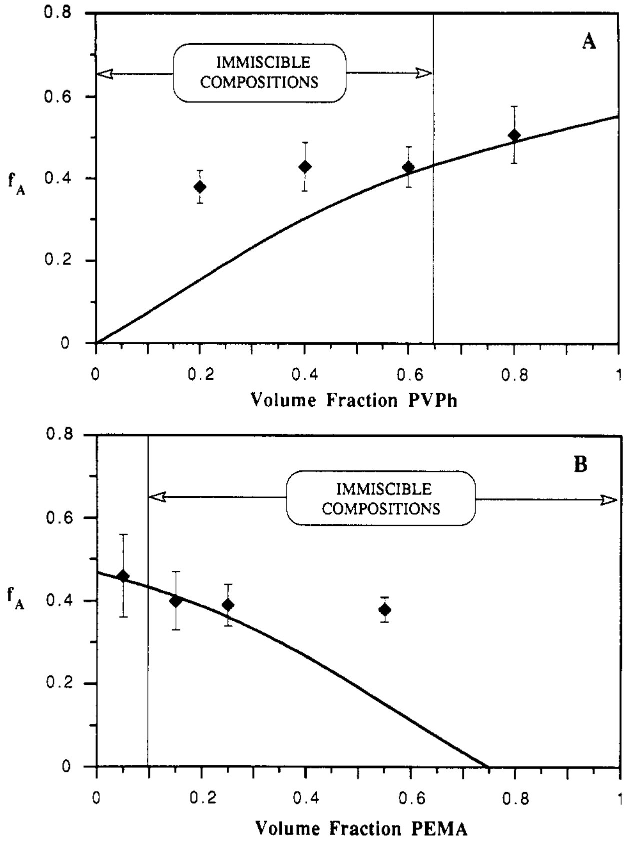

Figure 6. Comparison of the experimental fraction of hydrogen-bonded carbonyl groups of PMMA (f_A^{exp}) and the theoretical quantity (f_A^{theor}) for two representative cases of the ternary PMMA/PVPh/PEMA system at 165 °C: (A) constant ϕ_A/ϕ_C ratio ($\phi_A/\phi_C = 3/7$), (B) constant ϕ_A ($\phi_A = 0.25$).

Finally, by comparing the miscibility predictions of the association model for binary EMA-*co*-MMA/PVPh blends and ternary PEMA/PMMA/PVPh blends, we can state

Table III. Comparison of Theoretical and Experimental Fractions of Hydrogen-Bonded C═O Groups for Ternary PMMA (A)/PVPh (B)/PEMA (C) Blends[a]

$\phi_A/\phi_C = 6/4$

ϕ_B	f_T^{theor}	f_T^{exp}	f_A^{theor}	f_A^{exp}	f_C^{theor}	f_C^{exp}
0.20	0.158	0.14	0.151	0.28 ± 0.05	0.169	0.02 ± 0.05
0.40	0.311	0.27	0.299	0.45 ± 0.05	0.328	0.07 ± 0.04
0.60	0.424	0.38	0.410	0.40 ± 0.07	0.443	0.33 ± 0.07
0.80	0.505	0.48	0.491	0.45 ± 0.05	0.525	0.52 ± 0.05

$\phi_C = 0.25$

ϕ_A	f_T^{theor}	f_T^{exp}	f_A^{theor}	f_A^{exp}	f_C^{theor}	f_C^{exp}
0.05	0.484	0.45	0.456	0.41 ± 0.10	0.490	0.50 ± 0.10
0.15	0.433	0.41	0.412	0.42 ± 0.05	0.445	0.44 ± 0.06
0.25	0.377	0.32	0.361	0.44 ± 0.05	0.392	0.16 ± 0.05
0.35	0.312	0.27	0.299	0.45 ± 0.05	0.329	0.07 ± 0.04

[a] The estimated error in f_T^{exp} is about ±0.03 in all cases.

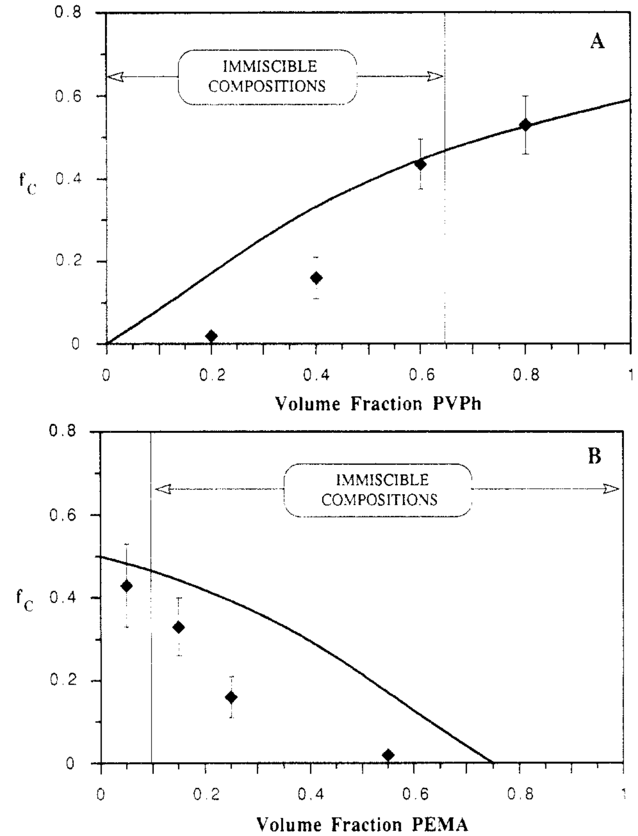

Figure 7. Comparison of the experimental fraction of hydrogen-bonded carbonyl groups of PEMA (f_C^{exp}) and the theoretical quantity (f_C^{theor}) for two representative cases of the ternary PMMA/PVPh/PEMA system at 165 °C: (A) constant ϕ_A/ϕ_C ratio (ϕ_A/ϕ_C = 3/7), (B) constant ϕ_A (ϕ_A = 0.25).

that a better agreement with experimental results[3,7] is achieved for binary systems than for ternary ones. However, further ternaries should be analyzed in order to ascertain the success and limitations of the association model extended to ternary polymer blends.

Summary and Conclusions

The association model extended to ternary polymer blends has been used to analyze the miscibility behavior and the degree of hydrogen bonding in ternary PMMA/PVPh/PEMA blends. It has been found that spinodal predictions in this system are very sensitive to the contributions to the free energy of mixing arising from weak physical forces. The lack of reliable interaction parameters corresponding to nonspecific forces prevents the determination of the precise miscibility boundary in terms of the association model for this system. However, the calculated interaction parameter of PMMA/PEMA blends, using this model and the experimental miscibility boundary, was found similar to that reported previously[7] from the classical Flory–Huggins theory and the miscibility diagrams of several ternaries involving the immiscible PMMA/PEMA pair.

FTIR measurements in the stretching region of the C═O group were performed in order to obtain information about hydrogen bonding in the ternary system and compare it to the model predictions. It has been found that the experimental overall fraction of hydrogen-bonded C═O groups (both of PMMA and PEMA) is in good agreement with the predicted one for miscible systems even for the immiscible compositions. This apparent contradiction has been attributed to the presence of a considerable amount of hydrogen-bonded carbonyl groups in each phase of the immiscible samples because PVPh is miscible with both PMMA and PEMA. Following a suitable curve-fitting procedure, the fraction of hydrogen-bonded C═O groups corresponding exclusively to PMMA and that of PEMA have been estimated. By comparing these experimental fractions to the theoretical ones from the model, ternary PMMA/PVPh/PEMA compositions where phase separation has taken place can be identified. In order to achieve a better insight into the success and the shortcomings of the association model extended to ternary polymer blends, other ternaries where experimental limitations such as strong band overlapping are not present should be analyzed.

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Appendix. Determination of f_A and f_C

Denoting the area of the band corresponding to hydrogen-bonded C═O groups of PMMA as $A_B^{(1)}$ and that of PEMA as $A_B^{(2)}$, the area of the band corresponding to free (non-hydrogen-bonded) C═O groups of both PMMA and PEMA is A_F^T. This latter band contains contributions from free C═O groups of PMMA ($A_F^{(1)}$) and PEMA ($A_F^{(2)}$), as given by

$$A_F^T = A_F^{(1)} + A_F^{(2)} \tag{A1}$$

The areas $A_B^{(1)}$ and $A_F^{(1)}$ are related to the fraction of hydrogen-bonded C═O groups of PMMA (f_A^{exp}) by the following equations:

$$A_B^{(1)} = a_B f_A^{\mathrm{exp}} \tag{A2}$$

$$A_F^{(1)} = a_F(1 - f_A^{\mathrm{exp}}) \tag{A3}$$

where a_B and a_F are the absorptivities for the hydrogen-bonded and free C=O bands, respectively. Similarly, for PEMA we have

$$A_B^{(2)} = a_B f_C^{\mathrm{exp}} \tag{A4}$$

$$A_F^{(2)} = a_F(1 - f_C^{\mathrm{exp}}) \tag{A5}$$

By using eqs A3 and A5, we can express eq A1 as

$$A_F^{T} = a_F(2 - f_A^{\mathrm{exp}} - f_C^{\mathrm{exp}}) \tag{A6}$$

Dividing eqs A2 and A4 by eq A6 gives

$$A_1 = \frac{A_B^{(1)}}{A_F^{T}} = \frac{a_r f_A^{\mathrm{exp}}}{2 - f_A^{\mathrm{exp}} - f_C^{\mathrm{exp}}} \tag{A7}$$

and

$$A_2 = \frac{A_B^{(2)}}{A_F^{T}} = \frac{a_r f_C^{\mathrm{exp}}}{2 - f_A^{\mathrm{exp}} - f_C^{\mathrm{exp}}} \tag{A8}$$

where $a_r = a_B/a_F$ is the absorptivity ratio. Hence, f_A^{exp} and f_C^{exp} can be determined in terms of the experimental quantities $A_B^{(1)}$, $A_B^{(2)}$, and A_F^{T} by solving eqs A7 and A8 above. The final expressions are

$$f_A^{\mathrm{exp}} = \frac{2A_1 a_r}{(A_1 + a_r)(A_2 + a_r) - A_1 A_2} \tag{A9}$$

and

$$f_C^{\mathrm{exp}} = \frac{2A_2 a_r}{(A_1 + a_r)(A_2 + a_r) - A_1 A_2} \tag{A10}$$

On the other hand, the expressions for the theoretical fractions of hydrogen-bonded C=O groups are given by the ternary association model as

$$f_A^{\mathrm{theor}} = 1 - \phi_{A_1}/\phi_A \tag{A11}$$

and

$$f_C^{\mathrm{theor}} = 1 - \phi_{C_1}/\phi_C \tag{A12}$$

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