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Equilibrium Constants and Predictions of Miscibility Windows and Maps for Polymer Blends Involving *p*-(Hexafluoro-2-hydroxy-2-propyl)styrene with Methacrylate and Acetoxy Groups

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ABSTRACT: Dimensionless equilibrium constants describing the self-association of the hexafluoro-2-phenyl-2-propanol (HFPP) group have been determined from infrared spectroscopic data. Corresponding values of these equilibrium constants for polymers containing the *p*-(hexafluoro-2-hydroxy-2-propyl)styrene (HFPS) group were calculated by taking into account differences in the molar volume of the model and what we define as the "specific repeat" of the polymer.[1] Equilibrium constants describing the interassociation of HFPS with methacrylate and acetoxy type carbonyl groups were obtained from spectroscopic studies of miscible poly[styrene-*co*-*p*-(hexafluoro-2-hydroxy-2-propyl)styrene] (STHFPS) blends with poly(*n*-butyl methacrylate) and an ethylene-*co*-vinyl acetate copolymer containing 70% vinyl acetate. Relative to vinylphenol, the self-association of HFPS is substantially weaker, while that of interassociation to aliphatic methacrylate and acetoxy type functionalities is roughly comparable. The equilibrium constant values were then used to calculate theoretical miscibility windows and maps for the complete range of blends of STHFPS with poly(*n*-alkyl methacrylates) and ethylene-*co*-vinyl acetate copolymers. In addition, calculations were also performed for poly[styrene-*co*-*p*-(hexafluoro-2-hydroxy-2-propyl)-α-methylstyrene] with poly(methyl methacrylate) and poly(*n*-butyl methacrylate). A comparison of the predicted miscibility windows and maps with those of the equivalent vinylphenol copolymer blends reveals that STHFPS blends have a much wider "window of miscibility", and this result is substantiated by experimental results reported in the literature and performed in our laboratories.

Introduction

Over the past 5 years or so the Penn State authors and their co-workers have developed a theoretical model that describes the free energy changes occurring in binary polymer mixtures containing strong directionally specific interactions.[1,2] Concurrently, experimental studies designed to assess the predictive capabilities of this model have been performed, with the emphasis placed on blends of polymers containing the 4-vinylphenol (VPh)[1] unit such as poly(4-vinylphenol) (PVPh) and styrene-*co*-vinylphenol (STVPh) as one component mixed with a series of poly(*n*-alkyl methacrylates) (PAMA),[3-7] ethylene-*co*-vinyl acetate (EVA),[8] ethylene-*co*-methyl acrylate (EMA),[8] and styrene-*co*-methyl acrylate (STMA)[9] polymers as the second component.

At the same time, the Polytechnic Institute authors and their co-workers have developed synthetic routes to produce polymers containing the *p*-(hexafluoro-2-hydroxy-2-propyl)styrene group (HFPS)[10-12] and examined various blends involving these materials. Styrene-*co*-*p*-(hexafluoro-2-hydroxy-2-propyl)styrene (STHFPS) copolymers containing varying amounts of HFPS were synthesized and found to be miscible with a wide variety of polymers including poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(*n*-butyl methacrylate) (PBMA), poly(vinyl acetate) (PVAc), polycarbonate (PC), and poly(vinyl methyl ether) (PVME). Perhaps the most interesting facet of this work, however, was the fact that it required <2% of HFPS units in polystyrene to render it miscible with PEMA or PBMA.[12] Similar results were subsequently observed for STVPh copolymers[1,5] and, more recently, polymer blends involving styrene-*co*-*p*-(hexafluoro-2-hydroxy-2-propyl)-α-methylstyrene (STHFPMS) copolymers.[13,14]

The primary motivation of the studies reported here was to determine whether or not the association model could predict the observed results reported for the STHFPS and STHFPMS polymer blend systems, and, if so, would there be unique predictions concerning the phase behavior of other blends involving these copolymers that would warrant further experimental investigation. To achieve these goals it is first necessary to determine equilibrium constants that can be used to describe the self-association and interassociation (hydrogen bonds between the different components) of blends of polymers containing the HFPS group. Experimental values of these parameters, which can be determined from infrared spectroscopic studies, are used in an association model, and the free energy of mixing, phase diagrams, and miscibility windows and maps of polymer blends can then be calculated.[1]

Experimental Section

Cyclohexane and 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol (HFPP) were purchased from Aldrich Chemical Co. and used without further purification. Styrene-*co*-*p*-(hexafluoro-2-hydroxy-2-propyl)styrene (STHFPS) containing 60 and 80 mol % of *p*-(hexafluoro-2-hydroxy-2-propyl)styrene (HFPS) were synthesized in the laboratories at the Polytechnic University of New York and have been previously described,[12] as have the poly(*n*-alkyl methacrylates) from methyl to decyl.[6,7] Other poly(*n*-alkyl methacrylates), including *n*-lauryl, *n*-hexadecyl, and *n*-octadecyl, together with the poly(ethylene-*co*-vinyl acetate) (EVA) copolymers with copolymer compositions ranging from 9

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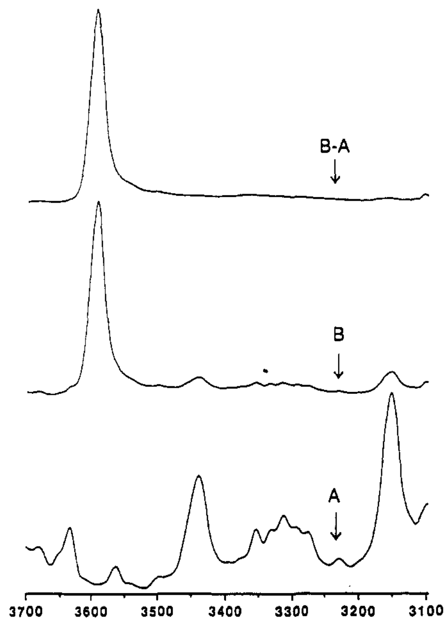


Figure 1. Infrared spectra in the hydroxyl stretching region of (A) pure cyclohexane and (B) a 0.8 mol/L solution of HFPP in cyclohexane and the difference spectrum B − A.

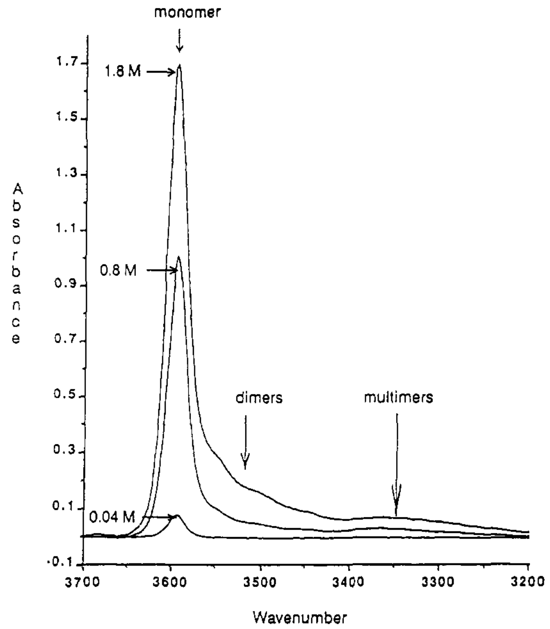


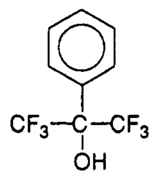
Figure 2. Infrared spectra in the hydroxyl stretching region of three different concentrations of HFPP in cyclohexane.

to 70 wt % and molecular weights exceeding 100 000 were purchased from Scientific Polymer Products Inc.

Infrared spectroscopic measurements were recorded on a Digilab Model FTS60 Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. For the model compound studies, mixtures of HFPP and cyclohexane of different concentrations were contained in a standard 0.02-mm KBr liquid cell at ambient temperature, and a total of 64 interferograms were signal averaged. To minimize potential errors from underlying overtone and combination bands attributable to cyclohexane, the spectrum of the pure solvent was subtracted from the spectra of the mixtures using the bands between 3100 and 3500 cm^{-1} as reference bands. This is illustrated in Figure 1. Note that the method we use to determine equilibrium constants[15] only requires accurate measurement of the absolute absorbance of the band at 3595 cm^{-1}, and thus we are only concerned with errors introduced by the relatively weak bands in the 3550–3650-cm^{-1} region. Polymer blend films for transmission FTIR were cast from a mixture of toluene and tetrahydrofuran (90:10 by volume) onto KBr windows. This solvent mixture was chosen in preference to pure THF to minimize solvent-induced phase separation. After the majority of the solvent had evaporated, the films were placed under vacuum at room temperature for at least 24 h, followed by 4 h at 120 °C, to completely remove residual solvent. We were careful to ensure that we attained equilibrium conditions by comparing infrared spectra recorded at different temperatures by cycling up and down from room temperature to 160 °C (well above the T_g's of the constituents of the blends). Films used in this study were sufficiently thin to be within an absorbance range where the Beer–Lambert law is obeyed.

Results and Discussion

Determination of Self-Association Equilibrium Constants. The determination of the equilibrium constants describing the formation of dimers (K_{c_2}) and higher multimers or "chainlike" complexes (K_c) from infrared spectroscopic measurements of hydroxyl-containing low molecular weight compounds is now well established.[1,15,16] Figure 2 shows representative infrared spectra in the hydroxyl stretching region of three different concentrations of hexafluoro-2-phenyl-2-propanol (HFPP (I)) in cyclohexane contained in a 0.02-mm path length cell at 25 °C.



HFPP (I)

Cyclohexane is essentially an inert diluent, and as its concentration is increased in the mixture the fraction of hydrogen-bonded hydroxyls decreases. Thus the dominant band at 3595 cm^{-1} is assigned to the "free" hydroxyl groups or non-hydrogen-bonded monomers, while the weak absorptions at approximately 3560 and 3350 cm^{-1} are attributed to hydrogen-bonded O–H dimers and multimers, respectively. If we compare these spectra to analogous phenol solutions of comparable concentrations,[1,16] we can immediately conclude from the very weak contributions from hydrogen-bonded dimers and multimers that the values of the equilibrium constants for HFPP (K_{c_2} and K_c) must be significantly less than those for phenol, which implies a much weaker overall degree of self-association.

To quantify this observation we employed the method of Coggeshall and Saier.[15] Quantitative measurements of the absorbance of the free hydroxyl band (obtained by measuring the intensity of the 3595-cm^{-1} band) as a function of concentration are listed in Table I. The intensity (absorbance) of the free hydroxyl band, I, is related to the absorptivity coefficient, ϵ, the concentration, c, and the path length, l, by the well-known Beer–Lambert law, $I = \epsilon l c$. Accordingly, from a plot of $I/(lc)$ versus c we can determine ϵ from the limit

$$\left| \frac{I}{cl} \right|_{\lim c \to 0} = \epsilon \qquad (1)$$

This is illustrated in Figure 3, from which a value of $\epsilon = 102.9$ (in appropriate units, where c is in mol/L, l is in mm, and I is in absorbance units) was determined by using a least-squares fitting of the data with a fifth-order polynomial, following Whetsel and Lady.[16] The experimental fraction of free monomers, f_m^{OH}, at any given

Table I
Data Pertaining to HFPP–Cyclohexane Solutions

c, mol L^{-1}	I	$I/(cl)$	I_0	f_m^{OH}	γ
0.0801	0.154	96.13	0.165	0.934	2.125
0.0995	0.189	94.97	0.205	0.923	2.201
0.198	0.346	87.37	0.407	0.849	1.892
0.303	0.491	81.02	0.624	0.787	1.767
0.413	0.625	75.67	0.850	0.735	1.688
0.500	0.722	72.20	1.029	0.702	1.650
0.610	0.833	68.28	1.255	0.664	1.597
0.702	0.905	64.46	1.445	0.626	1.475
0.798	0.978	61.28	1.642	0.596	1.399
0.902	1.056	58.54	1.856	0.569	1.354
1.002	1.131	56.44	2.062	0.548	1.335

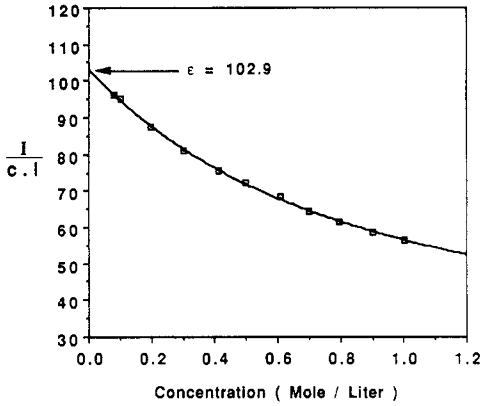


Figure 3. Graph depicting the extrapolation to zero concentration for the determination of the extinction coefficient ϵ.

concentration is then simply

$$f_m^{OH} = I/I_0 \quad (2)$$

where $I_0 = c\epsilon l$.

For the case where self-association is best described by two equilibrium constants, Coggeshall and Saier[15] derived an expression relating the general constant for the disassociation of hydrogen-bonded multimers to that of the disassociation of dimers, the fraction of unassociated hydroxylated molecules, and the concentration. Following some manipulation, in order to be consistent with our previous nomenclature,[1] K_c is related to K_{c_2}, f_m^{OH}, and c by the expression

$$K_c = \frac{2\left(\frac{1}{K_{c_2}} - \gamma\right)}{f_m^{OH} c\left[\frac{2}{K_{c_2}} - \frac{\gamma}{2} + \left(\frac{2\gamma}{K_{c_2}} + \frac{\gamma^2}{4}\right)^{0.5}\right]} \quad (3)$$

where

$$\gamma = \frac{2(f_m^{OH})^2 c}{1 - f_m^{OH}}$$

Coggeshall and Saier[15] noted that to evaluate K_c from eq 3 one must first evaluate K_{c_2}, which fortunately can be obtained by plotting γ versus c and extrapolating to zero concentration as

$$|\gamma|_{\lim c \to 0} = 1/K_{c_2} \quad (4)$$

Such a plot is shown in Figure 4, which yields a value of $K_{c_2} = 0.43$ L/mol. Again we employed a least-squares fitting of the data to a fifth-order polynomial in order to estimate the value of γ at $c = 0$. Substituting this value of K_{c_2} into eq 3 for each concentration, we obtain a mean value for K_c of 0.58 L/mol with a standard deviation of 0.12.

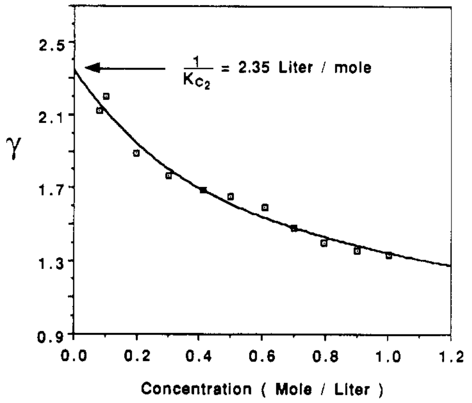


Figure 4. Graph depicting the extrapolation to zero concentration for the determination of the reciprocal of the equilibrium constant K_{c_2}.

It is informative to compare the values of K_{c_2} and K_c for HFPP in cyclohexane (0.43 and 0.58 L/mol, respectively) with those obtained by Whetsel and Lady[16] for phenol in the same inert solvent (2.10 and 6.68 L/mol, respectively). The significantly smaller values in the case of hexafluoro-2-phenyl-2-propanol confirms that this molecule has a much weaker propensity to self-associate than phenol. Both electronic and steric factors associated with the bulky trifluoromethyl groups presumably affect the ability of the molecule to form hydroxyl–hydroxyl intermolecular interactions. [Incidentally, Whetsel and Lady[16] used a somewhat different method to obtain K_{c_2} and K_c for phenol from that which we employ here.[15] Nonetheless, if we use the raw data reported by these authors and reduce it according to Coggeshall and Saier's method, we obtain K_{c_2} and K_c values of 2.20 and 6.56 L/mol, which is in good agreement and demonstrates self-consistency.]

For our purposes it is necessary to convert the above equilibrium constants, K_{c_2} and K_c, in unts of liter/mole to the *dimensionless* equilibrium constants K_2 and K_B, values that we employ in our association model. This we have described in detail before,[1] and the two sets of equilibrium constants are simply related by

$$K_2 = K_{c_2}\frac{1000}{V_B}$$

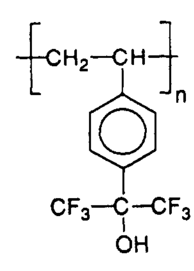
and

$$K_B = K_c\frac{1000}{V_B} \quad (5)$$

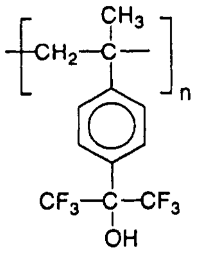
where V_B is the molar volume of hexafluoro-2-phenyl-2-propanol (in cm^3/mol), which was determined from the density at 25 °C to be 168.4. Thus we calculate values of $K_2 = 2.55$ and $K_B = 3.44$ for hexafluoro-2-phenyl-2-propanol at 25 °C.

The next step is to calculate the K_2 and K_B values for analogous polymers such as poly[*p*-(hexafluoro-2-hydroxy-2-propyl)styrene] (PHFPS (II)), poly[*p*-(hexafluoro-2-hydroxy-2-propyl)-α-methylstyrene] (PHFPMS (III)), and poly[styrene-*co*-*p*-(hexafluoro-2-hydroxy-2-propyl)styrene] (STHFPS[*y*] (IV)) from the values obtained for the model compound HFPP. This is again simply scaled to the molar volume of the "specific repeat", which we define as the average chemical unit containing one HFPP moiety.[1]

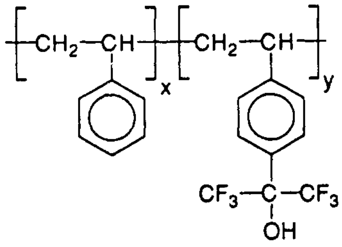
$$K_B^{\text{polymer}} = K_B^{\text{HFPP}}\frac{V_B^{\text{HFPP}}}{V_B^{\text{polymer}}} \quad (6)$$



PHFPS (II)



PHFPMS (III)



STHFPS[y] (IV)

The molar volumes of PHFPS and PHFPMS segments were estimated in the following manner. As we mentioned above, the molar volume of HFPP, 168.4 cm^3/mol, was obtained from density measurements. Using group molar volume constants,[1] the contribution from the hexafluoro-2-hydroxy-2-propyl group ($C(CF_3)_2OH$) was estimated by subtracting the phenyl group contribution from HFPP, to yield a value of 168.4 − 75.5 = 92.9. The molar volume of the PHFPS specific repeat was then calculated from the CH_2, CH, disubstituted phenyl, and hexafluoro-2-hydroxy-2-propyl group molar constants to be 170 cm^3/mol.

Similarly, the molar volume of PHFPMS was estimated to be 185 cm^3/mol. In forthcoming discussion we will consider polymer blends of two random STHFPS copolymers containing 80 and 60 mol % of HFPS, denoted STHFPS[80] and STHFPS[60], respectively. The calculated molar volumes of their respective specific repeats are 194 and 232 cm^3/mol (note that now the specific repeat unit contains some styrene units, according to copolymer composition). K_2 and K_B values for PHFPS, PHFPMS, STHFPS[80], and STHFPS[60] are listed in Table II.

Determination of Interassociation Equilibrium Constants. We now consider the determination of the interassociation equilibrium constant, K_A, between polymer mixtures containing the HFPP group and methacrylate or acetoxy type functionalities. The method employed here was identical to that we have previously used to determine K_A values for PVPh blends with polymers containing methacrylate, acrylate, ester, and acetoxy groups.[1,3-9] Miscible blends of STHFPS[80] and STHFPS[60] with poly(butyl methacrylate) (PBMA) and an ethylene-*co*-vinyl acetate copolymer (EVA[70]) were chosen for these studies.

Figure 5 shows typical infrared spectra obtained from films of STHFPS[80]–PBMA blends recorded at room temperature in the hydroxyl (3100–3700 cm^{-1}) and carbonyl (1650–1800 cm^{-1}) stretching regions. The spectrum of pure STHFPS[80] in the hydroxyl stretching region shows a major band at 3602 cm^{-1} attributed to "free" (non-hydrogen-bonded) OH groups with a broad shoulder at about 3520 cm^{-1} characteristic of the hydrogen-bonded OH dimer and multimers. As the STHFPS[80] is "diluted" with PBMA, both of these bands decrease in intensity and are replaced with a broad band centered at about 3380 cm^{-1}. This latter band is attributed to OH groups hydrogen bonded to the ester carbonyl groups of PBMA and has a frequency shift, as measured from the position of the free OH band, of some 220 cm^{-1}. This is a large shift and in marked contrast to analogous PVPh–PBMA mixtures where the frequency shift of the band attributed to OH - - - O=C interactions ($\approx$105 cm^{-1}) is observed to be less than that attributed to self-association ($\approx$155 cm^{-1}). Although quantitative correlations are difficult in this region of the spectrum, this is again consistent with, and a manifestation of, the differences between self-association and interassociation of the HFPP versus phenol groups. [It should be noted that frequency shifts relate only to the enthalpy of the interaction and, furthermore, frequency shift/enthalpy correlations are very system dependent.]

The "free" carbonyl band of pure PBMA is observed at 1731 cm^{-1}. With increasing concentration of STHFPS[80] in the blend, the relative contribution from this band decreases at the expense of a band at 1711 cm^{-1}, which is assigned to PBMA carbonyls hydrogen bonded to STHFPS[80] hydroxyl groups. [At first glance, it may appear that the 1731-cm^{-1} band is shifting significantly to lower

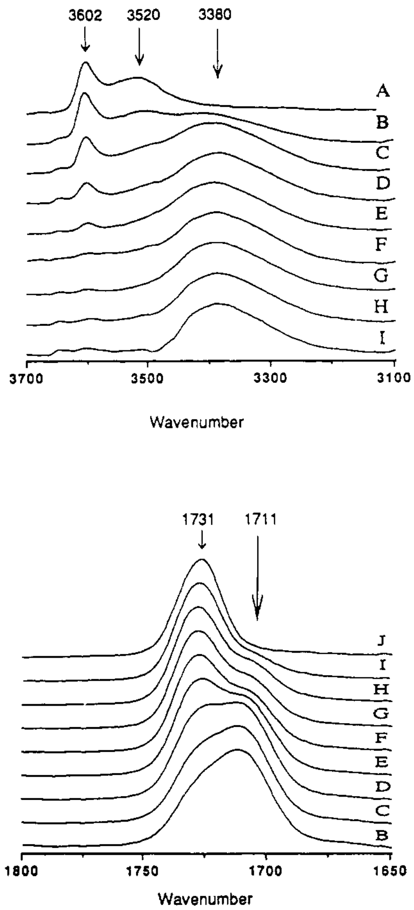


Figure 5. Infrared spectra in the hydroxyl stretching (top) and carbonyl stretching (bottom) regions of STHFPS–PBMA blends recorded at 25 °C: (A) 100:0, (B) 90:10, (C) 80:20, (D) 70:30, (E) 60:40, (F) 50:50, (G) 40:60, (H) 30:70, (I) 20:80, (J) 0:100 wt % STHFPS[80]:PBMA.

Table II
Self-Association Equilibrium Constants

polymer	K_2	K_B
PHFPS	2.53	3.41
PHFPMS	2.32	3.13
STHFPS[80]	2.21	2.99
STHFPS[60]	1.85	2.50

Table III
Curve-Fitting Results for Polymer Blends

	free C=O band			HB C=O band			
blend comp, wt %	ν, cm^{-1}	$w_{1/2}$, cm^{-1}	area	ν, cm^{-1}	$w_{1/2}$, cm^{-1}	area	$f_F^{C=O}$
STHFPS[80]–PBMA							
90:10	1731	23.2	3.469	1711	30.3	16.87	0.24
80:20	1731	21.9	4.898	1711	32.0	17.99	0.29
70:30	1730	21.5	5.278	1710	28.1	9.093	0.47
60:40	1730	21.5	3.493	1709	28.9	4.614	0.53
50:50	1731	21.8	3.826	1709	29.1	3.500	0.62
40:60	1730	21.8	33.12	1708	28.1	19.26	0.72
30:70	1730	23.6	10.5	1707	27.5	4.127	0.79
20:80	1729	20.1	29.51	1708	26.4	5.845	0.88
STHFPS[60]–PBMA							
80:20	1730	20.5	1.476	1710	26.6	3.800	0.37
70:30	1730	20.5	2.168	1710	26.2	3.984	0.45
60:40	1730	20.5	2.860	1709	26.4	3.831	0.53
50:50	1730	20.5	3.368	1709	26.4	2.642	0.66
40:60	1731	24.6	4.923	1707	26.1	2.993	0.71
20:80	1729	20.4	3.011	1709	26.4	1.040	0.82
STHFPS[60]–EVA[70]							
90:10	1740	19.9	0.318	1713	29.9	3.462	0.12
80:20	1740	20.5	1.870	1714	26.6	9.305	0.23
70:30	1739	19.5	2.379	1713	25.7	6.169	0.37
60:40	1739	19.4	2.677	1713	25.6	4.261	0.49
50:50	1739	21.7	4.949	1712	26.1	4.376	0.63
40:60	1739	21.6	17.04	1712	24.5	10.26	0.71
30:70	1738	20.7	3.399	1711	25.4	1.317	0.80
20:80	1737	19.8	2.100	1711	28.5	0.550	0.85

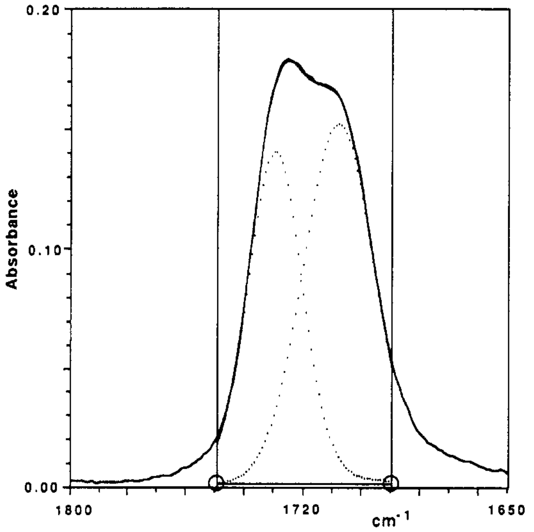


Figure 6. Example of curve fitting the infrared spectrum for a 60:40 wt % STHFPS[80]-PBMA blend sample.

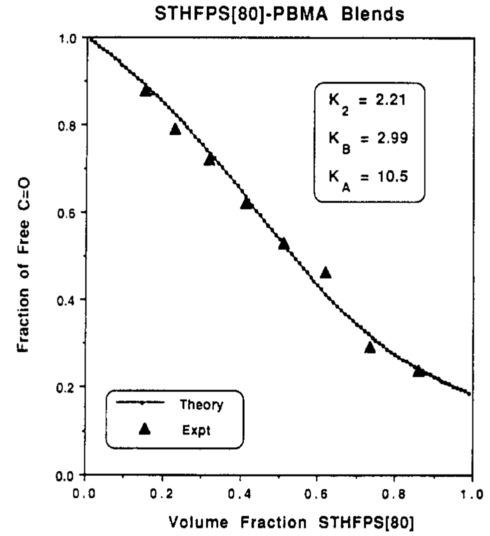


Figure 7. Graph showing the least-squares fitting of the stoichiometric equations to experimental results for the determination of K_A for STHFPS[80]–PBMA blends.

frequency with increasing concentration of STHFPS[80] in the blend, but this is an illusion caused by overlapping bands as the contribution from the 1711-cm^{-1} band becomes dominant.] The fraction of free carbonyls in STHFPS[80]–PBMA mixtures of a given concentration, $f_F^{C=O}$, can be quantitatively determined using a curve-fitting procedure that has been described previously (see Chapter 5, ref 1), and a typical example of the separation into the free and hydrogen-bonded carbonyl bands is shown in Figure 6. From a measurement of the areas of these bands and a knowledge of the absorptivity ratio, a_R, which reflects the difference between the absorptivities of the hydrogen-bonded and free carbonyl groups, we can readily calculate $f_F^{C=O}$. We have assumed a value for a_R = 1.5, the same value previously determined for mixtures involving phenolic hydroxyls and aliphatic esters.[1] [Since the frequency shift of the carbonyl band to lower frequency upon hydrogen bonding in STHFPS[80]–PBMA mixtures is similar to that of phenol–ester mixtures, we believe this to be a reasonable assumption and not the source of potentially large errors. Furthermore, we are bolstered in this conclusion by the fact that the combined area of these two bands in miscible STHFPS[80]–PBMA blends changes as a function of temperature, and these changes were duplicated, within error, using this value of a_R.] A summary of the curve-fitting results for the STHFPS[80]–PBMA and STHFPS[60]–PBMA mixtures at 25 °C is given in Table III.

The methodology used to determine K_A by least-squares fitting the stoichiometric equations to the $f_F^{C=O}$ data as a function of volume fraction of STHFPS[80] in the mixtures has been presented in detail previously.[1] Figure 7 shows the result of such an exercise for the STHFPS[80]–PBMA blends, which yields a value of K_A = 10.5. [Note that the curve does not appear to extrapolate to a value of $f_F^{C=O}$ = 0 at a volume fraction of STHFPS[80] = 1. In fact, at values of volume fractions extremely close to 1, the theoretical curve does approach zero, but these points are not displayed in the figure.]

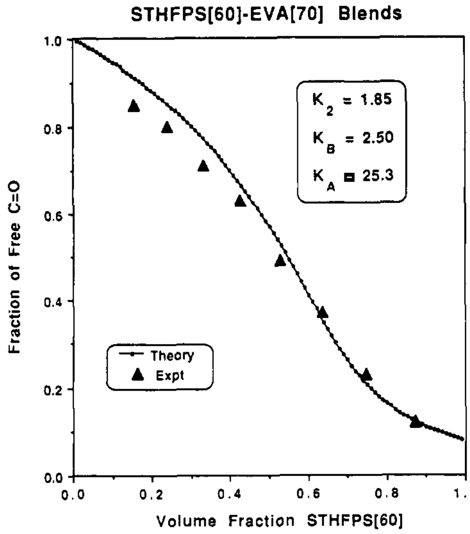


Figure 8. Graph showing the least-squares fitting of the stoichiometric equations to experimental results for the determination of K_A for STHFPS[60]-EVA[70] blends.

Table IV
Interassociation Equilibrium Constants

polymer	K_A methacrylates	K_A acetoxy
STHFPS[80]	10.5[a] (11.2)[b]	30.3[b]
STHFPS[60]	9.4[a]	25.3[a]
PHFPS ≡ STHFPS[100]	12.8[b]	34.5[b]
PHFPMS	11.8[b]	31.7[b]

[a] Experimental. [b] Calculated from STHFPS[60].

From a similar plot, a value of $K_A = 9.4$ was determined for the STHFPS[60]-PBMA blends. [Adjusting for molar volume differences yields a calculated value of (232/194) × 9.4 = 11.2 for the respective STHFPS[80]-PBMA blends, which is in reasonable agreement with the experimentally determined measurement.] Notice that the magnitude of K_A is approximately 4 times greater than K_2 or K_B, which again points to the relatively weak self-association of STHFPS[80] and relatively stronger interassociation of STHFPS[80] to PBMA.

In simple terms, if we scale the value of K_A to that equivalent to a reference molar volume equal to that of the repeat unit of poly(vinylphenol) (PVPh), we obtain a value of (194/100) × 10.5 = 20.4, which is not dissimilar in magnitude to that obtained for PVPh blends with polymethacrylates ($K_A = 37.1$) and suggests that the equilibrium constants describing *interassociation* are of the same order. However, to reiterate, the corresponding *self-association* equilibrium constants are very different.

Table III also summarizes the $f_F^{C=O}$ data as a function of composition for miscible blends of STHFPS[60] with EVA[70], from which we obtain a K_A value of 25.3 (Figure 8). The least-squares fit of the theoretical curve to the experimental data is not quite as good as that obtained for the STHFPS[80]-PBMA blends (Figure 7). However, potential errors in the determination of $f_F^{C=O}$ are greatest at compositional extremes and the experimental points in the middle range of compositions match the theoretical curve very well. The K_A value for the interassociation of STHFPS[60] with polymers containing acetoxy groups is somewhat larger than that of analogous polymers containing methacrylate groups (25.3 vs 10.5), a trend that we have noticed for the corresponding PVPh polymers (58.7 vs 37.1).[1] The K_A values are summarized in Table IV and include those calculated from STHFPS[60] for PHFPS and PHFPMS, after taking into account the differences in the molar volume, V_B, of the specific repeats;[1] i.e.

$$K_A^{\mathrm{PHFPS}} = K_A^{\mathrm{STHFPS[60]}} \frac{V_B^{\mathrm{STHFPS[60]}}}{V_B^{\mathrm{PHFPS}}} \tag{7}$$

Table V
Parameters Employed To Calculate Miscibility Windows and Maps

segment	molar vol, cm³/mol	sol. param, (cal cm^{-3})$^{0.5}$	equilib constant at 25 °C			
			K_2	K_B	K_A (methacrylate)	K_A (acetoxy)
HFPS	170	8.8	2.53	3.41	12.4	34.5
HFPMS	185	8.6	2.32	3.13	11.3	31.7
STHFPS[80]	194	8.9	2.21	2.99	10.5	30.2
STHFPS[60]	232	9.0	1.85	2.50	9.4	25.3
VPh	100	10.6	21.0	66.8	37.1	58.7
MMA	84.9	9.1				
BMA	134	8.7				
VAc (MA)	69.8	9.6				
CH_2	16.5	8.0				
ST	93.5	9.5				

Keep in mind that it is the molar volume of the self-associating species that is used as a reference volume and hence also affects the value of K_A.

Calculation of Miscibility Windows and Maps. Armed with equilibrium constants describing self-association and interassociation, we are now in a position to calculate theoretical miscibility windows and maps and compare the predictions to experimental observations that are in the published literature or that we have obtained in our laboratories. Since we have recently presented a comprehensive discourse on the subject of phase diagrams, miscibility windows, and maps for polymer blend systems involving hydrogen bonds and made available the necessary computer programs to calculate them,[1] we will move promptly to a discussion of the calculations we have performed. Values of the parameters used in the following calculations are summarized in Table V and we emphasize that we do not adjust these values. Note that we use carefully defined solubility parameters to determine non-hydrogen-bonding or "physical" interactions and we employ group contributions determined in our laboratories.[17] Those non-hydrogen-bonding parameters pertaining to the fluoromethyl group were not included in the original data base, however. Initial (tentative) values of the group molar volume, $V^* = 42.4$ cm³/mol, and molar attraction constants, $F^* = 270$ (cal cm^{-3})$^{0.5}$/mol, for the fluoromethyl group were determined from six model fluoroalkanes using the methodology described previously.[1,17] Solubility parameters of the specific repeat of the polymers considered are now readily calculated from $\delta = \sum F_i / \sum V_i$, while the average specific repeat for copolymers is determined using the equation attributed to Scott,[18] $\bar{\delta}_B = \Phi_1\delta_1 + \Phi_2\delta_2$.

We commence by comparing the theoretical predictions obtained for blends of poly(*n*-alkyl methacrylates) (PAMA) with styrene copolymers containing vinylphenol (STVPh) with those obtained by replacing VPh with *p*-(hexafluoro-2-hydroxy-2-propyl)styrene (STHFPS). This is most conveniently summarized using miscibility maps, which are shown in Figure 9. On the *x*-axis of both maps is the mole percent of styrene in the STVPh or STHFPS copolymer. The *y*-axis represents the PAMA homopolymers in terms of the number of methylene groups in the side chain (i.e., 0 corresponds to PMMA, 1 to PEMA, etc.) Our computer program utilizes parameters given in Table V to calculate, at a given temperature (in this study, 25 °C), whether or not a specific PAMA blend is theoretically

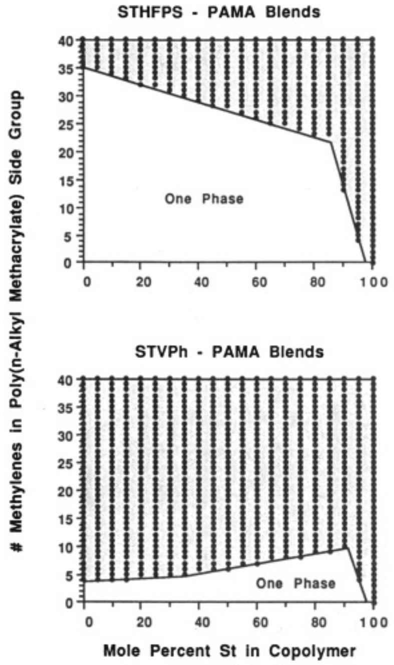


Figure 9. Comparison of the miscibility maps calculated at 25 °C for a homologous series of poly(*n*-alkyl methacrylate) blends with (top) STHFPS and (bottom) STVPh copolymers.

miscible with a particular copolymer (i.e., a single phase over the entire range of blend composition). The small black dots represent calculations (performed in this case at 5 mol % copolymer composition intervals) where two-phase systems are predicted. The predicted total area of miscibility is thus depicted by the unshaded portion of the miscibility map.

The PAMA–STVPh miscibility map has been published previously and its essential features have been verified experimentally.[1,7] It is included here primarily to underscore the stark difference in the predicted area of miscibility when HFPS is used as the comonomer with styrene rather than VPh. Our initial reaction to the theoretical PAMA–STHFPS miscibility map was one of concern, because it predicts the miscibility of STHFPS copolymers containing >20 mol % HFPS with PAMAs from PMMA to those having very long side chains (up to about 20 methylene units), and we were not aware of *any* miscible polymer blends containing PAMAs with >7 side group methylenes (POMA is miscible with STVPh over a very limited copolymer composition range[1,7]). However, we will defer for the moment any discussion of the experimental testing of this miscibility map until we have considered another theoretical miscibility map that is easily calculated with the parameters at hand.

We have pointed out in the past that in our association model no distinction is made between an amorphous homopolymer containing methylene units in a side group and the molar equivalent of a random methylene (or ethylene) copolymer. For example, poly(*n*-hexadecyl methacrylate), which has 15 methylenes in the side group, is equivalent in our scheme to a random copolymer of ethylene-*co*-methyl methacrylate containing ~32 wt % MMA. [Conceptually, we recognize that steric crowding must ultimately be a limiting factor and affect the actual equilibrium constants, but for the time being we wish to see how far we can push this assumption.] Accordingly, it follows that it is easier to experimentally test our predictions concerning the miscibility of STHFPS blends with copolymers containing ester type functionalities rather than synthesize PAMAs with very long side groups.

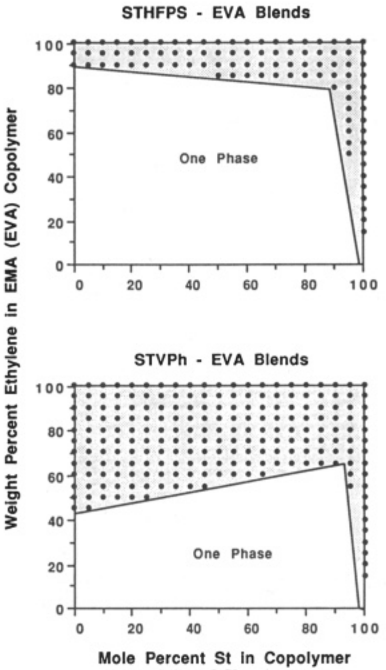


Figure 10. Comparison of the miscibility maps calculated at 25 °C for EVA copolymer blends with (top) STHFPS and (bottom) STVPh copolymers.

Figure 10 shows a comparison of the miscibility maps calculated at 25 °C from the data given in Table V for STHFPS and STVPh copolymers with ethylene-*co*-vinyl acetate (EVA) copolymers.[1,7] Again, the *x*-axis of both maps is the mole percent of styrene in the STVPh or STHFPS copolymer. The *y*-axis in this case is the EVA copolymer composition expressed in weight percent ethylene, and the predicted total area of miscibility is given by the unshaded portion of the miscibility map. We have previously shown experimentally that the miscibility map for STVPh–EVA blends is intrinsically correct.[1,7] In common with the PAMA blends discussed above, the one-phase region for the STHFPS–EVA blends is predicted to be considerably greater than that of their STVPh counterparts. For example, STHFPS copolymers with >10 mol % HFPS are predicted to be miscible with EVA (or EMA) copolymers containing up to about 80 wt % ethylene. This is very interesting because it predicts miscibility for blends of STHFPS copolymers containing >10% HFPS with, for example, EVA[25], a copolymer that we have studied previously and for which we have never found a miscible polymeric partner.

The number of experiments that we could perform to test the above predictions was limited by the small quantity of STHFPS copolymers available. Nevertheless, the initial results reported here are encouraging and indicate that the broad trends are correct. [More extensive studies are planned following the synthesis of a complete range of the STHFPS copolymers.] Blends (80:20% by weight) of STHFPS[60] with the polymethacrylates containing 3, 7, 9, 15, and 17 methylenes in the side groups (PBMA, POMA, PDMA, PHDMA, and PODMA) were studied by infrared spectroscopy. If we now calculate the theoretical miscibility window specifically for STHFPS[60] blends with PAMAs at 25 °C, we obtain the diagram shown in Figure 11. Following the line corresponding to an 80:20 wt % blend composition, we see that all the PAMA blends of this composition are predicted to be single phase and, in fact, we would have to examine a PAMA with >30 methylenes in the side group before a predicted two-phase

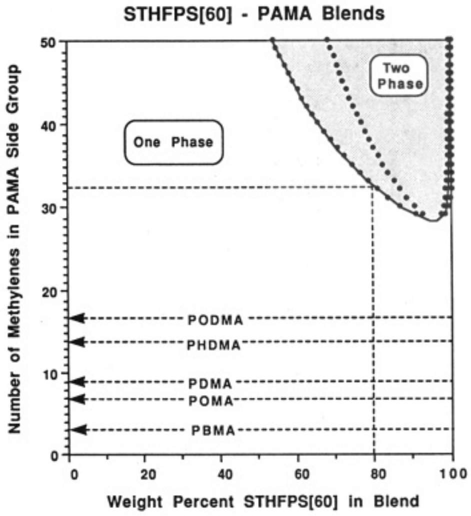


Figure 11. Miscibility window calculated at 25 °C for STHFPS-[60] blends with a homologous series of poly(*n*-alkyl methacrylates).

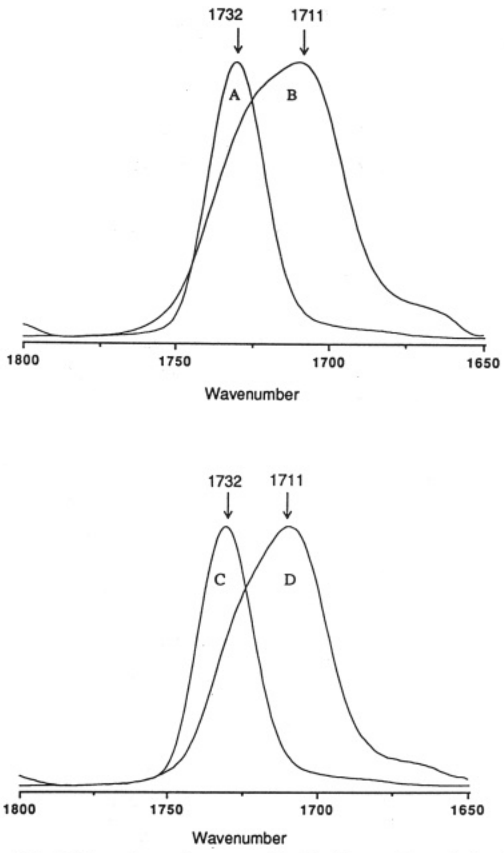


Figure 12. Infrared spectra recorded in the carbonyl stretching region at 25 °C for STHFPS[60] copolymer blends with PDMA (denoted B) and PODMA (D). Spectra A and C are of the pure PDMA and PODMA polymers, respectively.

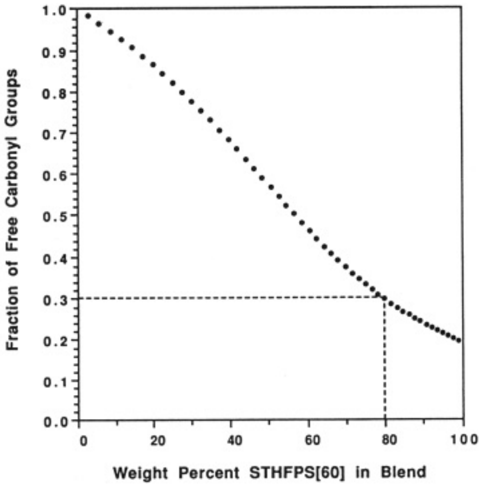


Figure 13. Calculated theoretical fraction of free carbonyl groups for STHFPS[60]–PDMA blends at 25 °C.

Table VI
Comparison of Theoretical and Experimental Values of $f_F^{C=O}$ for 80:20 wt % STHFPS[60]–PAMA Blends

	$f_F^{C=O}$	
polymer	theory	expt
PBMA	0.34	0.37
POMA	0.31	0.29
PDMA	0.30	0.30
PHDMA	0.27	0.22
PODMA	0.26	0.20

system was encountered. Figure 12 shows typical examples of infrared spectra obtained from films of 80:20 STHFPS-[60] blends with PAMAs. Specifically, the spectra of STHFPS[60] blends with PDMA and PODMA are shown in the carbonyl stretching region and it is immediately apparent, judging from the dominant contribution from the band at 1711 cm^{-1}, that significant molecular-level mixing of the two polymers has occurred. We have discussed in depth previously[1,6-8] how the fraction of free or bonded carbonyl groups in a *miscible* system can be calculated from the stoichiometric equations, if one has a knowledge of the equilibrium constants and the molar volumes of the respective polymer specific repeat units (see a typical example illustrated in Figure 13 for STHFPS-[60]–PDMA blends). Accordingly, we can readily calculate theoretical $f_F^{C=O}$ values for a series of hypothetical single-phase PAMAs blends with STHFPS[60] and compare these values to those determined experimentally by curve fitting spectra akin to those shown in Figure 12. This we have performed and the results are presented in Table VI.

The experimental results compare very favorably with the theoretical values of $f_F^{C=O}$ for single-phase blends, supporting the notion that STHFPS[60] is miscible with PAMAs having side groups up to at least 17 methylene groups. The experimental values of $f_F^{C=O}$ for PHDMA and PODMA are observed (within the probable bounds of error) to be *less than* that predicted for a single phase, which is unusual since phase separation into two amorphous phases inevitably leads to an increase in $f_F^{C=O}$ over that calculated for a single phase.[1] While we do not wish to overinterpret these results, it appears most likely that some crystallization of the long alkyl side chain occurs, and this would effectively increase the concentration of the STHFPS[60] in the amorphous portion of the blend, resulting in a smaller $f_F^{C=O}$ for the single-phase case.

The theoretical miscibility window for STHFPS[60] blends with EVA copolymers calculated at 25 °C is shown in Figure 14. Again, following the line corresponding to an 80:20 wt % blend composition, we see that EVA copolymers containing greater than ≈12% vinyl acetate are predicted to be single phase. Figure 15 shows typical examples of infrared spectra obtained from films of 80:20 STHFPS[60] blends with EVA copolymers containing 25 and 9 wt % VAc, and once more the spectra indicate that significant molecular-level mixing of the two polymers has occurred (note the dominant contribution from the band at 1713 cm^{-1}). In a manner similar to that described above, a typical calculation of the theoretical fraction of free carbonyl groups in a hypothetical *miscible* system for STHFPS[60]–EVA[18] blends was performed and is shown

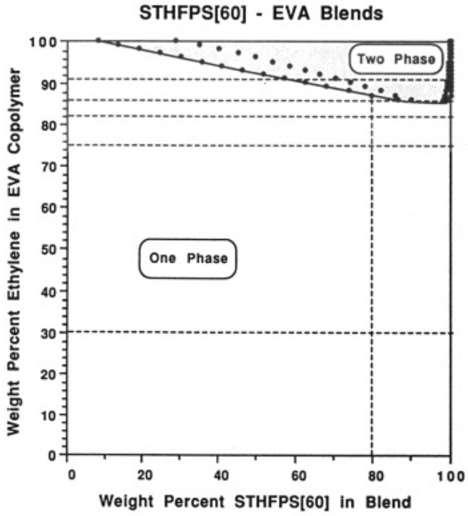


Figure 14. Miscibility window calculated at 25 °C for STHFPS-[60] blends with EVA copolymers.

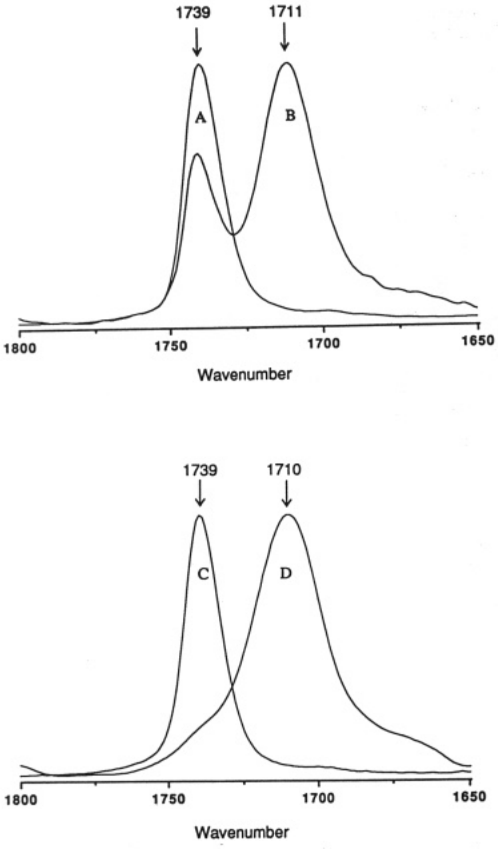


Figure 15. Infrared spectra recorded in the carbonyl stretching region at 25 °C for STHFPS[60] copolymer blends with EVA[9] (denoted B) and EVA[25] (D). Spectra A and C are of the pure EVA[9] and EVA[25] copolymers, respectively.

graphically in Figure 16. Experimental $f_F^{C=O}$ results obtained by curve fitting infrared spectra obtained as a function of blend composition are also shown. It is apparent that there is good agreement between theory and experiment, and we can confidently conclude that this particular system is indeed miscible. A comparison of the theoretical and experimental $f_F^{C=O}$ values for 80:20 wt % STHFPS[60] blends with the series of EVA copolymers is presented in Table VII. The results for the EVA[70], EVA[25], and EVA[18] blends are entirely consistent with single-phase systems, while that corresponding to the EVA[9] blend is consistent with a two-phase system (the observed $f_F^{C=O}$ is, within error, significantly greater than that predicted for a single phase). On the other hand, we cannot be so definitive about the STHFPS[60]–EVA[14] system and it appears to be just "on the edge of miscibility". This is quite remarkable considering that we had predicted (Figure 14) that blends of this composition should be miscible for EVA copolymers containing >12% vinyl acetate.

Finally, we can calculate theoretical miscibility windows for blends of PMMA and PBMA with STHFPMS copolymers using the parameters given in Table V and compare

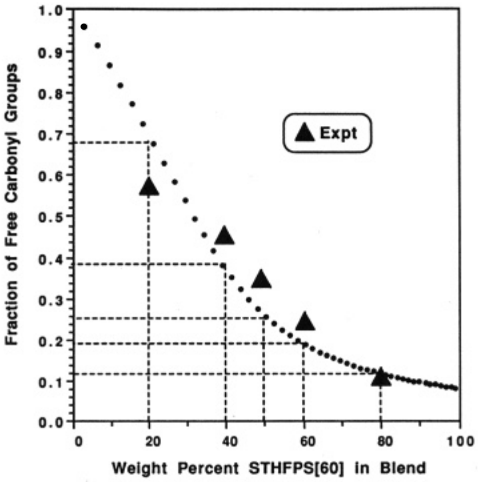


Figure 16. Comparison of the calculated theoretical fraction of free carbonyl groups with experimental results for STHFPS-[60]–EVA[18] blends at 25 °C.

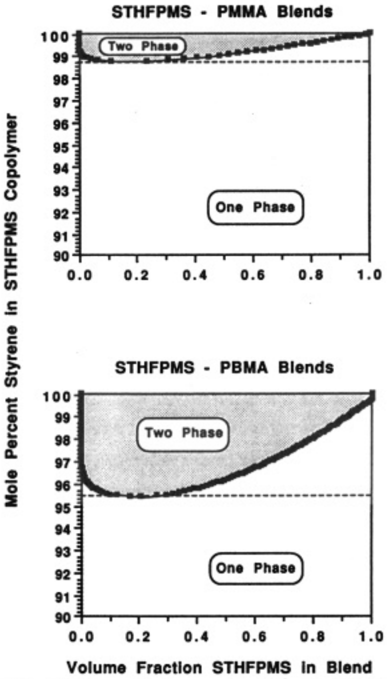


Figure 17. Miscibility windows calculated at 25 °C for STHFPMS copolymer blends with (top) PMMA and (bottom) PBMA.

Table VII
Comparison of Theoretical and Experimental Values of $f_F^{C=O}$ for 80:20 wt % STHFPS[60]–EVA Blends

	$f_F^{C=O}$	
polymer	theory	expt
EVA[70]	0.22	0.23
EVA[25]	0.13	0.11
EVA[18]	0.12	0.09
EVA[14]	0.12	0.18
EVA[9]	0.11	0.25

the predictions to the experimental results reported in the literature. Figure 17 shows the result of such an exercise. We have truncated the miscibility window to emphasize the range pertaining to styrene copolymers containing minor amounts of HFPMS, i.e., from PS to STHFPMS[10]. [For completeness, a single phase is predicted for all PMMA and PBMA blends with STHFPMS copolymers containing >10 mol % HFPMS.] Returning to Figure 17, PMMA and PBMA are predicted to be miscible (single phase across the entire blend composition range) at ambient temperature with STHFPMS copolymers containing >1.2 and >4.4 mol % HFPMS, respectively. This is in fine accord with the published results of Cao et al.,[13] who report that PMMA and PBMA are both immiscible with STHFPMS[0.8], STHFPMS[0.9], and STHFPMS[1.2] but miscible with STHFPMS[1.9] and STHFPMS[9.7].

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References and Notes

(1) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing, Inc.: Lancaster, PA, 1991.
(2) Painter, P. C.; Graf, J. F.; Coleman, M. M. *J. Chem. Phys.* **1990**, *92*, 6166.
(3) Coleman, M. M.; Lichkus, A. M.; Painter, P. C. *Macromolecules* **1989**, *22*, 586.
(4) Serman, C. J.; Painter, P. C.; Coleman, M. M. *Polymer* **1991**, *32*, 1049.
(5) Serman, C. J.; Xu, Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1989**, *22*, 2015.
(6) Xu, Y.; Graf, J. F.; Painter, P. C.; Coleman, M. M. *Polymer* **1991**, *32*, 3103.
(7) Xu, Y.; Painter, P. C.; Coleman, M. M. *Makromol. Chem., Macromol. Symp.* **1991**, *51*, 61.
(8) Coleman, M. M.; Xu, Y.; Painter, P. C.; Harrell, J. R. *Makromol. Chem., Macromol. Symp.* ESOPS Conference, Koln, Sept 1990, accepted.
(9) Coleman, M. M.; Zhang, H.; Xu, Y.; Painter, P. C. *Adv. Chem. Ser.*, submitted.
(10) Ting, S. P.; Pearce, E. M.; Kwei, T. K. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 201.
(11) Ting, S. P.; Bulkin, B. J.; Pearce, E. M.; Kwei, T. K. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1451.
(12) Pearce, E. M.; Kwei, T. K.; Min, B. Y. *J. Macromol. Sci., Chem.* **1984**, *A21*, 1181.
(13) Cao, X.; Jiang, M.; Yu, T. *Makromol. Chem.* **1989**, *190*, 117.
(14) He, M.; Liu, Y.; Feng, Y.; Jiang, M.; Han, C. C. *Macromolecules* **1991**, *24*, 464.
(15) Coggeshall, N. D.; Saier, E. L. *J. Am. Chem. Soc.* **1951**, *73*, 5414.
(16) Whetsel, K. B.; Lady, J. H. In *Spectrometry of Fuels*; Friedel, H., Ed.; Plenum: London, 1970.
(17) Coleman, M. M.; Serman, C. J.; Bhagwagar, D. E.; Painter, P. C. *Polymer* **1990**, *31*, 1187.
(18) Scott, R. L. *J. Polym. Sci.* **1952**, *9*, 423.