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Mapping the Phase Diagram of Polymer–Polymer Blends Using Infrared Spectroscopy. 2. The Poly(4-vinylphenol)–EVA[45] System

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ABSTRACT: Blends of poly(4-vinylphenol) and a poly(ethylene-*co*-vinyl acetate) copolymer containing 45% by weight of vinyl acetate were studied using infrared spectroscopy. The distribution of hydrogen bonds as a function of temperature and composition was followed by measuring the relative proportions of free and hydrogen-bonded acetate carbonyl groups. These measurements can then be used to map an experimental phase diagram for the system. The phase diagram so obtained is compared to optical microscopy and DSC results and to a theoretically predicted phase diagram based on an association model.

Introduction

In a previous publication[1] we introduced a novel methodology for mapping the experimental phase diagram of an amorphous polyamide blend using infrared spectroscopy. In essence, a comparison of the experimentally obtained fraction of "free" (non-hydrogen-bonded) amide carbonyl groups with that theoretically predicted for the single- and two-phase regions enabled us to draw a phase diagram for the blend system. A majority of the studies performed in our laboratory, however, have focused on the phase behavior of blends of homo- and copolymers of 4-vinylphenol (VPh) with a systematic series of homo- and copolymers of acrylates, methacrylates, esters, and acetates.[2] It is within the confines of polymer blend systems such as these where we have the highest confidence in our analysis of the infrared spectral data and, in turn, the values of the parameters required to calculate the free energy of mixing and phase diagrams using our association model (i.e., equilibrium constants describing both self-association and interassociation and enthalpies of hydrogen-bond formation). Theoretical predictions and experimental observations of phase behavior have been found to be in close agreement for a wide variety of VPh polymer blend systems.[2] Accordingly, we should be able to experimentally map the phase diagram of a poly(4-vinylphenol) (PVPh) blend using infrared spectroscopy with greater precision than we were able to do in the case of the amorphous polyamide blends. Blends of PVPh with a poly(ethylene-*co*-vinyl acetate) copolymer containing 45 wt % vinyl acetate (EVA[45]) were found to be excellent systems for our purposes and are the subject of this paper.

Experimental Section

The polymers employed in this study have been described previously.[3,4] PVPh with a molecular weight (undefined) range of 1500–7000 was purchased from Polysciences, Inc., and has a T_g of approximately 140 °C. EVA[45] with a reported (GPC) molecular weight of 100 000–120 000 and a T_g of −28 °C was procured from Mobay Chemical Co. Blend samples were prepared by mixing appropriate amounts of a 1% (w/v) solution of each of the polymers in methyl ethyl ketone. Samples for Fourier transform infrared spectroscopy (FTIR) and optical microscopy were prepared by casting films onto potassium bromide (KBr) windows and glass slides, respectively. After evaporation of the majority of the solvent at room temperature, the samples were placed in a vacuum oven at 100 °C for 24 h.

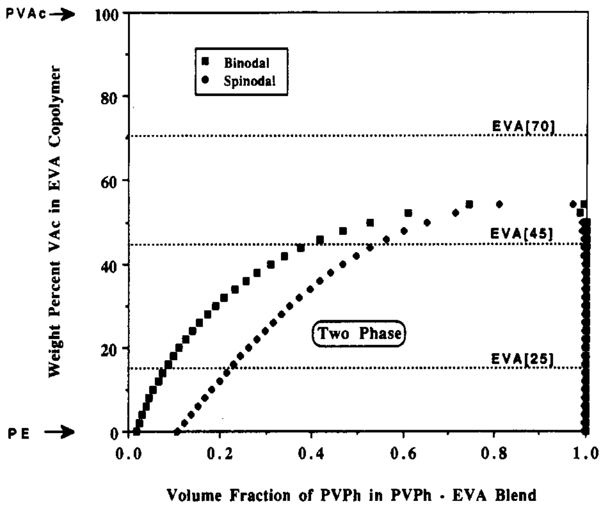

Figure 1. Miscibility map for the PVPh–EVA blend system at 100 °C.

Infrared spectra were recorded on a Digilab FTS-60 FTIR spectrometer at a resolution of 2 cm^{-1}. A minimum of 64 scans were signal averaged, and the spectra were stored on a magnetic disk system. Spectra recorded at elevated temperatures were obtained using a SPECAC high-temperature cell mounted in the spectrometer and a Micristar heat controller. This device has a reported accuracy of ±0.1 °C. Films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed (<0.6 absorbance units). Optical microscopy was conducted on a Olympus Model BHS polarizing microscope. Temperature studies were performed using a Mettler FP80 hot stage coupled to the microscope, and photographs were recorded on an Olympus PM10-ADS 35-mm camera.

Results and Discussion

In a series of recent papers we have described an association model[2,5–7] that accounts for free energy changes occurring in binary polymer mixtures containing strong specific interactions (hydrogen bonds). As a test of the predictive capabilities of this model, theoretical and experimental studies have been performed on PVPh–EVA blend systems.[2,8] Trends in the phase behavior of these types of blends can be conveniently expressed as miscibility "maps" or "windows". Figure 1 shows the theoretically predicted miscibility window for the PVPh–EVA blend system at 100 °C. The parameters employed in the calculations were all obtained a priori and are summarized in Table I. (The reader is referred to ref 8 for a complete

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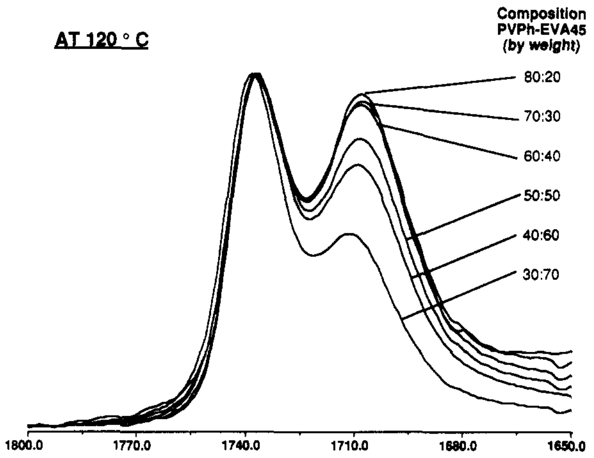

Figure 2. Scale-expanded spectra of the carbonyl stretching region as a function of PVPh–EVA[45] blend composition recorded at 120 °C.

Table I
Parameters Employed in Theoretical Calculations

segments	molar vol, cm^3/mol	mol wt	solubility param, $(cal{\cdot}cm^{-3})^{0.5}$	equilibrium constants of hydrogen-bond formation at 25 °C K_2	K_B	K_A
ethylene	16.5	14.0	8.0			
VAc	69.8	86.1	9.6			
VPh	100.0	120.0	10.6	21.0	66.8	58.7

enthalpy of hydrogen-bond formation:
h_2 = 5.6, h_B = 5.2, and h_A = 3.8 kcal/mol

analysis.) A single phase is predicted throughout the entire blend composition range (the definition of miscibility) for PVPh with poly(vinyl acetate) (PVAc) and EVA copolymers containing greater than about 55% vinyl acetate. On the other hand, blends of PVPh and EVA[25] are predicted to be grossly phase separated at equilibrium throughout the vast majority of the composition range and are thus immiscible. Experimental results performed in our laboratories are in excellent agreement with the trends presented above.[2-4,8,9] Of particular interest here is the PVPh–EVA[45] blend system, which is predicted to be two phase over a large part (~0.35–1.0 volume fraction of PVPh) of the composition range (and is thus an immiscible blend under the strict definition) but also contains a significant portion that is single phase (~0–0.35 volume fraction of PVPh). This type of polymer blend has been rather loosely referred to as "partially miscible".

Infrared spectra of PVPh–EVA[45] blends of differing composition were recorded at temperatures ranging from 100 to 200 °C. Of particular relevance to these studies are the stretching modes associated with the acetate carbonyl groups, as direct information about the nature and distribution of hydrogen-bonding interactions present in the system can be deduced from them. Representative examples of the infrared spectra obtained at 120 and 180 °C are shown in Figures 2 and 3, respectively. The carbonyl stretching band in these blends is recognized[2-4,8,9] as having two contributors, attributed to the free carbonyl groups (centered around 1738 cm^{-1}) and the hydrogen-bonded carbonyl groups (at ~1707 cm^{-1}). In order to quantitatively analyze the carbonyl stretching region, at least-squares fitting procedure was used to resolve individual spectra into their free and hydrogen-bonded carbonyl components. The fraction of hydrogen-bonded carbonyl groups can then be calculated from the relative areas under the free and hydrogen-bonded carbonyl bands by using an absorptivity coefficient ratio of $a_{HB}/a_F = 1.5$ (a value experimentally determined in previous works[2,3,9]). The results are summarized in Table II.

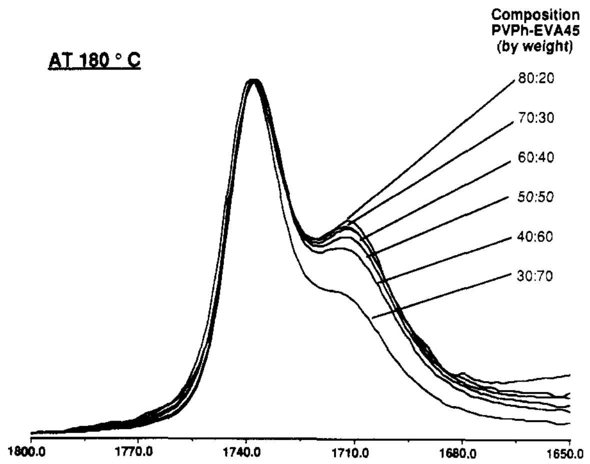

Figure 3. Scale-expanded spectra of the carbonyl stretching region as a function of PVPh–EVA[45] blend composition recorded at 180 °C.

Table II
Fraction of Hydrogen-Bonded Carbonyl Groups Determined by Curve Fitting the Carbonyl Stretching Region of the Infrared Spectra of PVPh–EVA[45] Blends at Different Compositions and Temperatures

temp, °C	composition (by wt) 80:20	70:30	60:40	50:50	40:60	30:70
100	0.57	0.58	0.57	0.55	0.52	0.44
120	0.55	0.57	0.56	0.54	0.52	0.42
140	0.54	0.56	0.54	0.53	0.51	0.41
160	0.51	0.54	0.52	0.51	0.48	0.34
180	0.49	0.51	0.50	0.50	0.47	0.38
200	0.47	0.48	0.48	0.48	0.45	0.36

In miscible PVPh–EVA blends, the phenolic hydroxyl group can hydrogen bond to itself (self-association), as well as with the acetate carbonyl groups (interassociation), resulting in the formation of hydrogen-bonded complexes or chains. In accord with the "chemical" theory of solutions, Prigogine[10] proposed that the formation of such complexes be treated by assuming a chemical equilibrium between the monomolecules of the bonded groups. We have applied these concepts to polymer mixtures and, using stoichiometric arguments, developed equations relating the fraction of bonded (associated) groups to the equilibrium constants of bond formation.[2] In other words, when functional groups in a blend are able to form hydrogen bonds according to their intrinsic proclivities (as in completely miscible blends) and are not constrained into separate domains by phase separation, then, using purely stoichiometric equations, the fraction of hydrogen-bonded carbonyl groups at any blend composition can be obtained from a knowledge of the equilibrium constants of self-association and interassociation. The results predicted by these stoichiometric equations are in excellent agreement with experimental values of the fraction of hydrogen-bonded carbonyl in miscible systems, as demonstrated in numerous experimental studies.[2,8,9] Values of the equilibrium constants of self-association between the phenol groups (K_2 and K_B) and interassociation between the phenol and carbonyl groups (K_A) can be obtained directly from previous experimental work,[2,8-12] permitting us to theoretically calculate the fraction of hydrogen-bonded groups for any miscible PVPh–EVA blends.

For a particular blend composition, the fraction of hydrogen-bonded carbonyl groups in a two-phase system

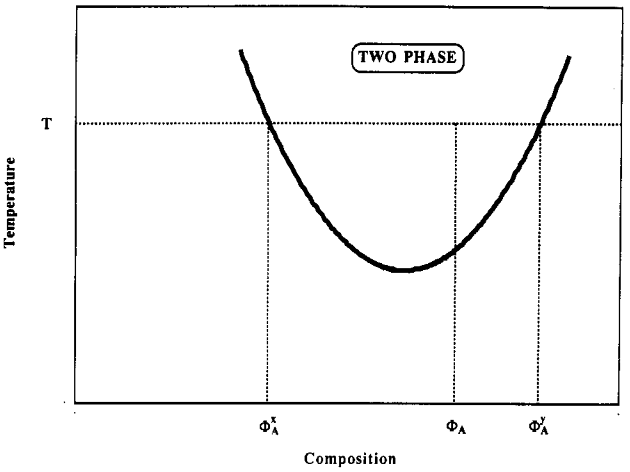

Figure 4. Schematic representation of a typical phase diagram.

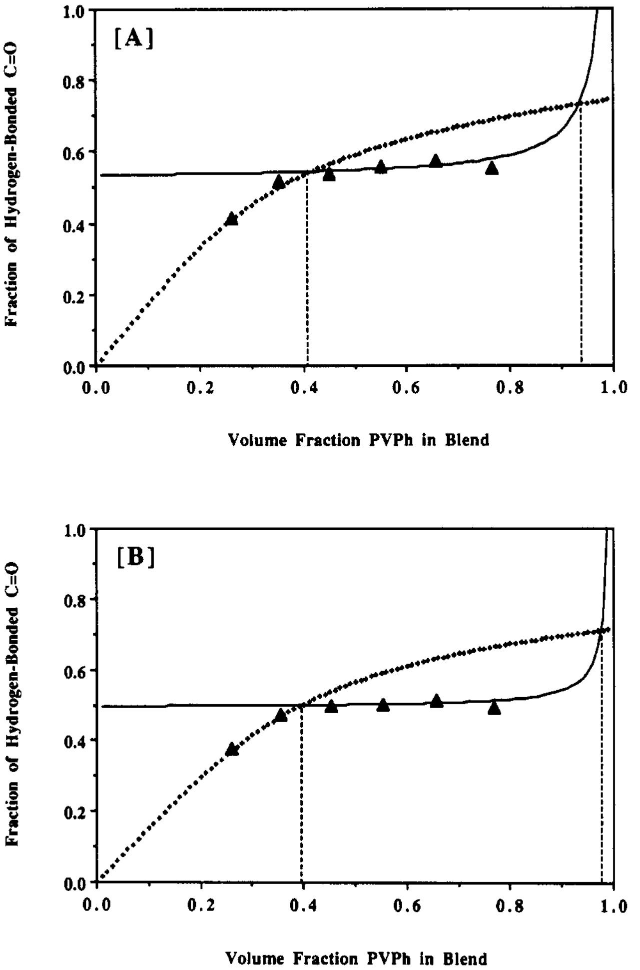

Figure 5. Comparison of the experimental data with the theoretical curves for the single- and two-phase systems for plots of the fraction of hydrogen-bonded carbonyl versus blend composition at (A) 120 °C and (B) 180 °C: (+++) theory, single phase; (—) lever rule, two phase; (▲) experimental data.

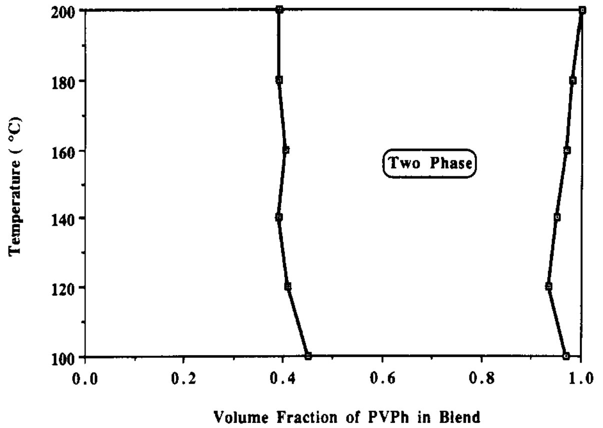

Figure 6. Experimental phase diagram of the PVPh-EVA[45] system as determined by infrared spectroscopy.

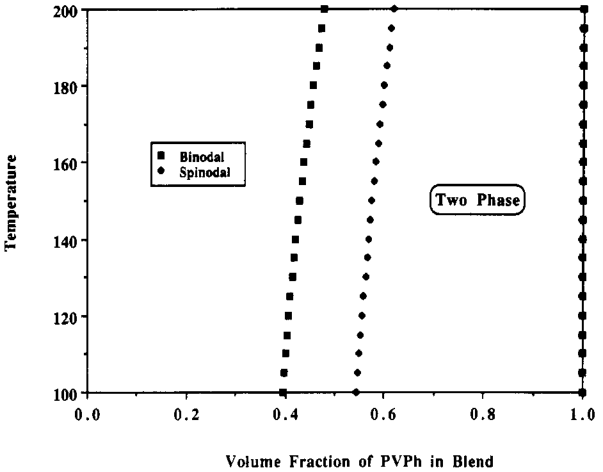

Figure 7. Theoretical binodal and spinodal phase diagrams of the PVPh-EVA[45] blend, as determined by the association model.

must necessarily be less than that present in the single-phase (miscible) counterpart. Although we have discussed the theoretical fraction of hydrogen-bonded carbonyl groups present at blend compositions within such a two-phase system,[1] it is worthwhile to briefly review some of the salient features. Consider the phase diagram shown in Figure 4. If, at blend composition Φ_A and temperature *T*, the system is in a two-phase region, then separation will occur into phases Φ_A^x and Φ_A^y as defined by the binodal. To be consistent with our previous nomenclature, the suffix A refers to the copolymer EVA[45]. The fraction of EVA[45] (or the fraction of carbonyl groups) present in the two phases, by the lever rule, is then given by

$$\frac{\Phi_A^y - \Phi_A}{\Phi_A^y - \Phi_A^x}\left[\frac{\Phi_A^x}{\Phi_A}\right] \quad \text{and} \quad \frac{\Phi_A - \Phi_A^x}{\Phi_A^y - \Phi_A^x}\left[\frac{\Phi_A^y}{\Phi_A}\right]$$

Now, if f_{HB}^x and f_{HB}^y are defined as the fraction of hydrogen-bonded carbonyl groups at compositions Φ_A^x and Φ_A^y, respectively, then the fraction of hydrogen-bonded carbonyl groups at Φ_A is given by

$$\Phi_A f_{HB} = \frac{\Phi_A^x \Phi_A^y (f_{HB}^x - f_{HB}^y)}{(\Phi_A^x - \Phi_A^x)} + \Phi_A \frac{(\Phi_A^y f_{HB}^y - \Phi_A^x f_{HB}^x)}{(\Phi_A^y - \Phi_A^x)} \tag{1}$$

Thus, for a blend system at a given temperature within a two-phase region at equilibrium, a plot of $\Phi_A f_{HB}$ versus Φ_A should yield a straight line with a slope ξ_1 and ξ_2, and the above equation simplifies to[1]

$$f_{HB} = \xi_1/\Phi_A + \xi_2 \tag{2}$$

In other words, within the two-phase region, at a given temperature, the relationship between the fraction of hydrogen-bonded carbonyl groups and blend composition Φ_A is given by this parabolic expression.

Mapping the Experimental Phase Diagram. Employing values of the equilibrium constants of hydrogen-bond formation (Table I) obtained in previous studies and employed here without alteration, the theoretical fraction

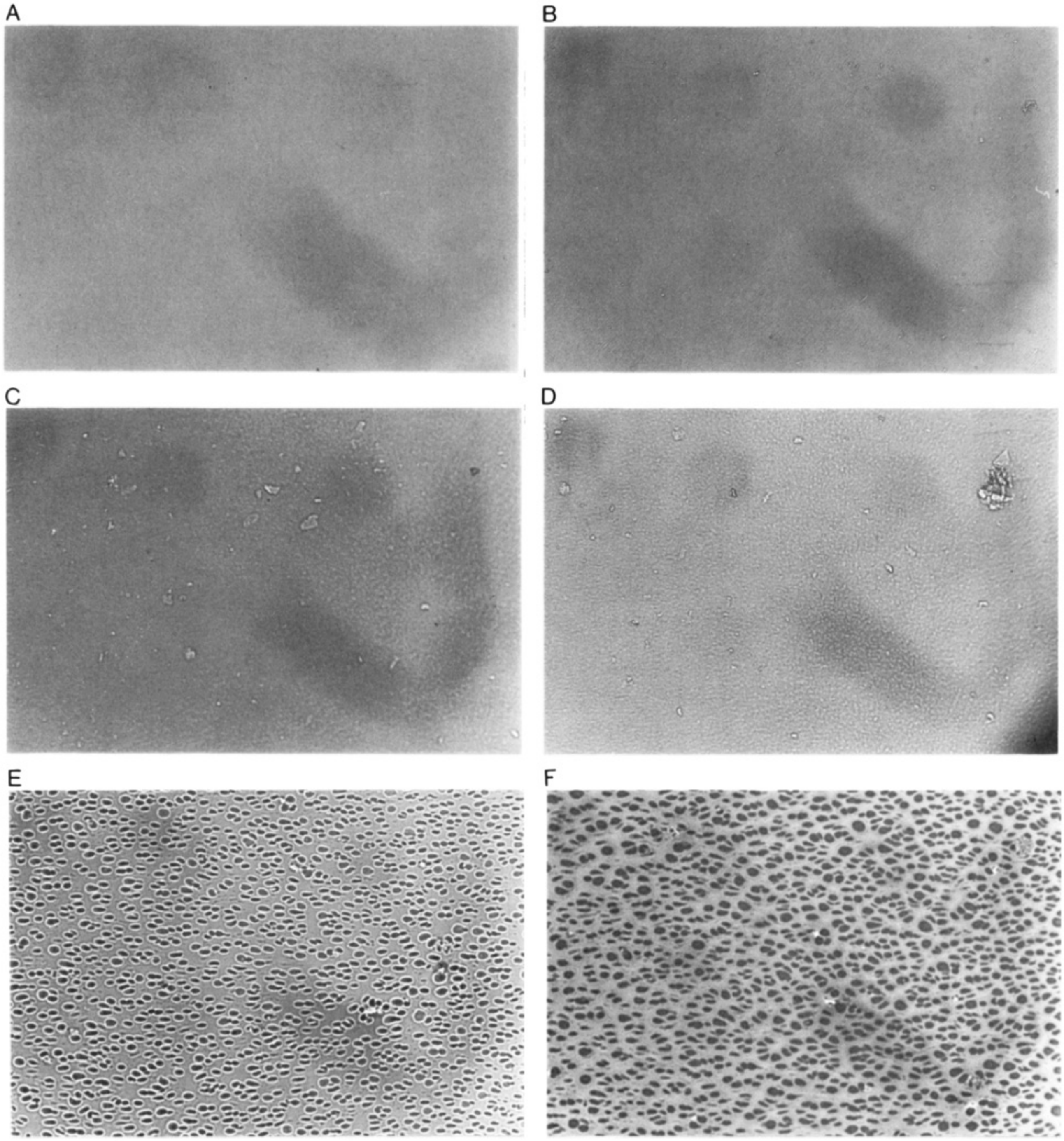

Figure 8. Optical micrographs of PVPh–EVA[45] blends of varying compositions (by weight): 30:70 at (A) 100 °C and at (B) 200 °C; 50:50 at (C) 100 °C and at (D) 200 °C; 80:20 at (E) 100 °C and at (F) 200 °C. All observations were made at magnifications of 100×.

of hydrogen-bonded carbonyl groups as a function of blend composition for *hypothetically completely miscible* PVPh–EVA[45] blends can be readily calculated.[2] Representative examples are illustrated in Figure 5. Also plotted are the experimental values of the fraction of hydrogen-bonded carbonyls obtained by curve resolving the carbonyl bands (Table II). Consider for analysis the results at 120 °C (Figure 5A). Two of the experimental data points (corresponding to volume fraction PVPh = 0.26 and 0.35) lie on the theoretical single-phase curve. The remaining experimental data points can be fitted to the parabolic two-phase lever rule curve (eq 2). The intersections of the theoretical single-phase curve and the lever rule two-phase curve represent compositions at which a transition occurs from a two-phase to a single-phase system. To reiterate, at a given temperature, the intercept of the two theoretical curves yields the composition limits of the two-phase region (the binodal). Applying this analysis at different temperatures permits us to map a phase diagram that has been derived from experimental infrared data, and this is illustrated in Figure 6.

Using the association model, the phase diagram for the PVPh–EVA[45] system can be theoretically calculated.[2] The parameters employed in the calculation are listed in Table I, and the resulting phase diagram, in the temperature range of interest, is shown in Figure 7. Without meaning to belabor the point, we lay emphasis on the fact that all the parameters used were predetermined and that the calculation uses no adjustable parameters. The agreement between theoretically predicted and experimentally observed phase behavior is clearly very good.

The use of infrared spectroscopy to probe the phase diagram of hydrogen-bonded mixtures is a new technique, but in support of our observations it should be noted that differential scanning calorimetry (DSC) studies conducted by Moskala et al.[4] indicated that PVPh–EVA[45] blends are a phase-separated system. Although interpretation is complicated due to a broad endotherm (associated with the melting of short sequences of ethylene-type crystallinity) superimposed on the thermograms, the authors conclude that the blend is a multiphased system, consisting of essentially a pure PVPh phase and a mixed PVPh and EVA[45] phase. Finally, optical microscopy studies were also performed on PVPh–EVA[45] blends, and the results are displayed in Figure 8. For the PVPh–EVA[45] 30:70 (by weight) blend, the optical micrographs were essentially featureless, inferring a homogeneous single-phase blend. The micrographs at 50:50 blend composition showed a granular character, probably signifying the onset of phase separation. At a composition of 80:20, the micrographs have the typical appearance of grossly phase-separated systems. Both these experimental techniques give results in complete accord with our experimental phase diagram.

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