Miscibility windows for poly(styrene-*co*-vinyl phenol) blends with poly(n-butyl methacrylate) and poly(n-hexyl methacrylate): a comparison of theoretical predictions with Fourier transform infra-red experimental data

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Employing parameters recently derived from studies of miscible poly(4-vinyl phenol) (PVPh) blends with poly(ethyl methacrylate) and poly(n-propyl methacrylate), spinodal phase diagrams and 'miscibility windows' have been calculated for blends of styrene-*co*-vinyl phenol (STVPh) copolymers with poly(n-butyl methacrylate) (PBMA) and poly(n-hexyl methacrylate) (PHMA) using an association model. Theoretical calculations predict that STVPh copolymers containing 0–~97% styrene are miscible with PBMA at ambient temperature. In contrast, PVPh is immiscible with PHMA at ambient temperature, but a miscibility window extending from ~32–94% styrene was predicted. Five random copolymers of STVPh were synthesized containing 75, 43, 25, 8 and 2 wt% vinyl phenol (VPh) and experimental studies were performed on blends of these copolymers with PBMA and PHMA. Quantitative analyses of the fraction of hydrogen-bonded carbonyl groups were obtained by Fourier transform infra-red spectroscopy and the data compared to the theoretical predicted values for miscible systems. In addition, the hydroxyl stretching region of the spectrum was compared qualitatively to the theoretical distribution of hydroxyl–hydroxyl, hydroxyl carbonyl and 'free' hydroxyl groups that would be present in a miscible blend. PVPh and the STVPh copolymers containing 75, 43, 25 and 8 wt% VPh were found to be miscible with PBMA, while the corresponding copolymer containing 2 wt% VPh was found to be immiscible. For the PHMA blends, PVPh and the two STVPh copolymers containing 75 and 2 wt% VPh were found to be immiscible with PHMA, while the corresponding copolymers containing 43, 25 and 8 wt% VPh were found to be miscible. These experimental results are in excellent accord with the theoretical predictions and lend support to the general validity of our association model approach.

(**Keywords: miscibility window; blends; *FT*i.r.**)

INTRODUCTION

Over the course of the past 3 years we have developed a theoretical model to describe the free energy changes occurring in binary polymer mixtures containing strong directionally specific interactions[1–3]. Concurrently, experimental studies have been performed designed to assess the predictive capabilities of the model[4–8]. Of particular relevance to the work reported here are the preliminary theoretical predictions we reported for styrene-*co*-vinyl phenol (STVPh) blends with a series of poly(alkyl methacrylates)[9], together with our more recent comprehensive theoretical and experimental studies of poly(4-vinyl phenol) (PVPh) blends with an homologous series of poly(n-alkyl methacrylates)[10] and the studies of Zhu *et al.*[11] on the STVPh poly(n-butyl acrylate-*co*-t-butyl acrylate) system. In this paper, we focus our attention on a comparison of experimental Fourier transform infra-red (*FT*i.r.) spectroscopic data to the theoretical predictions of miscibility windows for STVPh blends with poly(n-butyl methacrylate) (PBMA) and poly(n-hexyl methacrylate) (PHMA). These polymer blend systems were chosen as they provide an excellent test of the validity of the association model.

EXPERIMENTAL

Synthesis and characterization

Copolymer compositions, molecular weights and glass transition temperatures (T_g) of the polymers used in this study are summarized in *Table 1*. The amorphous PHMA was prepared by simple free radical solution polymerization and PBMA was prepared in our laboratories by group transfer polymerization described previously[9]. *N*,*N*-Dimethylformamide (DMF), tetrahydrofuran (THF), benzene, *p*-hydroxybenzaldehyde, t-butyldimethylsilyl chloride, methyl triphenylphosphonium bromide, tetrabutyl ammonium fluoride and styrene were purchased from Aldrich Chemical Company, Inc. Styrene was passed through a short column of neutral alumina and distilled from calcium hydride prior to use. DMF and THF, respectively, were distilled from magnesium sulphate and from sodium and benzophenone immediately before use. The other reagents were used without further purification. All glassware was flame-dried prior to use.

PVPh has been prepared by several synthetic methods, including cationic, anionic and free radical processes. It is difficult to prepare PVPh by direct polymerization of *p*-vinyl phenol (*p*-VPh), however, due to the occurrence

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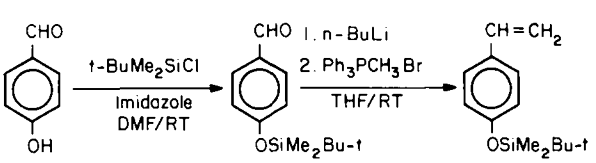
Table 1 Polymers used in this study

Polymer	Symbol	M_n[a]	T_g (°C)
Poly(n-butyl methacrylate)	PBMA	55000	21
Poly(hexyl methacrylate)	PHMA	~200000	−53
Poly(styrene[98]-*co*-*p*-vinyl phenol[2])	STVPh[2]	13000	102
Poly(styrene[92]-*co*-*p*-vinyl phenol[8])	STVPh[8]	14000	109
Poly(styrene[75]-*co*-*p*-vinyl phenol[25])	STVPh[25]	11000	133
Poly(styrene[57]-*co*-*p*-vinyl phenol[43])	STVPh[43]	13000	145
Poly(styrene[25]-*co*-*p*-vinyl phenol[75])	STVPh[73]	14000	166
Poly(4-vinyl phenol)	PVPh	38000	190

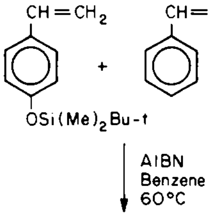
[a] By gel permeation chromatography

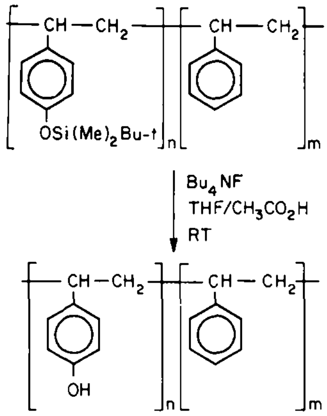
of side reactions involving the phenolic hydroxyl group during the polymerization[12]. Accordingly, protected monomers are commonly employed in this reaction. Protecting groups, such as acetyl[11,13,14], alkyl[15], trialkylsilyl[16] and t-butoxycarbonyl (t-BOC)[17], have all been used. The merit of a particular protecting group is basically determined by its stability during the polymerization reaction; the convenience and cost of monomer preparation; and the ease of the deprotecting step yielding the desired polymer.

After several preliminary studies we chose to concentrate our attention on the free radical polymerization of vinyl phenol with the hydroxyl group protected with the *p*-t-butyldimethylsilyloxyl group, because the synthesis of the homopolymer and essentially random copolymers with styrene was found to be very straightforward. The preparation and anionic polymerization of the monomer, *p*-t-butyldimethylsilyloxystyrene (t-BSOS), has been reported by Hirao *et al.*[18] but, to our knowledge, no previous information exists concerning the behaviour of this monomer during free radical homopolymerization or in the copolymerization reaction with styrene. We employed *p*-hydroxybenzaldehyde as the starting material and prepared t-BSOS in an overall yield of >75% from a preparation involving two steps; (1) protection of the hydroxyl group; and (2) olefination, as shown schematically below:



The protecting reagent t-butyldimethylsilyl chloride reacts with *p*-hydroxybenzaldehyde under very mild reaction conditions with high yield (>90%). The subsequent olefination was effected by the Wittig reaction using methyl triphenylphosphonium bromide (>85% yield). The copolymerization of styrene and t-BSOS was performed at 60°C in benzene using AIBN as an initiator. The chemistry is summarized below:





A range of copolymers were prepared at low (<10%) and high (>70%) conversions and the chemical compositions determined by ^{1}H nuclear magnetic resonance (n.m.r.) spectroscopy*. The copolymer composition was not found to be a strong function of the degree of conversion and is close to the initial monomer feed which suggests an essentially ideal copolymerization. Reactivity ratios for styrene and t-BSOS in benzene at 60°C were determined from the compositional data obtained from the polymers isolated at low conversions (<10%) yielding values of $r_{St} = 1.1$ and $r_{t\text{-BSOS}} = 0.6$. The product of the two reactivity ratios is 0.7 indicating that the two monomers are distributed in the copolymer in an essentially random fashion. The copolymers are very soluble in common organic solvents, such as THF and chloroform. The number and weight average molecular weights of the copolymers were determined by size exclusion chromatography (s.e.c.) and the results, based upon polystyrene standards, are included in *Table 1*. All

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* N.m.r. lines with chemical shifts at 0.16 and 0.95 ppm correspond, respectively, to the two methyl and one t-butyl groups in the t-BSOS monomer. Relatively broad lines appearing between 6.2 ppm and 7.2 ppm correspond to the aromatic protons which occur in both styrene and t-BSOS. The normalized area per proton corresponding to the t-BSOS chemical repeat, $A^{H}_{t\text{-BSOS}}$, may be determined from either:

$$A^{H}_{t\text{-BSOS}} = \frac{\text{Total area of 0.16 ppm line}}{6} = \frac{\text{Total area of 0.95 ppm line}}{9}$$

The normalized area per proton corresponding to the styrene chemical repeat, A^{H}_{St}, is given by:

$$A^{H}_{St} = \frac{\{\text{Total area of region from 6.2 to 7.2}\} - 4A^{H}_{t\text{-BSOS}}}{5}$$

Thus, the fraction of styrene in the copolymer is simply given by:

$$\text{Styrene (\%)} = \frac{A^{H}_{St}}{A^{H}_{St} + A^{H}_{t\text{-BSOS}}}$$

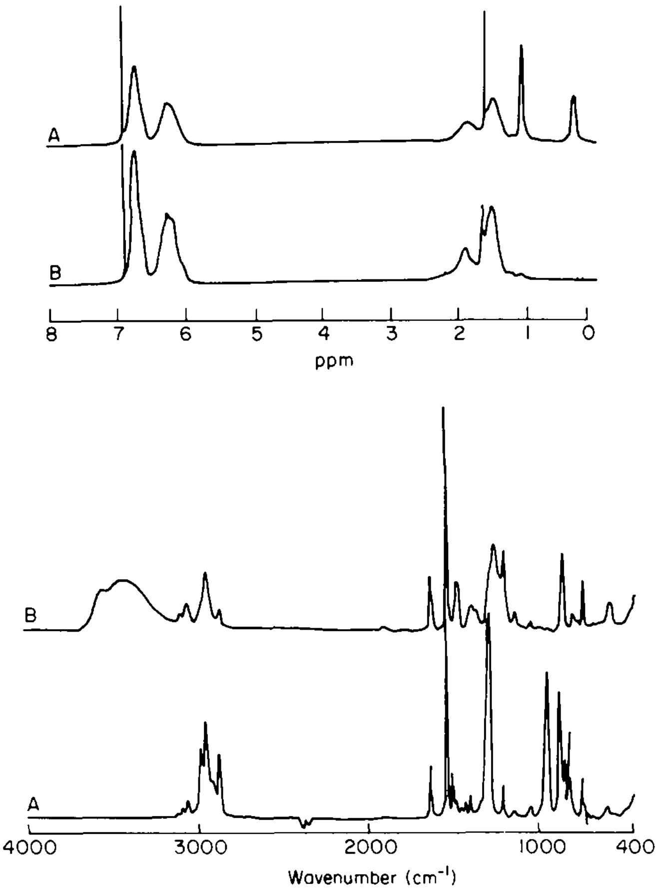

Figure 1 A comparison of ^{1}H n.m.r. (top) and *FT*i.r. (bottom) spectra before (A) and after (B) desilylation reaction

the s.e.c. curves were monomodal resembling normal distributions with polydispersities close to 2.0.

In general, silyl ether linkages are readily cleaved in the presence of fluoride ions, acids and bases[19]. Tetrabutylammonium fluoride was found to be an excellent desilylation reagent[20] completely removing the silyl group under very mild conditions (room temperature) and was applied to the various t-BSOS copolymers. ^{1}H n.m.r. and *FT*i.r. spectra of the copolymer containing 90 and 28 mol% styrene, respectively, before and after desilylation are shown in *Figure 1*. Of particular relevance is the disappearance of the n.m.r. lines at $\delta = 0.95$ and 0.16 ppm clearly indicating the elimination of the t-butyldimethylsilyl group. Similarly, the i.r. band seen at ~952 cm^{-1}, which is assigned to the Si O stretching modes is completely absent following desilylation. Further, the hydroxyl group can be clearly identified in i.r. studies and following desilylation the presence of the phenolic hydroxyl group is evident by the presence of the broad absorbance occurring between 3100 cm^{-1} and 3700 cm^{-1}.

We have tacitly assumed that the average degree of polymerization remains unchanged upon desilylation of the t-BSOS copolymers, because it is not feasible to obtain accurate molecular weights of STVPh copolymers directly from s.e.c. due to extensive interactions between the STVPh copolymers and the solvents and the stationary phase. Thermal analysis of the STVPh copolymers was performed using differential scanning calorimetry. A single, relatively sharp, T_g occurs between the T_gs of polystyrene (100°C) and PVPh (190°C). The temperature of this transition increases systematically with vinyl phenol concentration in these copolymers and, within error, the data obeys the simple Fox equation[21].

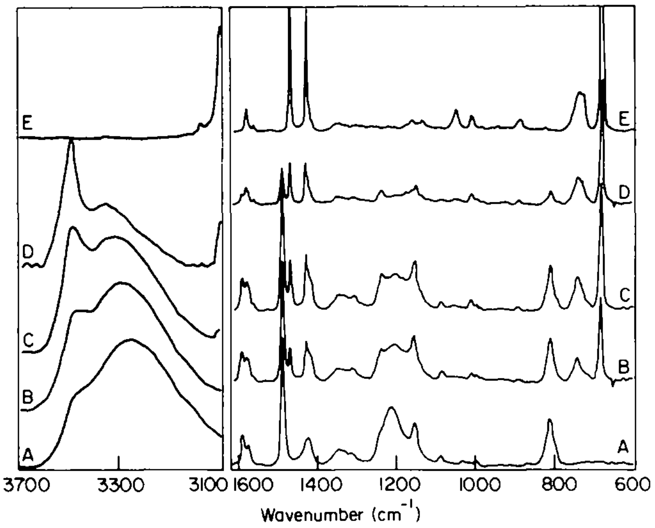

Figure 2 Scale expanded room temperature *FT*i.r. spectra in the hydroxyl stretching (3100–3700 cm^{-1}) and 'fingerprint' (600–1600 cm^{-1}) regions for STVPh copolymers containing (A) 100, (B) 75, (C) 43, (D) 8 and (E) 0 wt% VPh

Figure 2 shows scale expanded room temperature *FT*i.r. spectra in the hydroxyl stretching (3100–3700 cm^{-1}) and 'fingerprint' (600–1650 cm^{-1}) regions of atactic polystyrene, PVPh and three STVPh copolymers. As mentioned above, ^{1}H n.m.r. spectroscopy was employed to quantitatively determine the chemical composition of the t-BSOS copolymers. These copolymers may be used after desilylation as standards for an i.r. analytical method to determine the composition of STVPh copolymers*.

A comprehensive understanding of the changes occurring in the hydroxyl stretching region of the i.r. spectrum of the STVPh copolymers is particularly important for i.r. studies of the phase behaviour of polymer blends[8–10]. Included in *Figure 2* are room temperature i.r. spectra in the hydroxyl stretching region from 3100 to 3700 cm^{-1} of pure PVPh and three of the STVPh copolymers containing 28, 57 and 92 mol% styrene, respectively. PVPh strongly self-associates through intermolecular hydrogen bonding of the phenolic hydroxyl groups in the solid state and i.r. spectroscopy is particularly sensitive to this phenomenon. The i.r. band at 3525 cm^{-1} is assigned to 'free' (non-hydrogen-bonded) phenolic hydroxyls, while the broad envelope between ~3100 cm^{-1} and 3500 cm^{-1} reflects a broad distribution of hydrogen-bonded structures. These features have been considered in terms of two equilibrium constants[2,22] which describe the formation of dimers (K_2) and 'chain-like' structures (K_B).

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* Several characteristic i.r. bands can be used to identify and measure the amount of styrene or VPh chemical repeat units in the copolymers. The most convenient i.r. bands for quantitative analysis are those present at 1512 and 1492 cm^{-1}, which have very different absorption coefficients and are assigned to localized ring modes associated with the phenolic and phenyl groups, respectively. For our purposes we have prepared a calibration curve of STVPh copolymer composition based upon the intensity ratio, $I_{1492}/I_{1492} + I_{1512}$

respectively:

$$B_1 + B_1 \overset{K_2}{\leftrightarrows} B_2$$

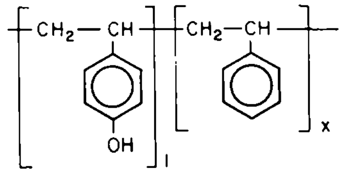
$$B_n + B_1 \overset{K_B}{\leftrightarrows} B_{n+1} \qquad (n \geqslant 2)$$

The fraction of 'free' phenolic hydroxyls, f_F°, may be calculated from the following relationship[2]:

$$f_F^\circ = \frac{1}{\bar{n}_H^\circ} = \frac{\left[1 - \frac{K_2}{K_B}\right] + \frac{K_2}{K_B}\left[\frac{1}{1 - K_B\Phi_{B_1}^\circ}\right]}{\left[1 - \frac{K_2}{K_B}\right] + \frac{K_2}{K_B}\left[\frac{1}{(1 - K_B\Phi_{B_1}^\circ)^2}\right]} \tag{1}$$

where $\Phi_{B_1}^\circ$ is the volume fraction, and $\bar{n}_H^\circ$ the number average hydrogen-bonded chain length of self-associated B units in pure B.

The incorporation of styrene into the polymer via copolymerization to form random STVPh copolymers effectively dilutes the system. This can be handled in two ways. The equilibrium constants can be defined in terms of the volume fraction of vinyl phenol units present, which is of course some fraction of the copolymer concentration in the blend. Alternatively, an average chemical repeat of the copolymer may be defined in such a manner that it contains one vinyl phenol unit[9], as illustrated below:



Knowing the values of the equilibrium constants, K_2 and K_B for pure PVPh, 21.0 and 66.8, respectively, it is a trivial task to calculate the corresponding equilibrium constant values for the STVPh copolymers by scaling using the ratio of the molar volumes of the chemical repeats of PVPh to STVPh[9,10]. The methods are entirely equivalent and give identical results. We will use the latter procedure and *Figure 3* shows the result of such an exercise, where f_F° is plotted as a function of the weight fraction of styrene in the STVPh copolymer. Increasing the concentration of styrene in the copolymer results in a sharp increase in the fraction of 'free' phenolic hydroxyls. This is reflected in the i.r. spectra shown in *Figure 2*. The relative intensity of 'free' phenolic hydroxyl band (3525 cm^{-1}) increases at the expense of the broad hydrogen-bonded band occurring in the range from 3100 to 3500 cm^{-1}. Note also that the number average length of the hydrogen-bonded phenolic 'chains' decreases with increasing styrene content, which is partially responsible for the shift in the peak frequency and narrowing of the band as the distribution of hydrogen-bonded structures varies.

Preparation of samples

Solutions (1% w/v) of STVPh, PBMA and PHMA were prepared in methyl ethyl ketone. Blends of various compositions were then made by mixing appropriate amounts of these solutions. Thin films for *FT*i.r. studies were obtained by solution casting onto potassium bromide windows at room temperature. The solvent was removed slowly under ambient conditions for a minimum of 24 h. The samples were then dried in a vacuum desiccator for an additional day before being placed in a vacuum oven at 110°C for 4 h to completely remove the residual solvent. To minimize water absorption, samples were stored under vacuum desiccation while awaiting study.

Instrumentation

I.r. spectra were obtained on a Digilab FTS-60 *FT*i.r. spectrometer using a minimum of 64 co-added scans at a resolution of 2 cm^{-1}. Spectra recorded at elevated temperatures were obtained using a heating cell mounted inside the sample chamber. Temperature was regulated by a Micristar 828D digital process controller which has a reported accuracy of ±0.1°C. All films were sufficiently thin to be within the absorbance range where the Beer–Lambert law is obeyed[23].

^{1}H n.m.r. spectra were recorded on a Bruker WP-200 FT-NMR spectrometer (200 and 300 MHz). Deuterated chloroform and acetone were used as solvents for the t-BSOS and STVPh copolymers, respectively. Molecular weights and molecular weight distributions based upon polystyrene standards were determined by s.e.c. using a Waters 150 C GPC/ALC chromatograph equipped with a refractive index detector and four μStyragel columns (100 000, 10 000, 500 and 100 Å) connected in series. Thermal analysis was conducted on a Perkin-Elmer differential scanning calorimeter (DSC-7) coupled to a computerized data station. A heating rate of 20°C min^{-1} was used in all experiments and T_g was taken as the midpoint of the heat capacity change.

RESULTS AND DISCUSSION

Theoretical calculations of spinodal phase diagrams and 'miscibility windows'

As a starting point for discussion we have reproduced (*Figure 4*) the previously published[10] theoretical spinodal phase diagrams for PVPh blends with a series of poly(n-alkyl methacrylates) (PAMA) ranging from methyl to n-hexyl. An important trend is predicted. If we

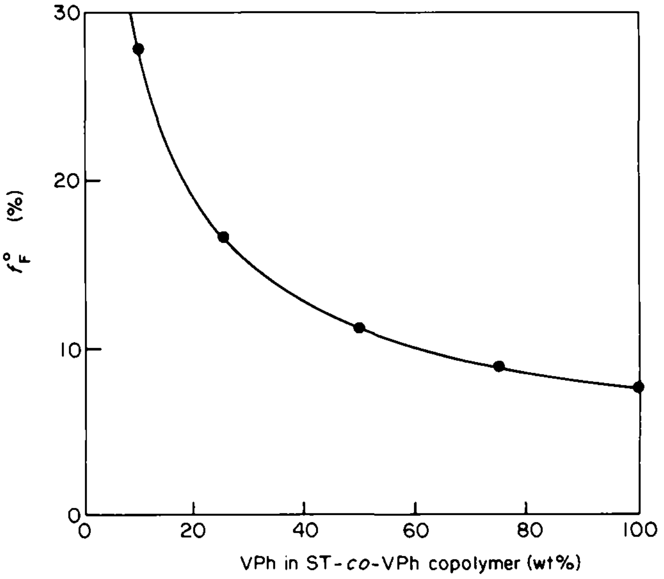


Figure 3 Calculated fraction of 'free' phenolic hydroxyl groups in STVPh copolymers as a function of the composition at 25°C

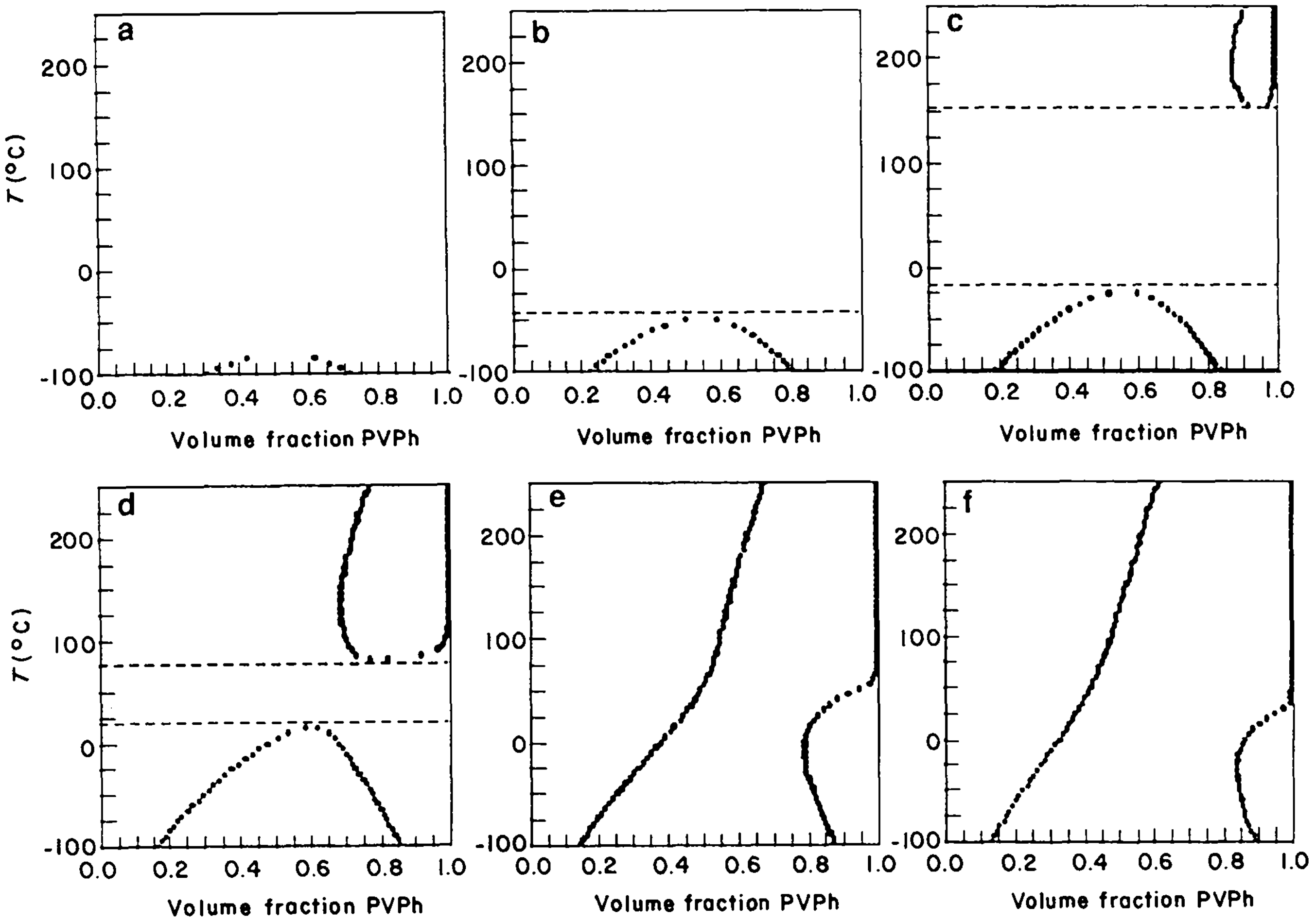


Figure 4 Theoretical spinodal phase diagrams for PVPh/poly(n-alkyl methacrylate) blends: (a) PMMA; (b) PEMA; (c) PPMA; (d) PBMA; (e) PPeMA; (f) PHMA

focus on the experimentally accessible temperature range of ambient to 250°C, systematically increasing the number of methylene groups in the side chain from zero to five leads to predicted changes in the phase behaviour of these blends that span the whole spectrum, from the completely miscible (PMMA, PEMA and essentially PPMA) to the completely immiscible (PPeMA and PHMA). The PVPh–PBMA blend system is predicted to be 'on the edge' of miscibility, with a single phase over the whole composition range at ambient temperature, but separating into two phases at elevated temperatures for compositions rich in PVPh. These predictions of the phase behaviour of PVPh–PAMA blends are in excellent accord with experiment[10].

'Miscibility windows', observed experimentally in certain blends that contain copolymers, are a convenient way of expressing the phase behaviour of polymer blend systems at a given temperature and have been previously described in terms of binary interaction models[24–26]. We have approached the problem from a different direction and have employed a Flory lattice model to obtain an expression for the free energy of mixing polymers that hydrogen bond[3]. A result of this approach is that unfavourable 'physical' contributions to the free energy of mixing, embodied in a Flory-type χ parameter, are separated from the favourable contribution emanating from the changing distribution of hydrogen bonds, $\Delta G_H/RT$ (in our original formulation[1,2] this was assumed, but we have recently obtained the same result in a more formal manner[3]). The free energy of mixing can be written:

$$\frac{\Delta G^M}{RT} = \frac{\Phi_A}{N_A}\ln\Phi_A + \frac{\Phi_B}{N_B}\ln\Phi_B + \Phi_A\Phi_B\chi + \frac{\Delta G_H}{RT} \qquad (2)$$

where Φ_A and Φ_B, and N_A and N_B, are the volume fractions and degrees of polymerization of polymers A and B, respectively. We use group contributions in calculating χ and consequently we make no conceptual distinction between the repeat unit of a homopolymer and the molar equivalent average repeat of a copolymer[27].

One of the more interesting and encouraging results of our previous preliminary calculations[9] was that we were able to predict with surprising accuracy the experimentally determined limits of miscibility of STVPh blends with PMMA, PEMA and PBMA[28]. The styrene in the copolymer was simply considered to be an inert diluent in the system and it was a relatively trivial task to obtain the parameters required to calculate the free energy of mixing and a phase diagram for a given STVPh–PAMA polymer blend from those describing the corresponding PVPh–PAMA system. Our methodology was described in detail previously[9] and will not be repeated here, but it is important to remember that both the magnitude of χ and the $\Delta G_H/RT$ terms change with copolymer composition. Using parameter values recently established (see *Table 2*) for PVPh–PAMA blends[10,29]

Table 2 Parameters used in this study^a

Polymer	V (cm^3 mol^{-1})	δ (cal cm^{-3})$^{1/2}$	$N_A = N_B$ (*DP*)	K_2	Equilibrium constant K_B	K_A
PBMA	134.4	8.7	500	-	-	-
PHMA	167.4	8.5	500	-	-	-
PVPh	100.0	10.6	500	21.0	66.8	37.1
STVPh[75]	134.7	10.3	371	15.6	49.6	27.5
STVPh[43]	224.5	10.0	223	9.4	29.8	16.5
STVPh[25]	381.7	9.8	131	5.5	17.5	9.7
STVPh[8]	1348	9.6	37	1.6	5.0	2.8
STVPh[2]	4701	9.5	11	0.5	1.4	0.8

^{a}Enthalpy of hydrogen bond formation: $h_2 = 5.6$, $h_B = 5.2$ and $h_A = 3.8$ (kcal mol^{-1})

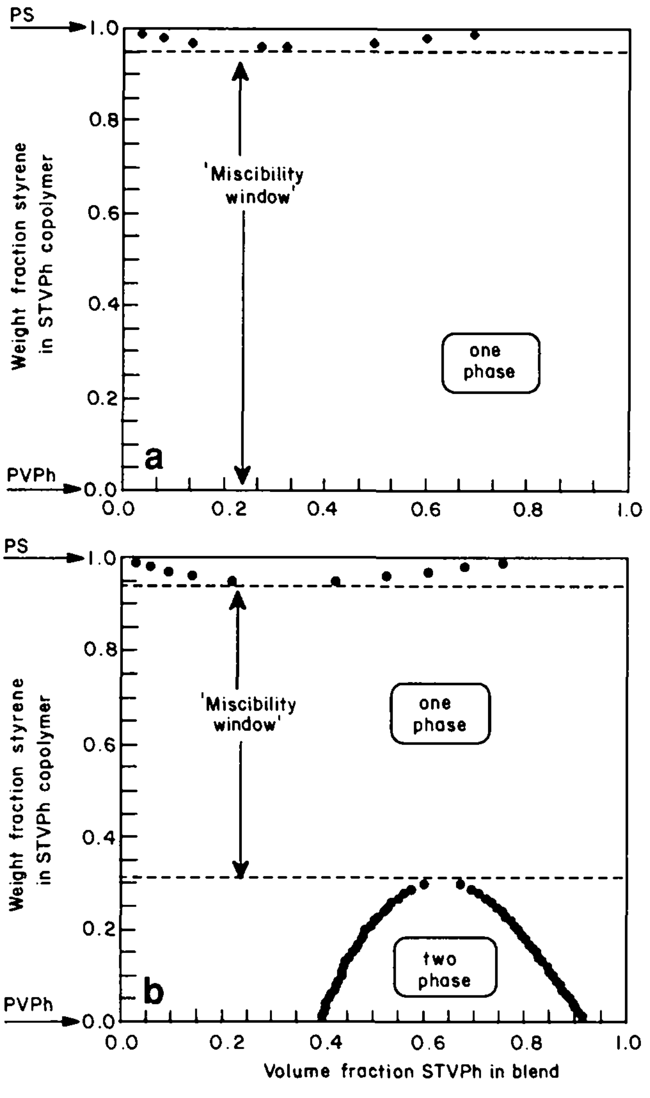


Figure 5 Theoretical 'miscibility window' calculated at 25°C for (a) PBMA and (b) PHMA blends with STVPh copolymers

employed to calculate the phase diagrams shown in *Figure 4*, 'miscibility windows' were calculated for PBMA and PHMA blends with STVPh copolymers[9]. These results are displayed in *Figure 5*. At the extremes on the *y* axis are the copolymer compositions corresponding to PVPh and essentially polystyrene (PS containing $<0.1\%$ VPh). A miscibility window for PBMA blends with STVPh copolymers ranging from ~0 to 97% styrene is calculated, while for the corresponding PHMA blends the window extends from ~32 to 94% styrene. It is these predictions that were tested experimentally.

Five essentially random STVPh copolymers containing 75, 43, 25, 8 and 2 wt% VPh, respectively, were synthesized and characterized in our laboratories. These copolymers are denoted STVPh[75], STVPh[43] etc. Theoretical spinodal phase diagrams for PBMA and PHMA blends with these specific STVPh copolymers were calculated using the procedure described previously[9] and from the parameters recently derived from the PVPh–PAMA blend system[10]. The results are displayed in *Figures 6* and *7*, respectively. For our purposes the most important conclusions are that PBMA is predicted to be miscible with PVPh, STVPh[75], STVPh[43], STVPh[25] and STVPh[8] and immiscible with STVPh[2] at ambient temperature. On the other hand, PHMA is predicted to be immiscible with PVPh and STVPh[75], miscible with STVPh[43], STVPh[25] and STVPh[8] and immiscible once again with STVPh[2].

To test the above predictions we have employed *FT*i.r. spectroscopy. In the past we have cautioned that even the presence of a prominent i.r. band attributed to an intermolecular interaction between groups of dissimilar polymers does not substantiate miscibility. Furthermore, a quantitative analysis of the fraction of hydrogen-bonded groups is insufficient to establish a single phase without a detailed knowledge of the stoichiometry and the equilibrium constants describing self- and inter-association[1–3]. Fortunately, in the case of the polymer blend systems considered here we have such information and if we assume that the mixture is a single phase (completely miscible), we can readily calculate the fraction of hydrogen-bonded carbonyl groups, $f_{HB}^{C=O}$; the fraction of hydrogen-bonded hydroxyl–hydroxyl groups (self-association), $f_{HB}^{OH/OH}$; the fraction of hydrogen-bonded hydroxyl–carbonyl groups (inter-association), $f_{HB}^{OH/CO}$, and the fraction of 'free' hydroxyl groups, f_F^{OH}. With this information we can compare the theoretical fraction of the various intermolecular interactions with those observed experimentally by *FT*i.r. spectroscopy. Should the theoretical values equal, within error, those determined experimentally, a miscible (single phase) blend can be confidently inferred. Conversely, if the theoretical values deviate significantly from that determined experimentally, an immiscible (two phase) mixture is indicated. At the extreme, when the two phases resemble essentially pure components, the theoretical

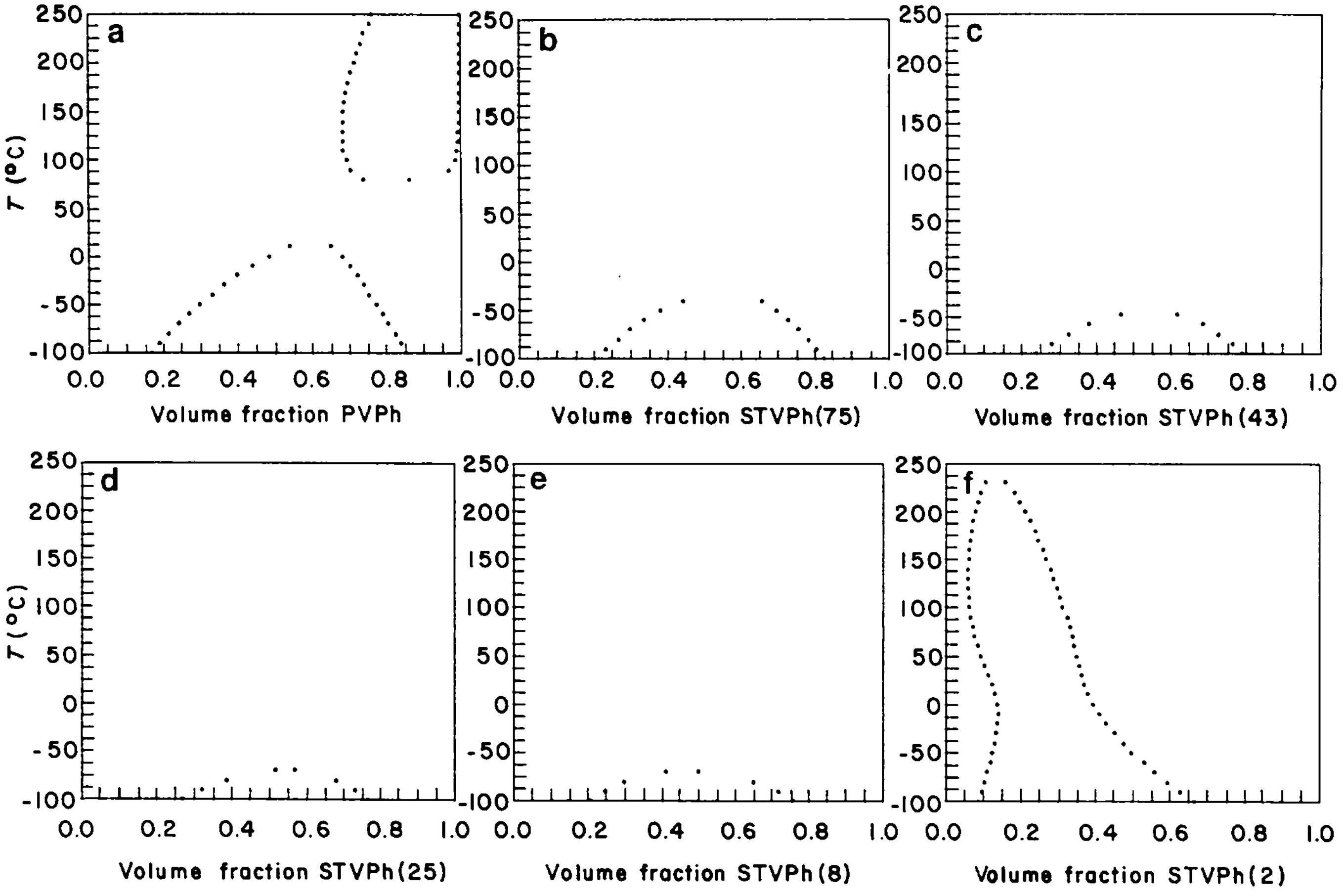


Figure 6 Theoretical spinodal phase diagrams for PBMA blends with: (a) PVPh; (b) STVPh[75]; (c) STVPh[43]; (d) STVPh[25]; (e) STVPh[8]; (f) STVPh[2]

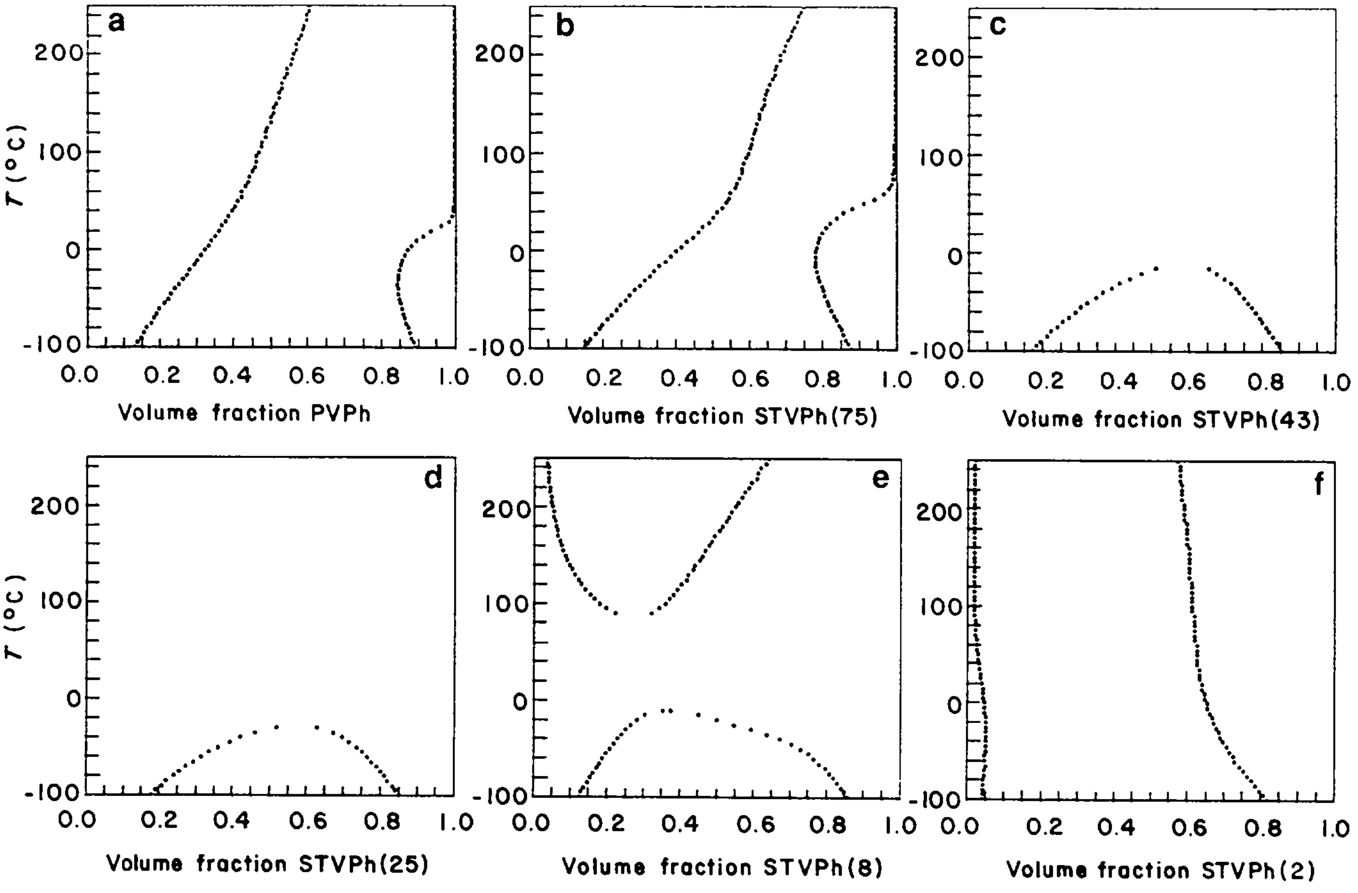


Figure 7 Theoretical spinodal phase diagrams for PHMA blends with: (a) PVPh; (b) STVPh[75]; (c) STVPh[43]; (d) STVPh[25]; (e) STVPh[8]; (f) STVPh[2]

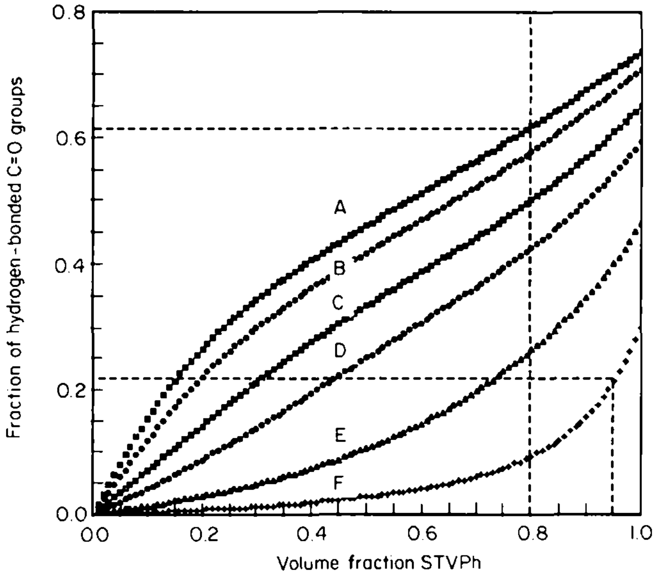


Figure 8 Fraction of hydrogen-bonded carbonyl groups calculated as a function of blend composition at 25°C for theoretically miscible blends of PHMA with: (A) PVPh; (B) STVPh[75]; (C) STVPh[43]; (D) STVPh[25]; (E) STVPh[8]; (F) STVPh[2]

values will approach those present originally in the pure materials.

If the polymer blend is truly miscible, the theoretical fraction of hydrogen-bonded carbonyl groups for PAMA blends with PVPh and the five STVPh copolymers as a function of blend composition at 25°C may be calculated from equation (3).

$$f_{\mathrm{HB}}^{\mathrm{C=O}} = 1 - \left\{ \frac{1}{\left[1 + K_A \Phi_{B_1} \left[\left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{(1 - K_B \Phi_{B_1})}\right)\right]\right]} \right\} \tag{3}$$

where Φ_{B_1} and Φ_{A_1} are the volume fractions of the totally 'free monomers' of the self-associating species B and the non-self-associating species A. K_2 and K_B are equilibrium constants describing the self-association of B while K_A corresponds to the equilibrium constant describing the inter-association of B with A[1-3,7,10]. The results of the calculations for the PHMA blends are displayed in *Figure 8* (the corresponding calculations for the PBMA blends differ somewhat in absolute values, but the form of the curves is very similar). In studying bands in the carbonyl stretching region of the i.r. spectrum we will concentrate on STVPh-rich blends, mainly 80:20 STVPh:PBMA (or PHMA) since the difference between the fraction of hydrogen-bonded carbonyl groups in a miscible mixture and pure PBMA or PHMA (none) is unambiguous. The theoretical curves presented in *Figure 8* illustrate an important point. Consider the vertical broken line passing through the curves at a composition of 80% STVPh. In a miscible blend of PHMA and STVPh[75] ~60% of the carbonyl groups would be hydrogen bonded, while corresponding values for miscible blends of PHMA and STVPh[25] or STVPh[8] are ~40 and 25%, respectively. To reiterate, the intermolecular interaction between the phenolic hydroxyl and the methacrylate carbonyl groups is identical in all cases, but the fraction of hydrogen-bonded carbonyl groups is a function of the stoichiometry and hence the equilibrium constants defining self- and inter-association (if defined in terms of an 'average' repeat unit).

In a similar manner, again assuming a single phase, the theoretical fraction of 'free' and hydrogen-bonded phenolic hydroxyl groups may be calculated as a function of blend composition at 25°C using equations (4)–(7).

$$f_{\mathrm{F}}^{\mathrm{OH}} = \frac{\Phi_{B_1}}{\Phi_B}\left[1 - \frac{K_2}{K_B} + \frac{K_2}{K_B}\left\{\frac{1}{1 - K_B \Phi_{B_1}}\right\}\right] \tag{4}$$

$$f_{\mathrm{HB}}^{\mathrm{OH}} = 1 - f_{\mathrm{F}}^{\mathrm{OH}} \tag{5}$$

$$f_{\mathrm{HB}}^{\mathrm{OH/CO}} = \frac{\Phi_{B_1}}{\Phi_B}\left\{\frac{\Phi_{A_1} K_A}{r}\right\}\left[1 - \frac{K_2}{K_B} + \frac{K_2}{K_B}\left\{\frac{1}{1 - K_B \Phi_{B_1}}\right\}\right] \tag{6}$$

$$f_{\mathrm{HB}}^{\mathrm{OH/OH}} = f_{\mathrm{HB}}^{\mathrm{OH}} - f_{\mathrm{HB}}^{\mathrm{OH/CO}} \tag{7}$$

where r is the ratio of the molar volumes of the chemical repeat units, V_A/V_B. The results of these calculations for the PHMA blends are displayed in *Figure 9* (again, the general form of the curves is very similar for the PBMA case). Unlike the carbonyl stretching region of the i.r. spectrum where there are only two bands attributed to 'free' and hydrogen-bonded carbonyl groups, in the hydroxyl stretching region there are (at least) three major contributors, and the variation of the fraction of the 'free' and two different hydrogen-bonded hydroxyl groups as a function of STVPh copolymer and blend compositions is rather complex. In this region of the spectrum the PBMA- or PHMA-rich blends (e.g. 20:80 STVPh:PHMA) will be particularly sensitive to differences in the phase behaviour of the blends. While a quantitative comparison between the theoretical and experimental fraction of the different species is feasible in the carbonyl stretching region, in the hydroxyl stretching region only a qualitative comparison can be made, because of the lack of reliable absorptivity coefficients and other complications.

Comparison of experimental FT*i.r. results to theoretical predictions*

I.r. spectra of PHMA and PBMA blends with PVPh and the five STVPh copolymers are displayed in *Figures 10–16*. With the exception of *Figure 16*, all show two separate regions of the i.r. spectrum. At the top are spectra recorded in the hydroxyl stretching region from 3100 to 3700 cm^{-1}, while at the bottom corresponding spectra recorded in the carbonyl stretching region from 1650 to 1800 cm^{-1} are displayed. For clarity, all spectra are scale expanded and plotted with respect to a relative absorbance scale; all the spectra were recorded from films that were sufficiently thin to ensure that maximum absorbances did not exceed 0.6 absorbance units.

Before we compare the experimental results with the theoretical predictions for each blend system, it is necessary to briefly discuss the problems associated with sample preparation. Whether or not a particular polymer mixture can be prepared in a state approaching thermodynamic equilibrium is always a source of concern. Thin films ($\approx$5–10 μm) for quantitative transmission i.r. analysis are usually cast from a dilute solution of a volatile solvent and it is well established that phase separation can be induced by the solvent during evaporation (the so-called $\Delta\chi$ effect[30]). If the T_gs of either or both phases are above the solvent evaporation

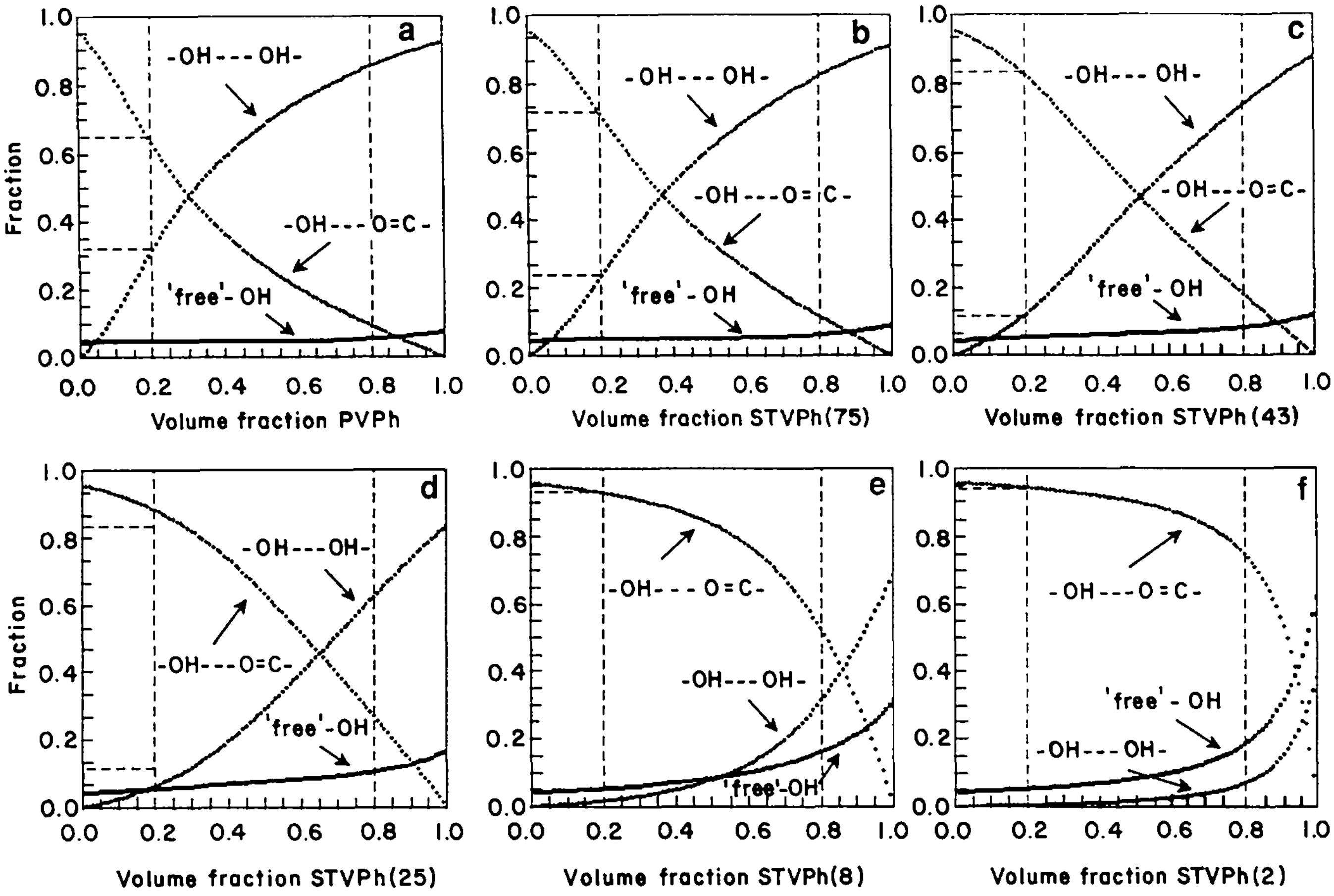


Figure 9 Fraction of 'free' and hydrogen-bonded hydroxyl groups calculated as a function of blend composition at 25°C for theoretically miscible blends of PHMA with: (a) PVPh; (b) STVPh[75]; (c) STVPh[43]; (d) STVPh[25]; (e) STVPh[8]; (f) STVPh[2]

temperature, a non-equilibrium multiphase material can be formed that is effectively 'frozen'; the components being prevented from mixing due to severely restricted mobility. Furthermore, there is also the possibility of trapping a homogeneous phase in systems that have high T_gs. STVPh copolymers have T_gs between 190°C (pure PVPh) and 100°C (pure PS) while PBMA and PHMA have T_gs of 21 and −53°C, respectively. We recognize that in blends rich in STVPh true equilibrium is impractical at room temperature and that additional complications will occur if we pass through a lower critical phase boundary during the heating cycle. Accordingly, we were careful to study the i.r. spectra of the blend samples at ambient temperature after preparation (see Experimental); at an elevated temperature of 200°C (above the T_g of all components) after an annealing period of ~15 min and again at ambient temperature upon cooling. The effect of non-equilibrium conditions on the observed fraction of hydrogen-bonded groups is tackled later, but for the purposes of this study the experimental complications mentioned above are not a serious problem.

PHMA blends with PVPh and STVPh[*75*]. *Figure 10* shows the *FT*i.r. spectra of blends containing 80:20 and 20:80 weight ratios of PVPh:PHMA together with those recorded for pure PVPh and PHMA. The interpretation of i.r. spectra of PVPh blends with carbonyl-containing polymers such as polyesters, polyacrylates, polymethacrylates, etc. has been discussed in detail previously[7,10,31-33] and only the essential features will be restated here. Pure amorphous PHMA (*Figure 10D*) is characterized by a carbonyl stretching vibration at 1735 cm^{-1}. If there were appreciable mixing at the molecular level in the PVPh–PHMA blend system then we would observe an additional band at ~1710 cm^{-1}, attributable to hydrogen-bonded carbonyl groups. The fraction of hydrogen-bonded carbonyl groups can be readily determined by measuring the relative areas of these two bands, after due consideration is given to differences in the respective absorptivity coefficients[7,10,33]. The top curve shown in *Figure 8* depicts the theoretical fraction of hydrogen-bonded carbonyl groups as a function of blend composition, assuming a miscible mixture. Thus, for a truly miscible 80:20 PVPh:PHMA blend, ~62% of the carbonyl groups would be hydrogen-bonded and a prominent 1710 cm^{-1} band would be observed (very similar to the spectra of the 80:20 miscible PVPh blends with the methyl, ethyl and propyl methacrylate polymers shown in ref. 10). Similarly, for a miscible 20:80 PVPh:PHMA blend ~27% of the carbonyl groups would be hydrogen bonded. An obvious band at 1710 cm^{-1} would be detected that could be easily measured quantitatively. Since there is no evidence of any significant contribution from an i.r. band at 1710 cm^{-1} in either blend spectrum (*Figure 10*), we conclude that these blends are grossly phase separated.

Figure 11 shows the *FT*i.r. spectra of blends containing 80:20 and 20:80 weight ratios of STVPh[75]:PHMA together with those recorded for pure STVPh[75] and PHMA. The interpretation of these i.r. spectra is very

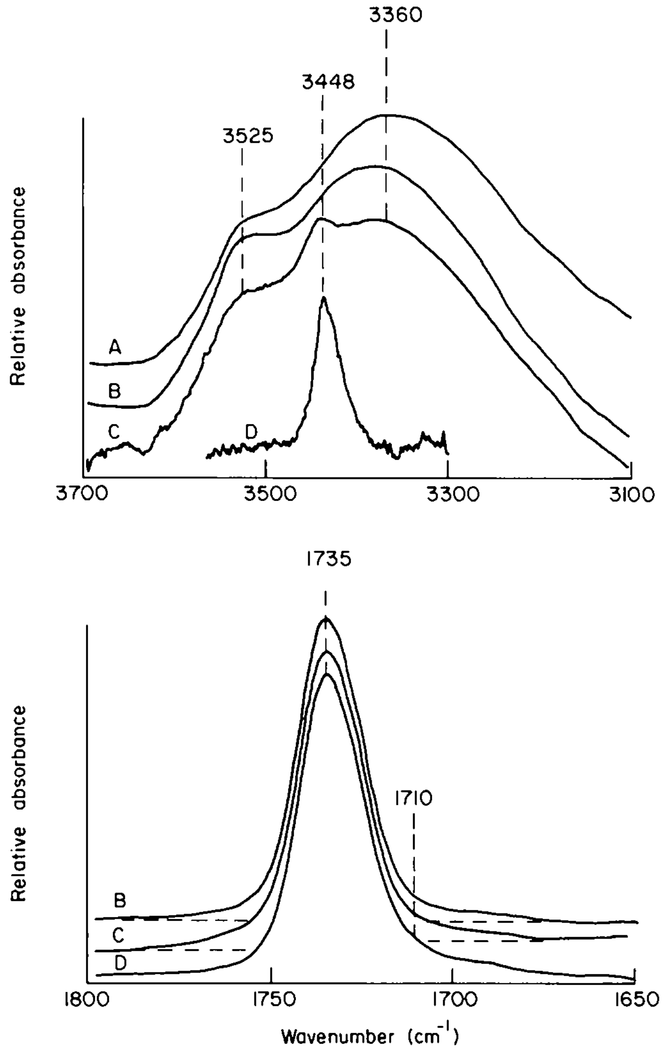


Figure 10 Scale-expanded *FT*i.r. spectra recorded at room temperature in the hydroxyl stretching (top) and carbonyl stretching (bottom) regions of blends of PVPh and PHMA: (A) pure PVPh; (B) 80:20 PvPh:PHMA; (C) 20:80 PVPh:PHMA; (D) pure PHMA

similar to that given above for the PVPh PHMA blends. Consulting *Figure 8*, we determine that for truly miscible 80:20 and 20:80 STVPh[75]:PHMA blends, ~58 and 22%, respectively, of the carbonyl groups would be hydrogen bonded. Since there is no evidence of any significant contribution from an i.r. band at 1710 cm^{-1} in either blend spectrum (*Figures 11B* and *C*), the conclusion is again that these blends are grossly phase separated.

Corroborating evidence for this conclusion is present in the hydroxyl stretching region shown at the top of *Figures 10* and *11*. Pure amorphous PVPh (*Figure 10A*) is characterized by 'free' and hydrogen-bonded (self-associated) hydroxyl stretching vibrations at 3525 and ~3360 cm^{-1}, respectively. An overtone of the carbonyl stretching vibration ($2 \times \nu_{C=O}$) of PHMA (*Figure 10D*) also occurs in this region of the spectrum at 3448 cm^{-1} and is conspicuous in PHMA-rich blends where there is a high relative concentration of carbonyl (non-hydrogen-bonded) to hydroxyl groups. This overtone can be removed by spectral subtraction, but is just as easily recognized and disregarded. More importantly, if there were appreciable mixing at the molecular level in the PVPh PHMA blends then we would observe an additional band in the spectra at ~3450 cm^{-1}, attributable to hydroxyl groups hydrogen-bonded to carbonyl groups[31,32]. In fact, for a truly miscible 20:80 PVPh:PHMA blend, we calculate (*Figure 9a*) that the fraction of hydrogen-bonded hydroxyl carbonyl (inter-association) and hydroxyl–hydroxyl (self-association) interactions would be ~0.64 and 0.32, respectively, with the remainder being 'free' hydroxyl groups. Corresponding fractions for a miscible 80:20 PVPh:PHMA blend are 0.1 and 0.84, respectively. Disregarding the overtone, the spectra of pure PVPh (*Figure 10A*) and the 80:20 and 20:80 PVPh:PHMA blends (*Figures 10B* and *C*) are almost identical. This is consistent with blend samples that are grossly phase separated where the PVPh in the blend is essentially isolated in its own domain.

Similarly, from *Figure 9B* we see that for a truly miscible 20:80 STVPh[75]:PHMA blend that the fraction of hydrogen-bonded hydroxyl–carbonyl and hydroxyl–hydroxyl interactions would be ~0.72 and 0.23, respectively, with the remainder being 'free' hydroxyl groups. Corresponding fractions for a miscible 80:20 STVPh[75]:PHMA blend are 0.12 and 0.82, respectively. Note that the incorporation of styrene into

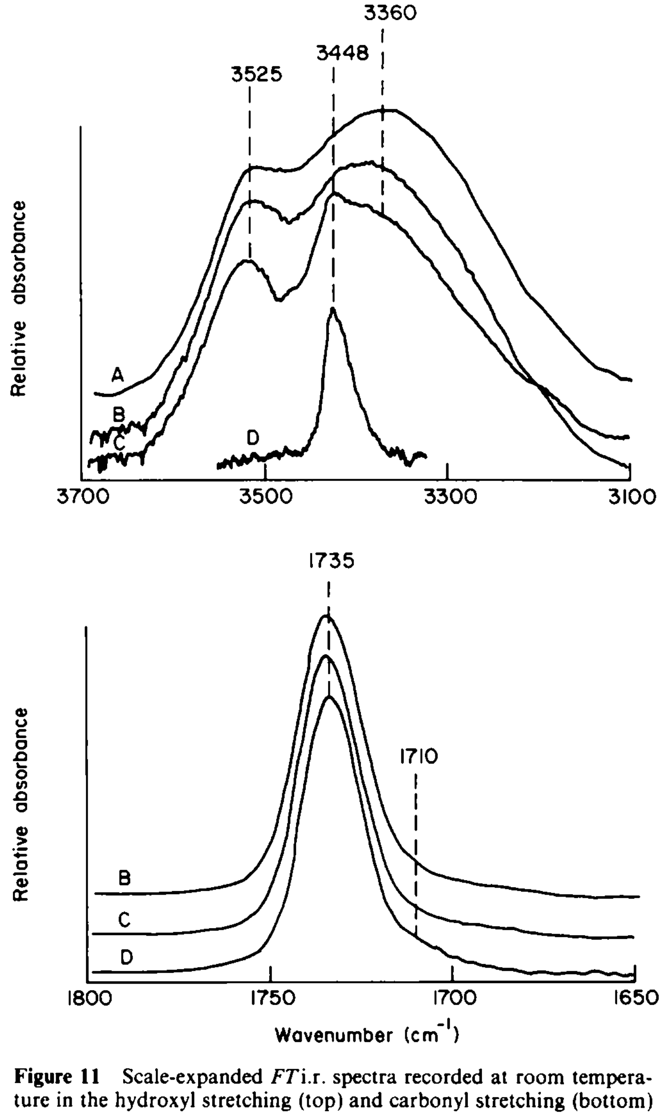


Figure 11 Scale-expanded *FT*i.r. spectra recorded at room temperature in the hydroxyl stretching (top) and carbonyl stretching (bottom) regions of blends of STVPh[75] and PHMA: (A) pure STVPh[75]; (B) 80:20 STVPh[75]:PHMA; (C) 20:80 STVPh[75]:PHMA; (D) pure PHMA

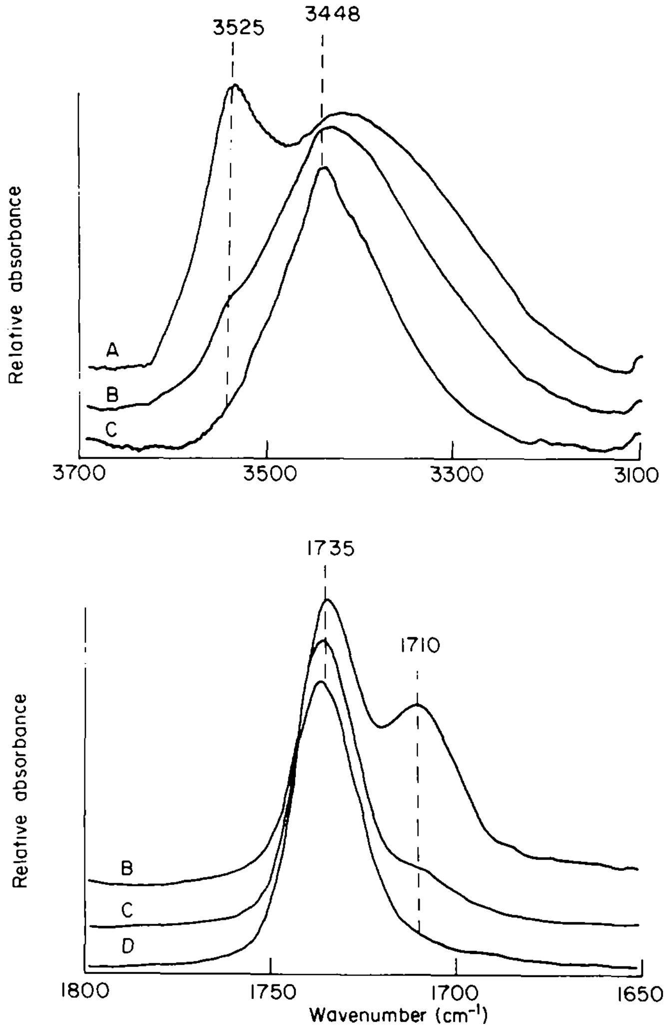


Figure 12 Scale-expanded *FT*i.r. spectra recorded at room temperature in the hydroxyl stretching (top) and carbonyl stretching (bottom) regions of blends of STVPh[43] and PHMA: (A) pure STVPh[43]; (B) 80:20 STVPh[43]:PHMA; (C) 20:80 STVPh[43]:PHMA; (D) pure PHMA

PVPh via copolymerization effectively dilutes the system. Accordingly, the values of the equilibrium constants describing self-association (as defined for a copolymer) decrease with increasing styrene concentration, which is reflected in an increase in the experimentally observed fraction of 'free' hydroxyl groups of the pure STVPh copolymers (see Experimental). This will be more obvious in the studies of other blends described below. In any event, if we disregard the overtone, the spectra of pure STVPh[75] (*Figure 11A*) and the 80:20 and 20:80 STVPh[75]:PHMA blends (*Figures 11B* and *C*) are very similar. This is again consistent with blend samples that are grossly phase separated.

In summary, experimental *FT*i.r. studies of PVPh and STVPh[75]-PHMA blends substantiate that the system is immiscible which is in accord with theoretical prediction (*Figures 5* and *7*).

PHMA blends with STVPh[43], STVPh[25] and STVPh[8]. *Figure 12* shows the *FT*i.r. spectra of blends containing 80:20 and 20:80 weight ratios of STVPh[43]:PHMA together with those recorded for pure STVPh[43] and PHMA. In marked contrast to the two previous blend systems considered, there is now definitive evidence for molecular mixing. There is an obvious contribution from an i.r. band at 1710 cm^{-1} in both blend spectra (*Figures 12B* and *C*). To reiterate, the obvious presence of a band attributed to hydrogen-bonded carbonyl groups is a necessary but insufficient requirement for a single phase (miscibility). Significant mixing is, of course, possible in the individual phases of multiphased systems. Nevertheless, referring to *Figure 8*, truly miscible 80:20 and 20:80 STVPh[43]:PHMA blends should have ~50 and 15%, respectively, of the hydrogen-bonded carbonyl groups. *Table 3* shows the results of a quantitative analysis[7,10,33] of the carbonyl stretching region of the 80:20 and 20:80 STVPh:PHMA blend spectra. Specifically, for the STVPh[43]-PHMA blends values of 46 and 14%, respectively, were determined. These results are equivalent, within error, to those calculated. Accordingly, we can confidently conclude that this blend system is miscible.

Figure 13 shows the *FT*i.r. spectra of blends containing 80:20 and 20:80 weight ratios of STVPh[25]:PHMA together with those recorded for pure STVPh[25] and PHMA. Here again we have definitive evidence for molecular mixing. The presence of an i.r. band at 1710 cm^{-1} in both blend spectra (*Figures 13B* and *C*) is

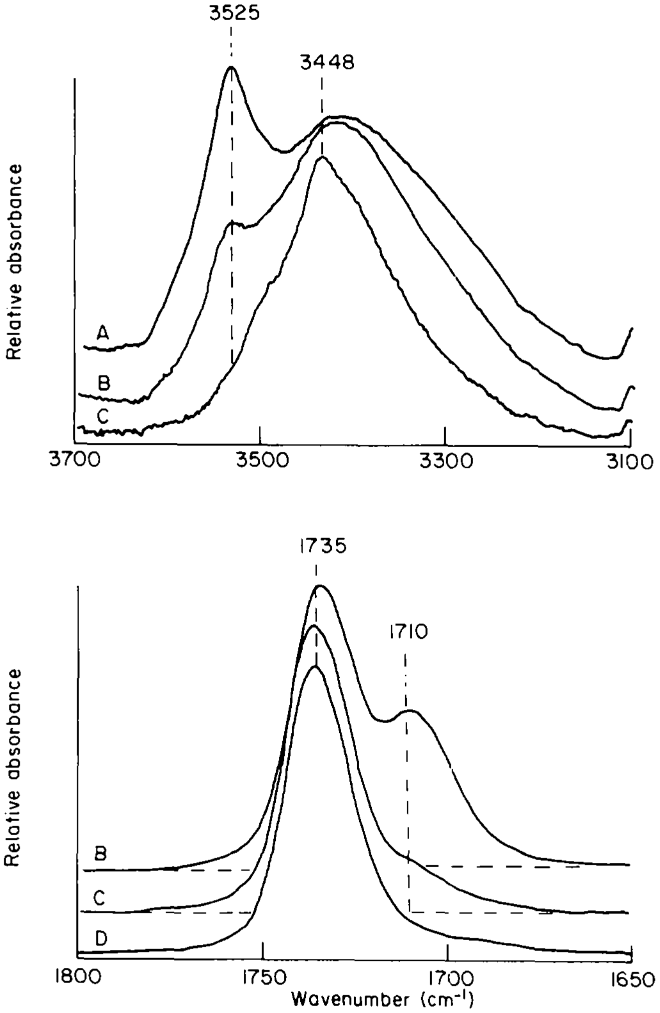


Figure 13 Scale-expanded *FT*i.r. spectra recorded at room temperature in the hydroxyl stretching (top) and carbonyl stretching (bottom) regions of blends of STVPh[25] and PHMA: (A) pure STVPh[25]; (B) 80:20 STVPh[25]:PHMA; (C) 20:80 STVPh[25]:PHMA; (D) pure PHMA

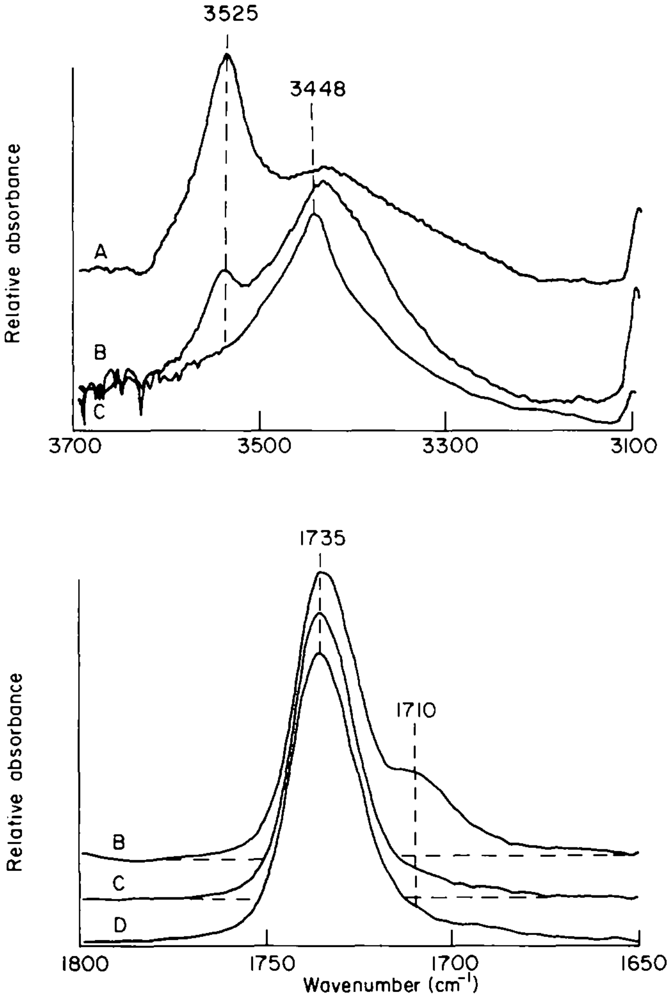


Figure 14 Scale-expanded *FT*i.r. spectra recorded at room temperature in the hydroxyl stretching (top) and carbonyl stretching (bottom) regions of blends of STVPh[8] and PHMA: (A) pure STVPh[8]; (B) 80:20 STVPh[8]:PHMA; (C) 20:80 STVPh[8]:PHMA; (D) pure PHMA

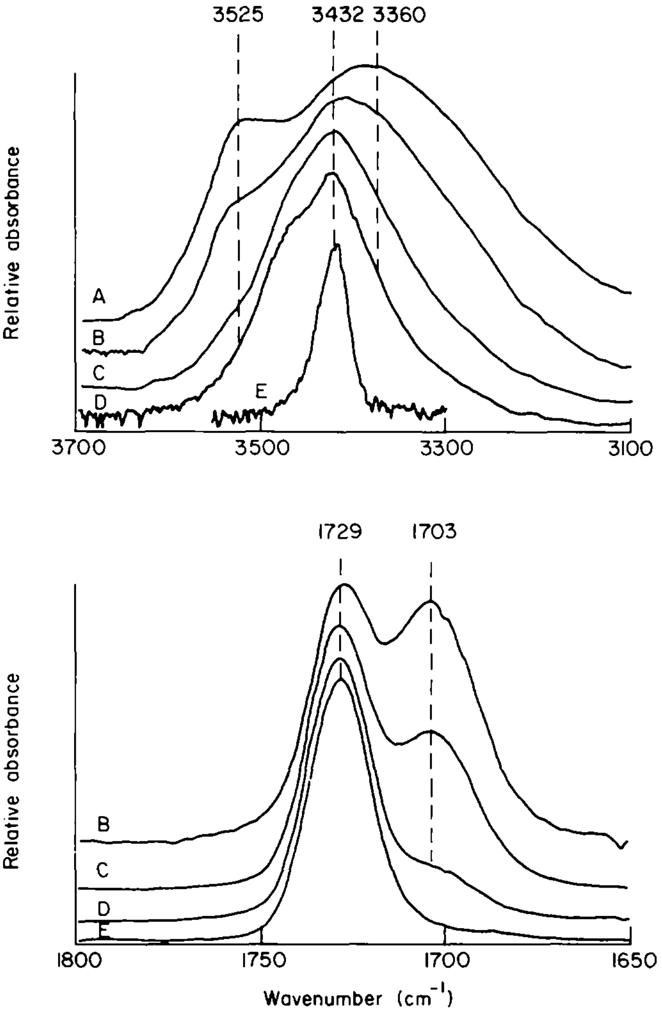


Figure 15 Scale-expanded *FT*i.r. spectra recorded at room temperature in the hydroxyl stretching (top) and carbonyl stretching (bottom) regions of blends of STVPh[75] and PBMA: (A) pure STVPh[75]; (B) 80:20 STVPh[75]:PBMA; (C) 50:50 STVPh[75]:PBMA; (D) 20:80 STVPh[75]:PBMA; (E) pure PBMA

obvious. Referring once more to *Figure 8*, there should be ~42 and 9%, respectively, of the hydrogen-bonded carbonyl groups in truly miscible 80:20 and 20:80 STVPh[25]:PHMA blends. Quantitative analysis (*Table 3*) yields values of 39 and 13%, respectively, comparable within experimental error to the calculated values which implies a miscible system. Similarly, *Figure 14* shows the *FT*i.r. spectra of blends containing 80:20 and 20:80 weight ratios of STVPh[8]:PHMA. Molecular mixing is definitely indicated; 21 and 3%, respectively, of the carbonyl groups present in miscible 80:20 and 20:80 STVPh[8]:PHMA blends should be hydrogen bonded (*Figure 8*). Quantitative analysis (*Table 3*) yields values of 21 and <5% (detectable, but below the limit of accurate measurement), respectively. This excellent agreement again implies a miscible blend system.

Corresponding and dramatic changes in the hydroxyl stretching region of the spectra of the PHMA blends with STVPh[43], STVPh[25] and STVPh[8] indicate extensive molecular mixing and qualitatively support miscibility. As mentioned above, quantitative analysis is unfortunately impractical. *Figure 12A* shows the spectrum of pure STVPh[43] with a now prominent 'free' hydroxyl band reflecting the dilution effect of the styrene comonomer. Using the graph shown in *Figure 9c* we see

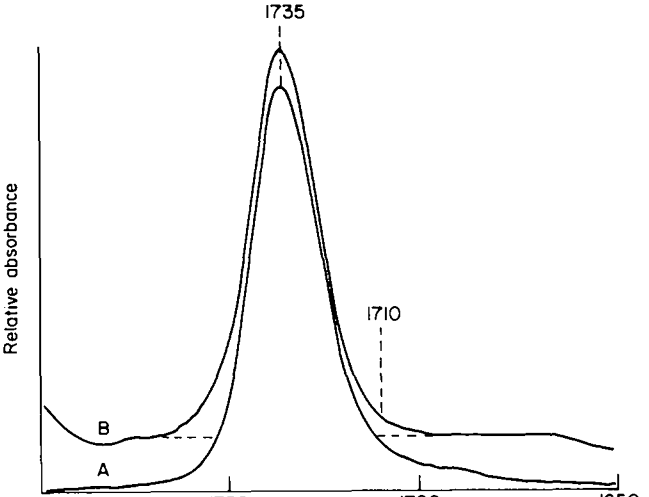


Figure 16 Scale-expanded *FT*i.r. spectra recorded at room temperature in the carbonyl stretching region of (A) pure PHMA and (B) a blend of 95:5 STVPh[2]:PHMA

Table 3 Curve resolving data for PHMA–STVPh blends

Blend (by weight)	'Free' C=O band			Hydrogen-bonded C=O band			Fraction of hydrogen-bonded C=O groups	
PHMA:STVPh[x]	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area	Expt	Theory[a]
PHMA:STVPh[8]								
20:80	1735	19	3.01	1710[b]	25[b]	0.96	0.2[illegible]	0.21
80:20	1735	21	8.41	1710	–		<0.05[c]	0.03
PHMA:STVPh[25]								
20:80	1735	18	1.24	1710	25	1.09	0.39	0.42
80:20	1735	20	4.82	1710[b]	25[b]	1.13	0.12	0.09
PHMA:STVPh[43]								
20:80	1735	20	4.05	1710	25	3.08	0.47	0.50
80:20	1735	22	2.49	1710[b]	25[b]	10.3	0.14	0.15

[a] See *Figure 8*
[b] Fixed parameters
[c] Limit of detection

that for a truly miscible 20:80 STVPh[43]:PHMA blend that the fraction of hydrogen-bonded hydroxyl–carbonyl, hydroxyl–hydroxyl interactions and 'free' hydroxyl groups would be ~0.83, 0.13 and 0.04, respectively. The spectrum shown in *Figure 12C* (top) is in excellent qualitative agreement with these theoretical calculations. A dominant band attributable to hydroxyl carbonyl interactions is observed at 3450 cm^{-1} together with a minor underlying contribution from the hydroxyl–hydroxyl band ($\approx$ 3400 cm^{-1}) and a very small contribution from the 'free' hydroxyl band (3525 cm^{-1}). Corresponding theoretical fractions for a miscible 80:20 STVPh[43]:PHMA blend are 0.20, 0.73 and 0.07, respectively, which compare favourably with the relative increase in the contributions from the hydroxyl hydroxyl and 'free' bands over that of the hydroxyl–carbonyl band as shown in *Figure 12B* (top). In this case the spectrum of pure STVPh[43] (*Figure 12A*) and the 80:20 and 20:80 STVPh[43]:PHMA blends (*Figures 12B* and *C*) are very different. This is in accord with a blend system that is well mixed and possibly miscible.

In a similar manner, from *Figure 9d* the fraction of hydrogen-bonded hydroxyl–carbonyl, hydroxyl–hydroxyl and 'free' hydroxyl groups is calculated at ~0.89, 0.07 and 0.04, respectively, for a miscible 20:80 STVPh[25]:PHMA blend. The spectrum shown in *Figure 13C* (top) appears to be in good qualitative agreement with these theoretical calculations. The hydroxyl carbonyl band is paramount with only very minor underlying contributions from the hydroxyl hydroxyl and 'free' hydroxyl bands. Corresponding theoretical fractions for a miscible 80:20 STVPh[25]: PHMA blend are 0.27, 0.62 and 0.11, respectively. The spectral features shown in *Figure 13B* (top) qualitatively reflect such a distribution. Once more, the spectrum of pure STVPh[25] (*Figure 13A*) and the 80:20 and 20:80 STVPh[25]:PHMA blends (*Figures 13B* and *C*) are very different and in accord with a blend system that is well mixed and possibly miscible.

Finally, from *Figure 9E* the fraction of hydrogen-bonded hydroxyl–carbonyl, hydroxyl hydroxyl and 'free' hydroxyl groups is calculated at ~0.93, 0.02 and 0.05, respectively, for a miscible 20:80 STVPh[8]:PHMA blend. *Figure 14C* (top) reflects a distribution such as this with the hydroxyl–carbonyl band totally dominant. Corresponding theoretical fractions for a miscible 80:20 STVPh[8]:PHMA blend are 0.52, 0.32 and 0.16, respectively. The spectral features shown in *Figure 14B* (top) reflect such a distribution. For the last time, the spectrum of pure STVPh[8] (*Figure 14A*) and the 80:20 and 20:80 STVPh[8]:PHMA blends (*Figures 14B* and *C*) are very different and in accord with a blend system that is well mixed and possibly miscible.

In summary, experimental *FT*i.r. studies of PHMA blends with STVPh[43], STVPh[25] and STVPh[8] indicate that these systems are miscible which is again in agreement with theoretical prediction (*Figures 5* and *7*).

PBMA blends with PVPh, STVPh[75], STVPh[43], STVPh[25] and STVPh[8]. Above we have demonstrated that PHMA blends with PVPh and STVPh[75] are immiscible but, as mentioned previously, PVPh is miscible (albeit only just so) with PBMA at ambient temperature[10]. The spectral differences between the PHMA and PBMA systems are dramatically illustrated if one compares *Figures 11* and *15*. *Figure 15* shows the *FT*i.r. spectra of blends containing 80:20, 50:50 and 20:80 weight ratios of STVPh[75]:PBMA together with those recorded for pure STVPh[75] and PBMA. Pure amorphous PBMA (*Figure 15E*) is characterized by a carbonyl stretching vibration at 1729 cm^{-1}. If there were appreciable mixing at the molecular level in the STVPh[75] PBMA blend system then we would observe an additional band at ~1703 cm^{-1}, attributable to hydrogen-bonded carbonyl groups. For a truly miscible 80:20 STVPh[75]:PBMA blend, ~55% of the carbonyl groups should be hydrogen bonded (equation (3)) and a prominent 1703 cm^{-1} band would be observed. Similarly, for miscible 50:50 and 20:80 STVPh[75]:PBMA blends ~39 and 19% of the carbonyl groups would be hydrogen bonded, respectively. *Table 4* shows the results of a quantitative analysis[7,10,33] of the carbonyl stretching region of the STVPh–PBMA blend spectra. Specifically, for the STVPh[75] PBMA blends described above, values of 52, 38 and 18% were determined, respectively.

Table 4 Curve resolving data for PBMA–STVPh blends

Blend (by wt)	'Free' C=O band			Hydrogen-bonded C=O band			Fraction of hydrogen-bonded C=O groups	
PBMA:STVPh[*x*]	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area	ν (cm^{-1})	$W_{1/2}$ (cm^{-1})	Area	Expt	Theory[a]
PBMA:STVPh[8]								
20:80	1728	20	3.82	1703	28	1.40	0.20	0.22
50:50	1728	20	11.9	1703	22	1.75	0.09	0.09
80:20	1728	21	19.1	1703[b]	22[b]	1.48	0.04	0.03
PBMA:STVPh[25]								
20:80	1729	20	1.94	1703	28	1.78	0.38	0.41
50:50	1729	20	15.0	1703	26	7.16	0.24	0.24
80:20	1729	21	10.3	1703[b]	22[b]	1.88	0.10	0.08
PBMA:STVPh[43]								
20:80	1729	19	1.08	1703	29	1.43	0.47	0.48
50:50	1729	20	14.0	1703	27	8.94	0.30	0.32
80:20	1729	21	8.41	1703	22	2.00	0.14	0.13
PBMA:STVPh[75]								
20:80	1729	19	0.87	1703	29	1.33	0.52	0.54
50:50	1729	19	6.92	1703	28	6.22	0.38	0.39
80:20	1729	20	9.53	1703	28	3.14	0.18	0.19

[a] From equation (3)
[b] Fixed parameters

These results are equivalent, within error, to those calculated. Accordingly, we can confidently conclude that this blend system is miscible. We do not show the corresponding spectra for the STVPh[43]–PBMA, STVPh[25]–PBMA and STVPh[8]–PBMA blends but they resemble the analogous PHMA blend spectra (*Figures 12–14*). As shown in *Table 4*, the quantitative experimental results are comparable, within error, to the theoretical calculations of the fraction of hydrogen-bonded carbonyl groups. This is consistent with miscibility in all these blends.

We have cautioned that the blend can only be expected to attain equilibrium above a temperature exceeding that of the component with the highest T_g in the system. Even in the case of a miscible blend the fraction of hydrogen-bonded carbonyl groups experimentally determined may depend upon thermal history. For example, a miscible 80:20 STVPh[75]:PBMA blend has a T_g of ~135°C (Fox equation). Accordingly, one would expect to observe the equilibrium fraction of hydrogen-bonded carbonyl groups at, say, 200°C (above T_g), but upon cooling to room temperature a non-equilibrium situation exists and the fraction of hydrogen-bonded carbonyl groups determined reflects that of the equilibrium value found close to T_g. Fortunately, as we know the three enthalpies of hydrogen bond formation (*Table 2*) we can easily calculate the theoretical fraction of hydrogen-bonded carbonyl groups at elevated temperatures by assuming that the van't Hoff relationship is obeyed[10]. *Figure 17* shows graphically the theoretical fraction of hydrogen-bonded carbonyl groups as a function of blend composition calculated at 25°C and at a temperature exceeding the T_g of the pure STVPh copolymers (equation (3)). The area bounded by these two curves is important as it sets the experimental limits. If the blend is in an equilibrium state at 25°C then the experimental fraction of hydrogen-bonded carbonyl groups should fall, within error, on the theoretical curve calculated at 25°C. However, if the T_g of the miscible blend exceeds room temperature then the experimental fraction of hydrogen-bonded carbonyl groups will fall in the range between the two curves. Thus we can be confident that the results displayed in *Figure 17* are consistent with miscible blend systems.

Dramatic changes in the hydroxyl stretching region of the spectra of the PBMA with STVPh[75] (*Figure 15*) and the other STVPh[43], STVPh[25] and STVPh[8] blends (not shown, but which resemble those of the analogous PHMA blends) indicate extensive molecular mixing and qualitatively support miscibility. For a truly miscible 20:80 STVPh[75]:PBMA blend the fraction of hydrogen-bonded hydroxyl–carbonyl, hydroxyl–hydroxyl interactions and 'free' hydroxyl groups should be ~0.76, 0.19 and 0.05, respectively. The spectrum shown in *Figure 15D* (top) is in excellent qualitative agreement with these theoretical calculations. A dominant band attributable to hydroxyl–carbonyl interactions is observed at ~3450 cm^{-1} together with a minor underlying contribution from the hydroxyl–hydroxyl band (≈ 3400 cm^{-1}) and a very small contribution from the 'free' hydroxyl band (3525 cm^{-1}). Corresponding theoretical fractions for miscible 50:50 and 80:20 STVPh[75]–PBMA blends are (0.39, 0.57 and 0.04) and (0.16, 0.81 and 0.03), respectively, which compare favourably with the relative increase in the contributions from the hydroxyl–hydroxyl and 'free' bands over that of the hydroxyl–carbonyl band as shown in *Figures 15C* and *B* (top). In any event, the spectra of the pure STVPh[75] (*Figure 15A*) and the 80:20, 50:50 and 20:80 STVPh[75]:PBMA blends (*Figures 15B, C* and *D*) are very different. This is in accord with a blend system that is miscible. A similar comparison of the results for the STVPh[43], STVPh[25] and STVPh[8] blends to the theoretical calculations leads to an identical conclusion.

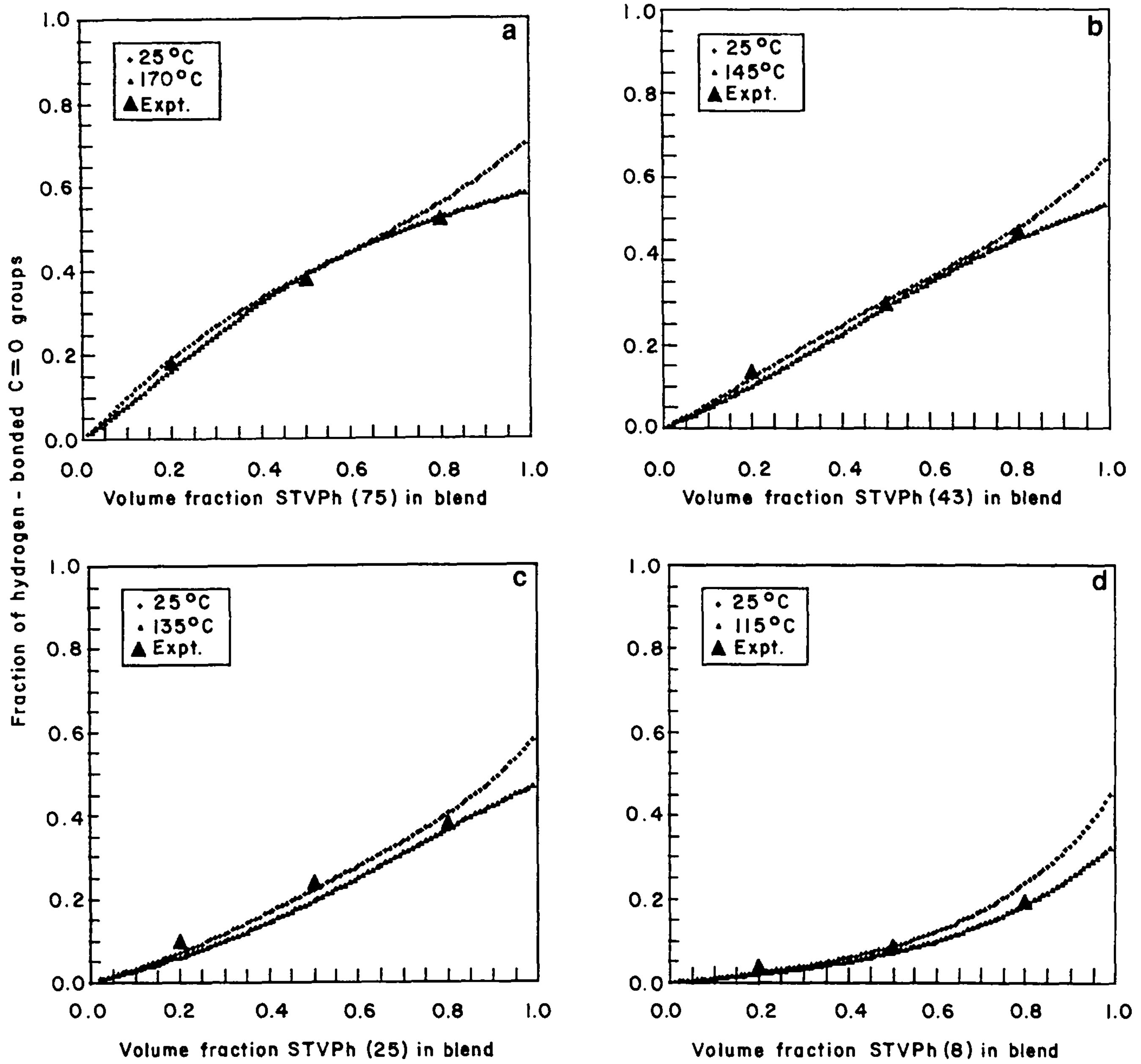


Figure 17 Comparison of the experimentally determined and theoretically calculated fraction of hydrogen-bonded carbonyl groups as a function of blend composition for miscible blends of PBMA with: (a) STVPh[75]; (b) STVPh[43]; (c) STVPh[25]; (d) STVPh[8] at 25°C and at a temperature just above the T_g of the pure STVPh copolymers

In summary, experimental *FT*i.r. studies of PBMA blends with PVPh and the STVPh copolymers containing 75, 43, 25 and 8 wt% VPh support systems that are miscible which is in accord with theoretical prediction (*Figures 5* and *6*).

PHMA and PBMA blends with STVPh[2]. With this blend system we are fast approaching the limit of reasonable experimental *FT*i.r. measurements. In fact, we failed to obtain meaningful spectra of STVPh[2]–PHMA or PBMA blends in the hydroxyl stretching region where it is necessary to examine PHMA- or PBMA-rich blends. The hydroxyl group concentration is very low, requiring large scale spectral expansion with the result that the spectra recorded were very noisy, of poor quality and fraught with complications arising from the PHMA or PBMA overtone band. We had more success in the carbonyl stretching region of the spectrum, however. Here only blends very rich in STVPh[2] (>90%) can be tested, since there are relatively few of the carbonyl groups that are hydrogen bonded, even in the best case of a truly miscible system (*Figure 8*). Accordingly, *Figure 16* shows the *FT*i.r. spectra of a blend containing 95:5 weight ratio of STVPh[2]:PHMA together with that recorded for pure PHMA. The corresponding PBMA blend spectra were essentially identical. If these blends were miscible ≈22% of the carbonyl groups should be hydrogen bonded (*Figure 8*) and the spectrum should resemble that of the 80:20 STVPh[8]:PHMA blend spectrum shown in *Figure 14B* (bottom). However, it does not. In fact, we do not detect any contribution from the 1710 (1703) cm^{-1} band in the 95:5 STVPh[2]:PHMA or STVPh[2]:PBMA spectra which strongly implies that these systems are immiscible.

In summary, experimental *FT*i.r. studies of STVPh[2]–PHMA and STVPh[2]–PBMA blends in the

Table 5 Glass transition temperature (T_g) of PHMA–STVPh blends

Blend (50:50 by wt)		T_g (°C)	
PHMA:PVPh	−50		180
PHMA:STVPh[75]	−48		168
PHMA:STVPh[43]		18	
PHMA:STVPh[25]		15	
PHMA:STVPh[08]		11	
PHMA:STVPh[02]	−50		107

carbonyl stretching region suggest that the system is immiscible which is again in concert with theoretical prediction (*Figures 5* 7).

Thermal analysis

As i.r. spectroscopy has not in the past been employed to determine the miscibility of polymer blends it was suggested by a reviewer that we include some corroborating glass transition data. *Table 5* shows the results of thermal analyses performed on the STVPh–PHMA blend system. Two T_gs at temperatures close to those of the pure components were observed for the PHMA blends with PVPh, STVPh[75] and STVPh[2]. Conversely, a single T_g close to that estimated from the Fox equation was observed for the corresponding blends with STVPh[43], STVPh[25] and STVPh[8]. These results are entirely consistent with the *FT*i.r. analysis described above.

CONCLUSIONS

'Miscibility windows' for PBMA and PHMA blends with STVPh copolymers extending from ~0 to 97% and 32 to 94% styrene, respectively, were predicted from theoretical calculations using an association model and parameters derived from previous studies of miscible PVPh–PAMA blends. Experimental *FT*i.r. studies of these blend systems were found to be in accord with these theoretical predictions supporting the general validity of the theory.

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