

Effect of Steric Restrictions on the Enhancement of Miscibility through Hydrogen Bonding in Blends of Modified Poly(α -methyl styrene) with Polymers Containing Acceptor Sites

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SYNOPSIS

Two series of copolymers have been prepared from α -methylstyrene and α -methylstyrene units modified by the incorporation of the hydrogen-bond donor units, methyl carbinol and trifluoromethyl carbinol, designated P α MS (I) and P α MS (II), respectively. It has been observed that if the concentration of the donor unit exceeds 4 mol %, one-phase blends can be prepared with a series of polymers containing hydrogen-bond acceptor sites such as poly(vinyl acetate), poly(vinyl pyrrolidone), poly(4-vinyl pyridine), and some poly(alkyl acrylate)s, none of which are miscible with the unmodified P α MS. All the one-phase blends formed are stable at temperatures above the glass transition temperature, T_g , of the blend, but eventually phase separate when the temperature is increased sufficiently. These lower critical cloud-point curves have been measured for a wide range of the blends and act as an indicator of the effectiveness of the hydrogen bonds in enhancing one-phase blend formation. The T_g 's of the blends are in many cases higher than those calculated from the simple rule of mixtures and reflect the reduction in chain mobility in the blends caused by extensive hydrogen bonding. The results demonstrate the effect that specific interactions have in enhancing miscibility in binary polymer blends. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In the search for new materials, the study of polymer blends has proved to be a popular approach because of the initially deceptive simplicity of mixing polymers with attractive properties in the hope that the mixtures produced may be equally good or better materials than are the individual components. The reality is more restrictive, as it has been found that the majority of commodity polymers do not mix to form one-phase systems. The reason for this becomes evident on inspection of the basic thermodynamics used to describe mixtures. To the first approximation, the fundamental requirement for the formation of a one-phase mixture is that the free

energy of mixing ΔG^M must be negative. This can be expressed as

$$\Delta G^M = \Delta H^M - T\Delta S^M \quad (1)$$

where ΔH^M is the enthalpy of mixing and ΔS^M is the entropy of mixing, both of which contribute to the overall value of ΔG^M . In small molecule mixtures, or polymer–small molecule mixtures, the main driving force favoring mixing comes from the ΔS^M term, which is positive, whereas mixing is usually opposed by the normally positive, unfavorable, ΔH^M component. On the basis of the Flory–Huggins lattice model for polymer mixtures, eq. (1) can be expanded and the entropy contribution is essentially combinatorial, given by

$$\Delta S^M = -RV \left\{ \frac{\phi_1 \ln \phi_1}{V_1} + \frac{\phi_2 \ln \phi_2}{V_2} \right\} \quad (2)$$

Here ϕ_i and V_i are the volume fraction and molar

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volume of the i th component, respectively, and V is the total volume of the system. The heat of mixing term is usually expressed through the dimensionless interaction parameter, χ_{ij} , by

$$\Delta H^M = \frac{RTV}{V_R} \chi_{ij} \phi_i \phi_j \quad (3)$$

where V_R is a reference segment volume, often approximated by selecting it to represent the volume of the smallest polymer repeat unit. The final expression for ΔG^M is then

$$\Delta G^M = \frac{RTV}{V_R} \left\{ \frac{\phi_1 \ln \phi_1}{r_1} + \frac{\phi_2 \ln \phi_2}{r_2} + \chi_{12} \phi_1 \phi_2 \right\} \quad (4)$$

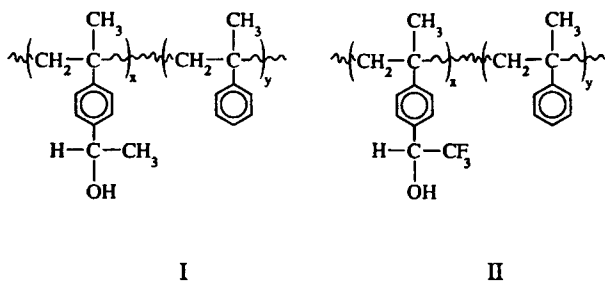
where the degree of polymerization r_i of component i is

$$r_i = (V_i/V_R) \quad (5)$$

Inspection of eq. (4) shows that when r is large the combinatorial entropy term becomes vanishingly small and miscibility is increasingly dependent on the nature of the ΔH^M contribution.

To encourage the formation of a one-phase system in polymer blends, it is necessary to ensure that favorable specific intermolecular interactions exist between the two components of the blend. Ideally, one polymer should have a donor site and the other an acceptor site on the chain. These may be present in the natural structure of the polymer, but if not, then the components may have to be modified chemically in one of a number of ways. The most commonly used interactions are of the general acid-base type, i.e., hydrogen-bonding,¹⁻³ ion-dipole,⁴⁻⁶ or charge-transfer⁷⁻⁹ interactions.

We have reported previously¹⁰ the synthesis of modified poly(α -methyl styrene) in which acidic hydrogen-bonding sites were incorporated in the phenyl rings. Two series of copolymers, poly[α -methylstyrene-*ran*-4-(2-hydroxyethyl) α -methylstyrene] structure **I** and poly[α -methylstyrene-*stat*-4-(1,1,1-trifluoro-2-hydroxyethyl) α -methylstyrene] structure **II**, were prepared:



It was observed that these copolymers form one-phase blends with a number of polymers having different base-acceptor sites. In this study, the glass transition temperatures and phase behavior of mixtures of these copolymers with poly(vinyl acetate), poly(alkyl acrylate)s, poly(4-vinyl pyridine), and poly(vinyl pyrrolidone) have been examined. The points of interest are (a) to assess the effect of the different strengths of acidic hydrogen-bonding sites on the blend behavior and (b) to determine whether the accessibility of the hydrogen-bonding sites may control the level of intermolecular interaction and, hence, the phase equilibria.

EXPERIMENTAL

Polymers and Copolymers

The syntheses of poly{ α -methylstyrene-*ran*-4-(2-hydroxyethyl) α -methylstyrene}, P α MS (**I**), and poly{ α -methylstyrene-*stat*-4-(1,1,1-trifluoro-2-hydroxyethyl) α -methylstyrene}, P α MS (**II**), copolymers, whose structures are shown above, have been described in detail elsewhere.¹⁰

The acceptor polymers used in this study were poly(vinyl acetate), $M_n = 90,000$; poly(4-vinyl pyridine), $M_n = 50,000$; and poly(vinyl pyrrolidone), $M_n = 40,000$, all purchased from Poly Science, and a series of poly(alkyl acrylate)s, synthesized as described elsewhere,¹¹ comprising the methyl ($M_n = 57,000$), ethyl ($M_n = 28,000$), *n*-propyl ($M_n = 29,000$), *n*-butyl ($M_n = 32,000$), and *t*-butyl ($M_n = 42,000$) derivatives.

Sample Characterization

A Knauer membrane osmometer was used to measure the number-average molecular weights M_n . The glass transition temperatures, T_g , were determined by differential scanning calorimetry, on a Perkin-Elmer DSC2. The T_g was taken to be the temperature of the onset of a base-line shift in the thermograms that were obtained, using a heating rate of 20 K min⁻¹.

Blends were prepared by first dissolving both polymers in a common solvent (e.g., toluene, tetrahydrofuran, dichloromethane), then spreading the solution on a Teflon sheet to form a film. The film blends were then dried thoroughly under vacuum before use.

The phase stability of the one-phase blends was estimated by measuring the lower cloud-point temperatures (LCPT). One-phase blends usually

Table I Characteristics of the Modified Poly(α -methyl styrene) Samples

P α MS (I) mol % OH group ^a	T_g /K	P α MS (II) mol % OH group	T_g /K	$10^5 \times M_n$
0	441	0	441	1.15
11	447	4	442	1.47
28	451	7	443	1.72
59	461	16	444	1.57
94	468	40	462	1.78
		53	466	1.63
		77	471	1.09
		100	472	1.24

^a All samples had an M_n of approximately 1.1×10^6 .

formed clear films, which were heated slowly on a hot stage; the temperature at which the films began to show opacity was taken to be the LCPT.

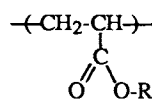
RESULTS AND DISCUSSION

Compositions and glass transition temperatures characterizing the two series of P α MS copolymers used to prepare the blends are shown in Table I. We demonstrated previously¹⁰ that the strength of the hydrogen bonds formed between the trifluoromethyl carbinol groups in the P α MS (II) and the acceptor polymers is relatively greater than those resulting from interactions between the methyl carbinol unit in P α MS (I) and the acceptor polymers, because the hydrogen on the hydroxyl group is more acidic in the former. This affects the ability of the modified P α MS copolymers to form one-phase blends with polymers that are not miscible with the P α MS homopolymer. As will be demonstrated here, it is usually necessary to have a greater concentration of the methyl carbinol units in the copolymer to produce comparable levels of miscibility with the acceptor polymers than of the trifluoromethyl carbinol unit, as judged by the phase stability of the one-phase blends.

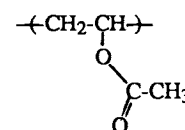
It has been shown^{10,11} that the formation of one-phase blends, when modified P α MS samples are mixed with polymers incorporating suitable groups, is a result of specific intermolecular hydrogen bonding. It must be remembered that the average length of a hydrogen bond is 240–290 pm, and so the accessibility of the acceptor group to the donor moiety can also influence the number of bonds that can form and their stability to subsequent molecular motion within the blend. The importance of this factor can be gauged by examining the blending characteristics of polymers with acceptor groups

spaced at different distances from the main chain or shielded by a bulky side group.

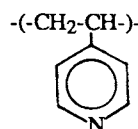
In this study, we have used four different types of acceptor polymer:



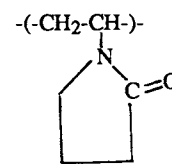
III



IV



V



VI

the poly(alkyl acrylate)s III, poly(vinyl acetate) IV, poly(vinyl pyridine) V, and poly(vinyl pyrrolidone) VI. These have either nitrogen or a carbonyl unit as the main acceptor site, and blends of these with the modified P α MS (I) and P α MS (II) donors were found to be mainly one-phase when the concentration of the modified donor units in the P α MS copolymers exceeded 4 mol %.

Glass Transition Temperatures

Glass transition temperatures for the one-phase blends were measured for a range of blend compositions. Typical examples of the observed trends of T_g with blend composition are shown in Figures 1 and 2, and as all the one-phase blends behaved in a similar fashion, they will not be reported in detail.

In Figure 1, the data for blends of poly(methyl acrylate) with P α MS (I) and P α MS (II) are shown,

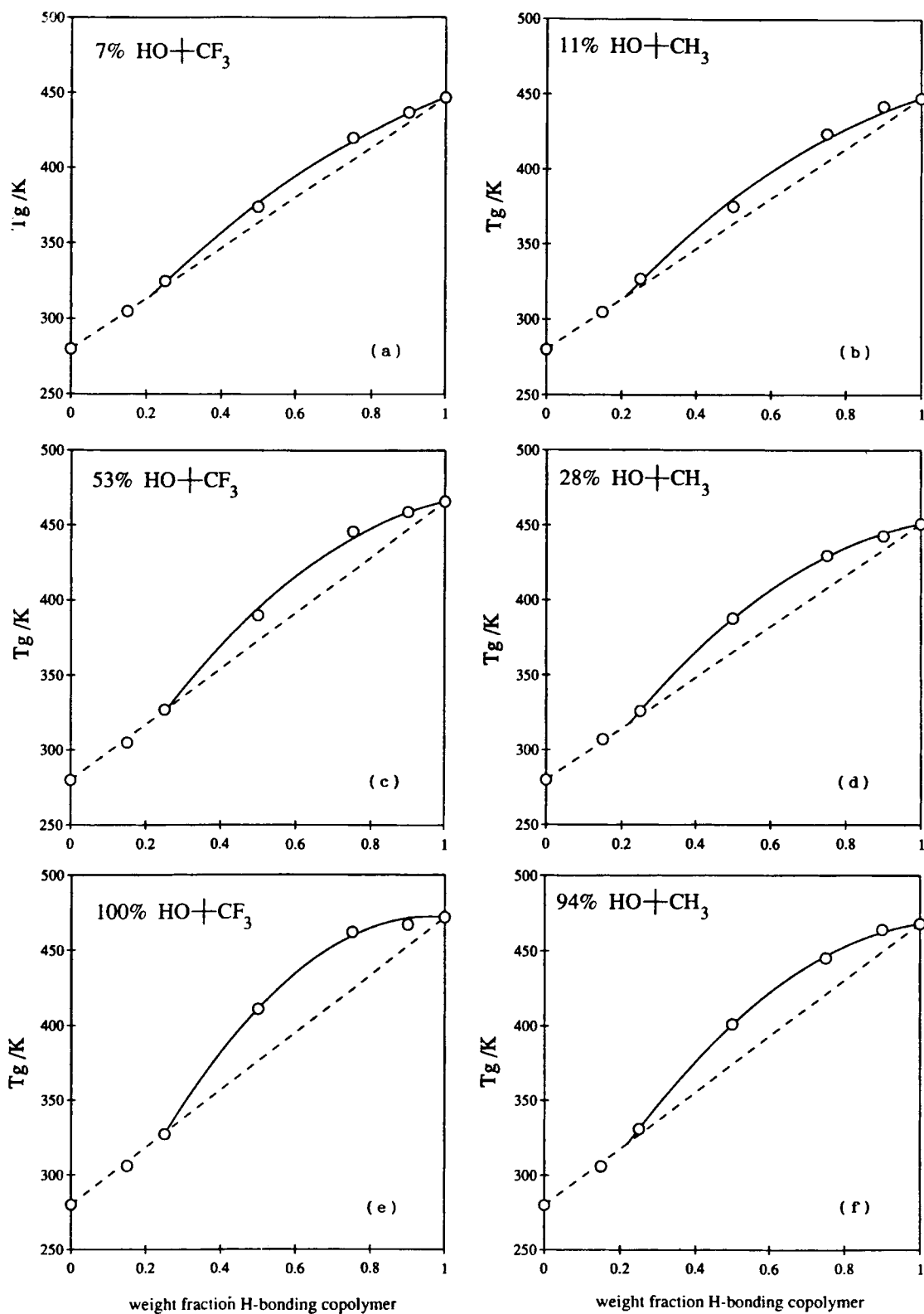


Figure 1 The dependence of T_g on the composition of the blend for poly(methyl acrylate) blended with P α MS (I) right-hand column and P α MS (II) left-hand column. The mol % of the modified unit in the P α MS copolymers is shown in each diagram. The P α MS copolymers are referred to as the H-bonding copolymer in the diagrams.

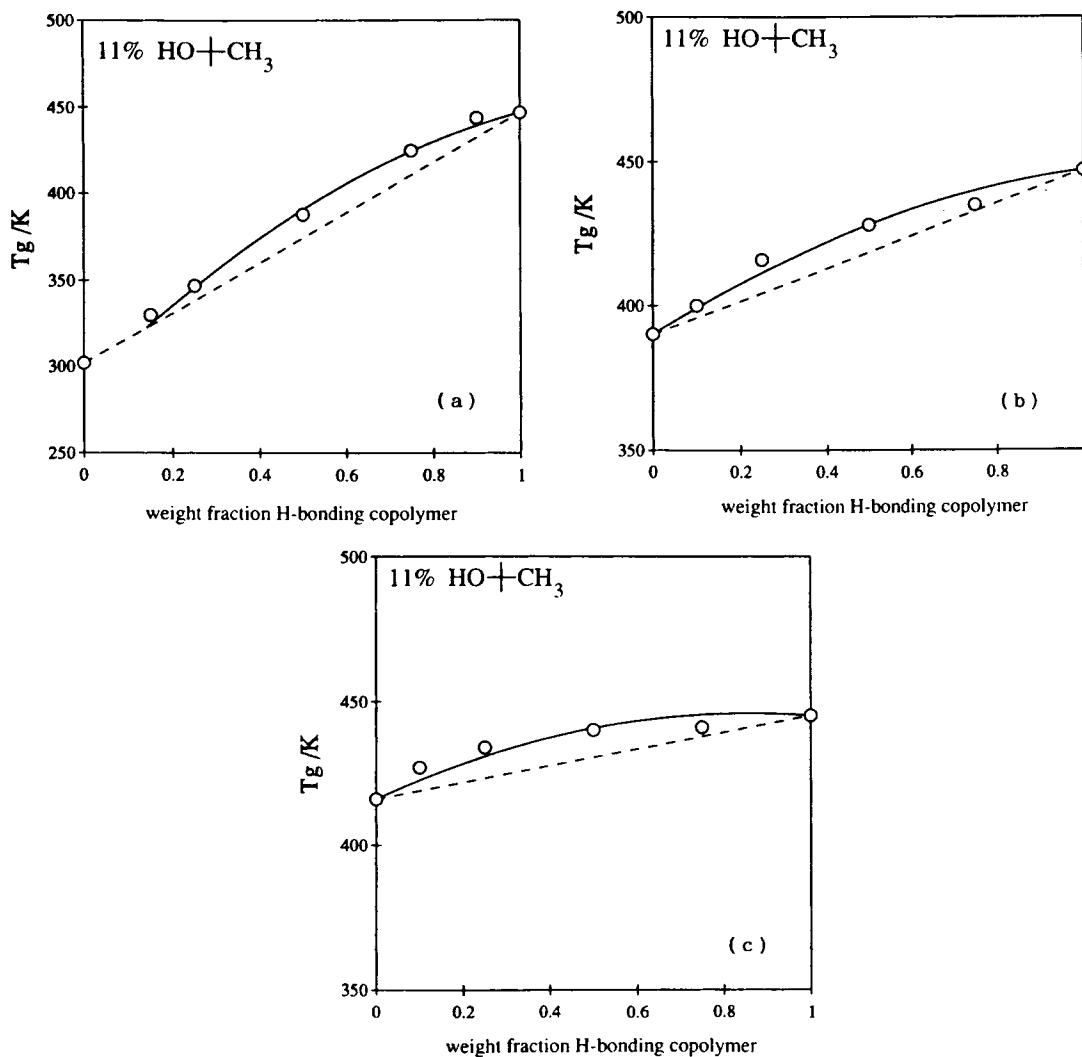


Figure 2 Variation of T_g with blend composition for blends of P α MS (I), 11 mol %, with (a) poly(vinyl acetate), (b) poly(vinyl pyrrolidone), and (c) poly(vinyl pyridine).

in which the mol % of the modified unit in the P α MS samples is varied in both concentration and bonding strength. In the blends where the weight fraction of the P α MS component is less than 0.25, the T_g follows the simple rule of mixtures, viz.

$$T_g = w_A T_g^A + w_B T_g^B \quad (6)$$

where T_g , T_g^A , and T_g^B are the glass transition temperatures of the blend and the individual homopolymers A and B, and w_i are the weight fractions of the blend components. As the amount of P α MS increases, positive deviations in T_g are observed where the values are now much higher than predicted by eq. (6). These higher T_g values reflect a decrease in chain mobility and free volume and are caused by the increasing hydrogen bonding between compo-

nent chains, which will act as cross-links in the blend. There is probably also a contribution from some intramolecular hydrogen bonding at high concentrations of the P α MS copolymers, which will tend to self-associate to some extent. This behavior has been reported in other blends where specific intermolecular interactions are known to exist^{9,12-14} and again is seen in the blends of the modified P α MS with the other acceptor polymers studied here (Fig. 2). Minor differences are observed in that the blends involving polymers containing a nitrogen acceptor, poly(vinyl pyridine) and poly(vinyl pyrrolidone), show a higher T_g than predicted by eq. (6) over the complete composition range, whereas the blends with poly(alkyl acrylate)s and poly(vinyl acetate) only deviate at higher concentrations of the modified P α MS.

The positive deviations in T_g can be described by using the Kwei equation¹⁵:

$$T_g = \frac{w_A T_g^A + k w_B T_g^B}{w_A + k w_B} + q w_A w_B \quad (7)$$

where k and q are adjustable parameters. The solid lines in Figures 1 and 2 were calculated using $k = 1$ and allowing q to vary, but for poly(methyl acrylate) and poly(vinyl acetate), the data can only be fitted over part of the composition range and not where eq. (6) is adequate.

This asymmetric behavior for the latter group may reflect the efficiency of hydrogen-bond formation at low donor concentrations. Thus, the nitrogen-containing polymers seem capable of generating strongly hydrogen-bonded structures over the complete blend composition range. This is a consequence of either the easier accessibility of the acceptor sites or that nitrogen is a better acceptor than is oxygen. Steric restrictions in the formation of hydrogen bonds play an important part in determining miscibility in these blends as the hydrogen bond can form only if the donor and acceptor groups are the appropriate distances from each other. These effects are more clearly seen if the phase equilibria in the blends are examined.

Lower Cloud-point Curves

All the one-phase blends studied were observed to phase separate on raising the temperature some distance above the temperature of the glass transition. The temperature at which the cloud point was detected varied with the strength and number of hydrogen-bonding interactions that formed and helped to stabilize the system. Typical examples of the LCP curves, for blends of P α MS (**I**) with each of the acceptor polymers, are shown in Figure 3, where the phase-separation temperatures for a range of blend compositions are plotted. These illustrate two points: An increase in the mol % of the methyl carbinol unit in P α MS (**I**) is accompanied by an increase in the temperature at which phase separation occurs. This reflects the larger proportion of hydrogen bonds formed in the blends with increasing concentrations of the donor groups, which will stabilize the one-phase system to higher temperatures before thermal agitation eventually ruptures a sufficient number to lead to phase separation. Second, a comparison of the relative phase-separation temperatures reveals differences in behavior among the blends with different acceptor polymers. Using the blends with P α MS (**I**) containing 11 mol % of the

modified unit as the reference, the relative order of increasing phase-separation temperatures is poly(methyl acrylate) **III**, < poly(vinyl acetate) **IV**, < poly(vinyl pyridine) **V**, \leq poly(vinyl pyrrolidone) **VI**. This order can be rationalized in terms of the relative ease of approach of the donor group to the acceptor. The carbonyl groups and the nitrogen atoms can be considered as the primary acceptor sites, and in the case of the former, this is situated adjacent to the main chain in **III**, whereas there is a two bond spacing away from the main chain in **IV** and **VI**.

Consequently, the steric restrictions to the approach of the donor groups are less in **IV** and **VI** than in **III**, so fewer H bonds may be able to form in the latter. For structure **V**, even though the phenyl ring is a bulky unit, the nitrogen in the 4-position of the phenyl ring will be easily accessible and so the number of interactions should be correspondingly larger. The observation that the phase behavior of **V** and **VI** is similar must be a consequence of the presence of two strong acceptor sites in **VI**, which, though less accessible than the pyridyl nitrogen, increases the probability of hydrogen bonds being able to form.

The effect of steric restrictions on the contributions of the total hydrogen-bonding strengths to the phase stability of the blends can also be demonstrated by examining the overall contribution to the heat of mixing of the blend ΔH_B . If it is assumed that this comprises the sum of the dispersive force, ΔH_D , and specific interaction, ΔH_{SI} , energies, then $\Delta H_B = \Delta H_D + \Delta H_{SI}$, and for the blend to be one-phase, ΔH_B should be negative. As ΔH_D is normally positive, the miscibility behavior will depend on the magnitude of ΔH_{SI} (neglecting any residual entropic contributions), and this will have to be sufficiently large and negative if a one-phase blend is to be formed.

An estimate of ΔH_D can be made from the solubility parameters δ_i of the polymer components, as it will be proportional to the difference between them. The values of δ_i can be estimated from group contribution methods,¹⁶ and in units of $(\text{J cm}^{-3})^{1/2}$, these are for P α MS (**I**): 11 mol %, $\delta = 18.5$; for **III**: $\delta = 19.6$; for **IV**: $\delta = 19.6$; for **V**: $\delta = 20.2$; and for **VI**: $\delta = 20.9$. Thus, the order of magnitude for the ΔH_{SI} term even to just counterbalance ΔH_D increases as **III** = **IV** < **V** < **VI**, if there are no other effects altering the ability of the polymers to form one-phase blends. Thus, for polymer pairs, with an equivalent number of hydrogen-bonding sites, more bonds have to form if **VI** is to be miscible with P α MS and produce one-phase blends than if **III** is used as the blend component. This would be true if all the

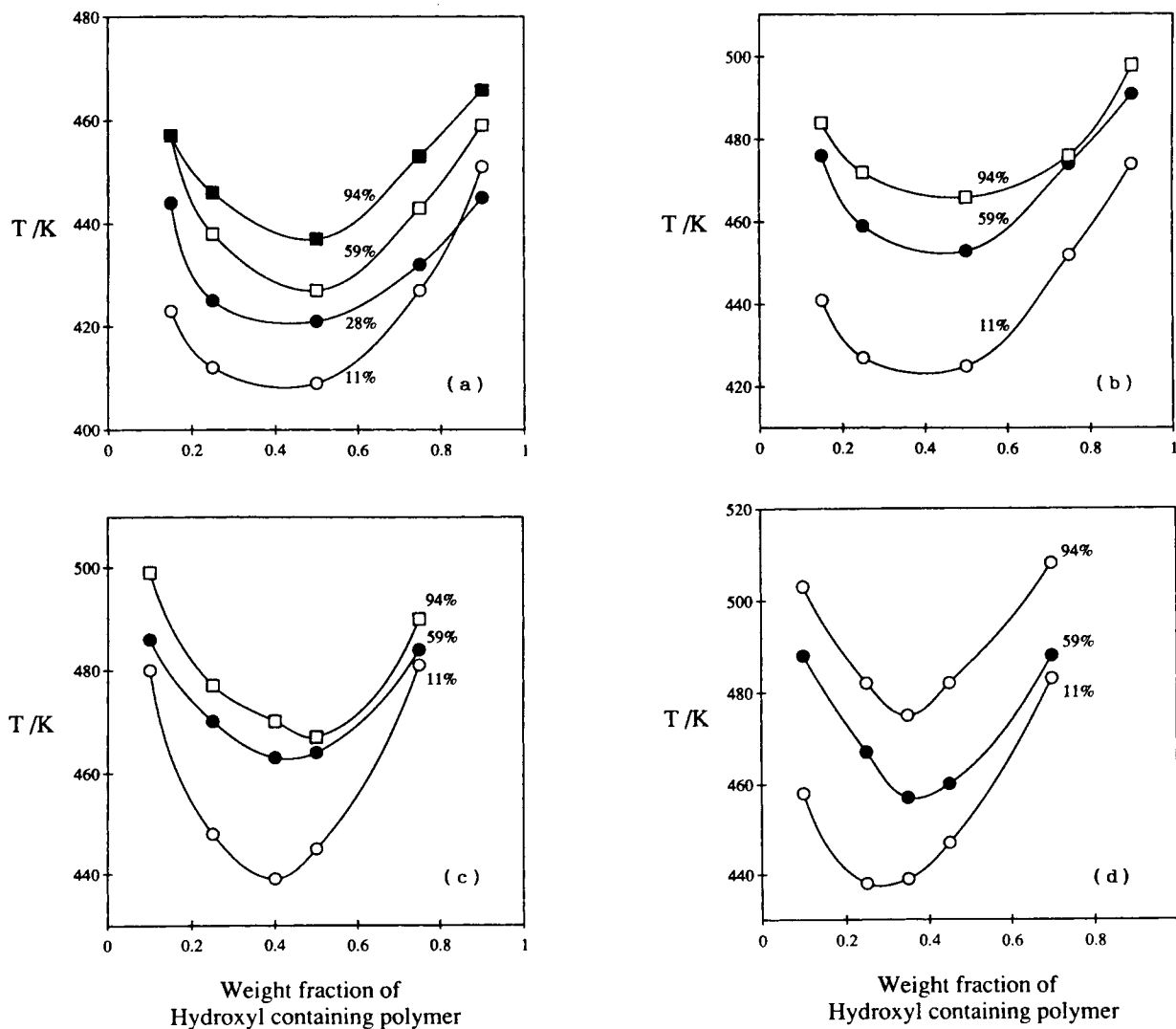


Figure 3 Lower cloud-point curves for blends of P α MS (I), containing the mol % of the hydrogen-bond donor group as shown on the diagram, and (a) poly(methyl acrylate), (b) poly(vinyl acetate), (c) poly(vinyl pyrrolidone), and (d) poly(vinyl pyridine). Lines mark the boundaries between a one-phase blend at lower temperatures and a two-phase blend at temperatures above the boundary.

hydrogen bonds formed with equal ease in each of the blends, but the LCP temperatures have a relative order of increasing phase stability of **III** < **IV** < **V** < **VI**, so some other effect must be superimposed on the simple ability to form a hydrogen bond. The steric effects discussed above would certainly account for this and clearly must be a powerful influence in determining the proportion of hydrogen-bond formation in the blend and, hence, the total contribution to ΔH_{St} .

The influence of steric restrictions on the number of hydrogen bonds formed is also seen in the phase behavior of a series of poly(alkyl acrylate)s blended

with P α MS (**II**) as illustrated in Figure 4. It was found that one-phase blends were obtained with the methyl, ethyl, and *t*-butyl derivatives but that the *n*-propyl and *n*-butyl derivatives gave two-phase blends. Focusing on the cloud-point curves for the blends with P α MS (**II**) (7 mol %), the order of increasing phase-separation temperature is *t*-butyl < ethyl < methyl. This mirrors the decreasing steric restrictions caused by the length and bulk of the side chain that shields the carbonyl unit. The *n*-propyl and *n*-butyl chains are longer and prevent the donor group from coming close enough for the hydrogen bonds to have the opportunity to form in

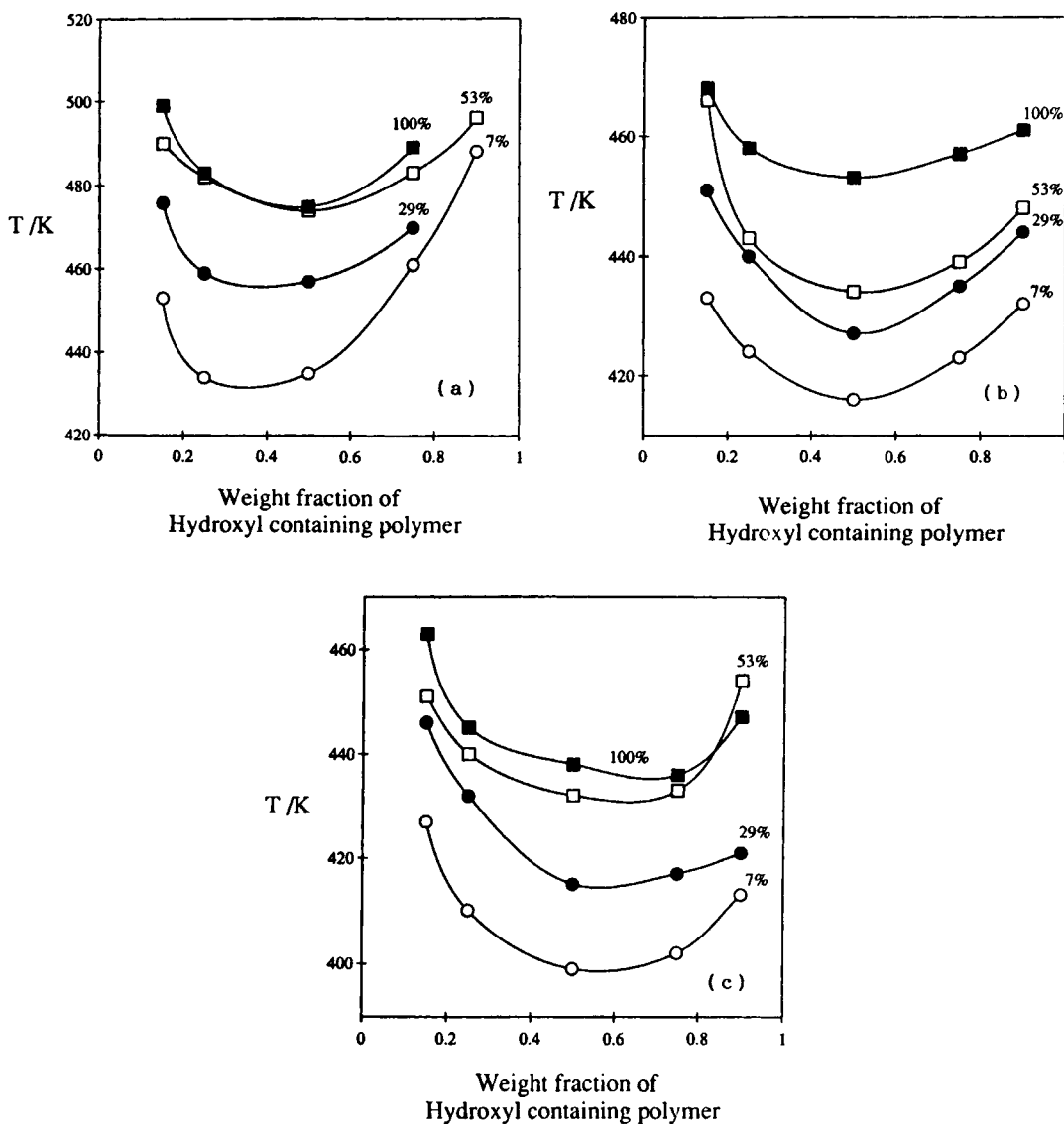


Figure 4 Lower cloud-point curves for blends of P α MS (II) (copolymer compositions with respect to the hydrogen-bond donor group are shown in each diagram) and (a) poly(methyl acrylate), (b) poly(ethyl acrylate), and (c) poly(*t*-butyl acrylate).

sufficient numbers, if at all, and create a one-phase blend. Although the *t*-butyl group is bulky, it is only as long as an ethyl unit, in any direction, and so the secondary bonding can form in blends incorporating poly(*t*-butyl acrylate) but not poly(*n*-butyl acrylate).

One further point of comparison between the data plotted in Figures 3(a) and 4(a), for blends of PMA with P α MS (I) and P α MS (II) respectively, shows that phase separation for blends with P α MS (II), 7 mol %, occurs at higher temperatures than for those with P α MS (I), 11 mol %. This demonstrates that the strength of the hydrogen bonds formed with P α MS (II) are greater than with P α MS (I), and

so a lower concentration of the trifluorocarinol will be required to produce a one-phase blend than if the methyl carbinol is used.

CONCLUSIONS

It has been shown that by modifying poly(α -methyl styrene) chemically, such that a hydrogen-bond donor group is incorporated into the chain, stable one-phase blends can be formed with polymers containing an acceptor site. It has also been shown that, because a hydrogen bond can form only when the correct spacing between donor and acceptor sites is

achieved, steric restrictions can alter the effectiveness of this method for creating one-phase blends from inherently immiscible binary polymer mixtures. Finally, it has been shown that the strength of the hydrogen bond will be important in determining how extensive the polymer modification needs to be. Thus, strong H-bonding sites will be more effective at low concentrations in forming one-phase blends than will the weaker moieties.

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Received April 17, 1992

Accepted April 22, 1992