Enhancement of miscibility in blends of poly(vinyl methyl ether) and poly(α-methylstyrene)s modified by incorporation of hydrogen-bonding sites

J. M. G. Cowie* and A. A. N. Reilly
Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, UK
(Received 13 December 1991; revised 2 March 1992; accepted 25 March 1992)

Poly(α-methylstyrene) and poly(vinyl methyl ether) do not form one-phase blends when mixed together. This situation can be changed if the poly(α-methylstyrene) is modified by introducing hydrogen-bond donor groups into the phenyl ring. Two groups of differing donor strength, methylcarbinol and trifluoromethylcarbinol, were selected, and modified poly(α-methylstyrene) samples, with varying degrees of substitution of these groups, were prepared. If the amount of the modifying group incorporated exceeded 4 mol% then one-phase blends of these copolymers with poly(vinyl methyl ether) could be prepared. The effect of the number and strength of these hydrogen-bonding sites on the phase stability of the blends was measured by locating the lower critical phase separation temperature in each blend. The glass transitions of the blends were found to be normally higher than those predicted from a simple rule of mixtures and reflect the extent of hydrogen-bond formation in the blends. This behaviour could, in part, be described by the Kwei equation.

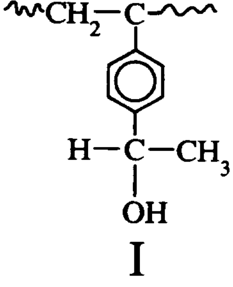
(Keywords: miscibility; hydrogen-bonded blends; poly(α-methylstyrene); poly(vinyl methyl ether); lower critical phase boundaries; blend glass transitions)

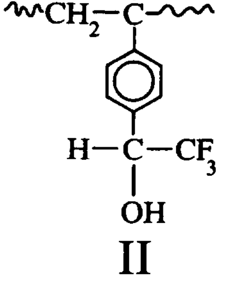
INTRODUCTION

The likelihood that one-phase binary polymer blends can be prepared is greatly enhanced if the components in the blend can interact with one another, through the formation of secondary intermolecular bonding forces, such as hydrogen bonds, cation–anion interactions or charge-transfer complexation. This is a necessary prerequisite in the majority of polymer mixtures, where one must rely on a favourable enthalpy of mixing contribution to produce the negative free energy of mixing required to achieve a one-phase system, because the normally favourable entropy of mixing term is vanishingly small in mixtures of high-molecular-weight polymer chains. In many cases, suitable donor–acceptor groups are not present in the structure of the component polymers, and the practice of modifying one or both components has been adopted by several workers[1–3].

For totally immiscible polymer pairs, the secondary interactions that have to be introduced to produce one-phase mixtures may have to be either quite powerful or alternatively numerous, or both, and for this reason the incorporation of hydrogen-bonding sites has proved popular. Pearce *et al.*[1,4–7] have been prominent in using this approach, and have modified polystyrene and polyethylene by introducing the hexafluorodimethylcarbinol group, which is one of the stronger H-bonding units. This has allowed them to prepare one-phase blends of the modified structures with a wide range of polymers having an acceptor site as a component part of the chain.

Very little work has appeared in which poly(α-methylstyrene) is used as a component in polymer blending. This polymer has the attraction that its glass transition temperature T_g ($\sim$441 K) is considerably higher than that of polystyrene, and consequently it could be a useful component when high-T_g blends are of interest. Our previous work[8,9] has shown that, despite the similarities in structure, polystyrene only forms miscible blends with poly(α-methylstyrene), over the complete composition range, when the sample molecular weights are less than 80 000. It has also been observed that, unlike polystyrene, attempts to form one-phase blends of poly(α-methystyrene) (PαMS) and poly(vinyl methyl ether) (PVME) have proved unsuccessful. This, then, is an interesting system to use to initiate work on modified poly(α-methylstyrene), and it was decided to incorporate in the polymer two types of H-bonding site that differed in strength and whose structures are shown as PαMS I and PαMS II:


I


II

---

*To whom correspondence should be addressed

0032-3861/92/224814-07

This allows one to study the effect of both the H-bond strength and their number on the miscibility, by using a range of copolymers containing variable quantities of the structures shown. Both of these groups are weaker hydrogen-bonding units than the hexafluorodimethylcarbinol group, as will be demonstrated, but they have the advantage that they are cheaper to prepare and are sufficiently effective for the purpose of forming a range of one-phase blends.

EXPERIMENTAL

Synthesis of p-trifluoroacetyl-α-methylstyrene

The solvent for the reaction, tetrahydrofuran (THF), was dried using a two-stage process. First, it was refluxed over calcium hydride overnight, then distilled; lithium aluminium hydride was added to the distillate in aliquots until it reached a concentration of 8 g dm^{-3} THF. It was then redistilled from this mixture prior to use.

A chloroform solution of 4-chloro-α-methylstyrene was dried using an alumina column and the $CHCl_3$ was later removed by rotary evaporation. The dry monomer was finally distilled under reduced pressure, then stabilized with a small amount of 3,5-t-butylcatechol.

Anhydrous THF (25 cm^3) was added to magnesium turnings (9.2 g) in a clean dry flask and ethyl bromide (3 cm^3) was added slowly dropwise. A solution of 4-chloro-α-methylstyrene in THF (30.5 g/100 cm^3) was introduced slowly into the nitrogen-purged system, producing a green coloration indicative of the formation of the Grignard reagents. The solution was refluxed for a further 30 min, after which a THF solution of trifluoroacetic acid (8 g/60 cm^3) was added dropwise. The initial rate of addition had to be very slow as the reaction is highly exothermic. The resulting yellow solution was refluxed for 30 min, cooled, then poured into a mixture of ice and concentrated hydrochloric acid. The organic layer was extracted with diethyl ether, which was subsequently removed, leaving a viscous yellow oil. The required product was isolated by distillation under reduced pressure (10 mmHg); boiling range 379–381 K; yield 37%. The structure was confirmed by i.r. and n.m.r. spectroscopy.

*Synthesis of poly{α-methylstyrene-*stat*-[4-(1,1,1-trifluoro-2-hydroxyethyl)-α-methylstyrene]}*

Copolymers of α-methylstyrene and 4-trifluoroacetyl-α-methylstyrene were prepared by conventional cationic techniques. Conversions were kept as low as possible to avoid composition drift. A graph of the copolymer composition (F_1) against the composition of the feed (f_1) is shown in *Figure 1*, and the corresponding reactivity ratios are r_1(trifluoroacetyl-α-methylstyrene) = 0.85, r_2(α-methylstyrene) = 1.63.

The required polymer was obtained by subsequent reduction of the carbonyl group in the trifluoroacetyl unit using lithium aluminium hydride. Copolymer compositions were estimated in two ways: the hydroxyl proton signals in ^{1}H n.m.r. spectra were used to determine the comonomer concentration, or infra-red measurements were used. In the latter, the ratio of the carbonyl absorption of the trifluoroacetyl group (1720 cm^{-1}) to that of the aromatic C–H stretch (1605 cm^{-1}) in the copolymer was used, with the ratio of the two comparable peak areas in the poly(trifluoroacetyl-α-methylstyrene) homopolymer spectrum as the standard. Both methods were in good agreement.

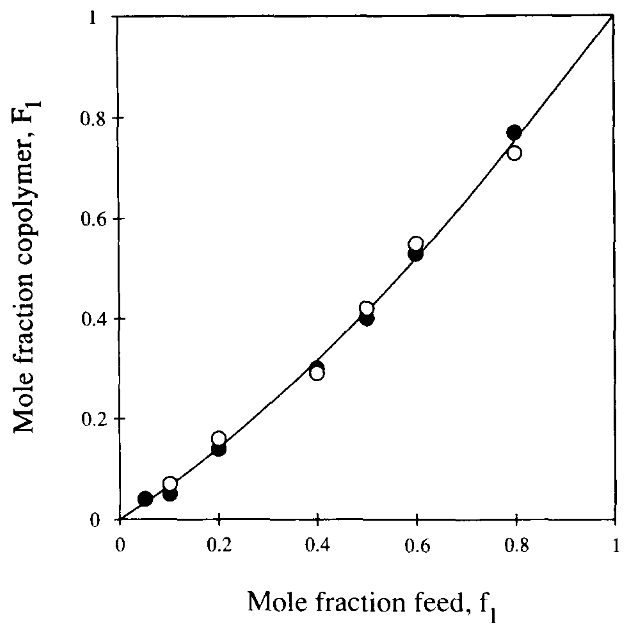


Figure 1 Copolymer composition, expressed as F_1, the mole fraction of the modified monomer in the poly(α-methylstyrene) copolymer, plotted against the mole fraction of the trifluoroacetyl-α-methylstyrene in the feed, f_1

*Synthesis of poly[α-methylstyrene-*ran*-4-(2-hydroxyethyl)-α-methylstyrene]*

The preparation of the monomer of 4-acetyl-α-methylstyrene proved difficult, so the easier and more direct polymer analogous reaction route was employed. Acetylation of poly(α-methylstyrene), Polysciences standard M_n = 115 000, was carried out following the method of Kenyon and Waugh[10]. A solution of the polymer in carbon disulphide (1.3 g/15 cm^3) was added slowly to a mixture of aluminium trichloride (2.6 g) and acetyl chloride (1.2 g) in CS_2 (15 cm^3). Differing degrees of acetylation were obtained by refluxing the solution for different lengths of time. Thus 3–43 min gave degrees of acetylation ranging from 11% to 94%. The copolymers were isolated by pouring the reaction mixture onto ice and concentrated HCl. The precipitate was dissolved in acetone, reprecipitated in methanol and dried under vacuum. The molecular weights of the copolymer were the same as those of the parent material, within experimental error, indicating that no significant degradation had occurred. Compositions were analysed as described above on the unreduced copolymer, and the final product was again obtained by reduction of the acetyl group using $LiAlH_4$.

Other blend components

The sample of poly(vinyl methyl ether) (PVME) used was a commercial sample that was purified by reprecipitation, then fractionated to remove the higher- and lower-molecular-weight components. The middle fraction, M_n = 44 000, was used in all the blends.

Table 1 Characteristics of the modified poly(α-methylstyrene) samples

PαMS I (mol% OH group)[a]	T_g (K)	PαMS II (mol% OH group)	T_g (K)	$10^5 M_n$
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 1.1×10^5

Table 2 Frequency shifts measured by *FT*-i.r. for the bonded OH absorption in the copolymer and in the copolymer/PVME blends

H-bonding group	Bonded OH copolymer (cm^{-1})	Bonded OH blend (cm^{-1})	$\Delta\nu$ (cm^{-1})
I	3457	3442	15
II	3441	3316	54
III	3440	3316	124
IV	3513	3200	313

Sample characterization

Number-average molecular weights (M_n) were measured using a Knauer membrane osmometer. Glass transition temperatures (T_g) were determined by differential scanning calorimetry with a Perkin–Elmer DSC 2. The heating rate was 20 K min^{-1}, and T_g was taken as the point at which the baseline shift first occurred, characteristic of the transition. Lower critical cloud-point temperatures were measured by heating clear films of the blends slowly on a hot-stage microscope and observing the temperature at which the films began to turn opaque.

Blend preparation

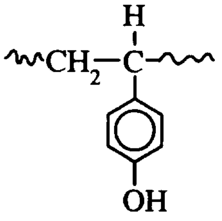
Blends were prepared by dissolution of the polymers in a common solvent (toluene, THF), followed by film casting on a Teflon sheet. The films were rigorously dried in a vacuum oven before use.

Some of the sample characteristics are shown in *Table 1*.

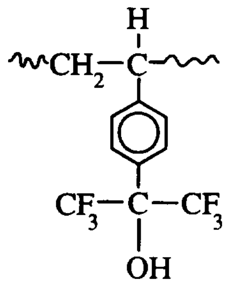
RESULTS AND DISCUSSION

Relative strength of H-bonding groups

It is possible to obtain an estimate of the relative strengths of different H-bonding sites, introduced into a polymeric structure, using *FT*-i.r. spectroscopy. This can be achieved by measuring the frequency shifts in the absorption band most sensitive to H-bonding, which in these systems is the O–H stretch frequency around the 3500 cm^{-1} region. Coleman *et al.*[11] have pointed out that it is possible to distinguish three absorption bands in this area corresponding to the 'free' OH, the 'self-associated' OH and the 'intermolecularly hydrogen-bonded' OH. In another context we have examined blends of PVME with several modified polystyrene samples; details will be published elsewhere[12] but are summarized here to put the present work in context. The polystyrenes were modified in four different ways: two had the analogous structures to PαMS I and PαMS II, while the other two, shown here as III and IV, were copolymers of styrene with vinylphenol, and with the hexafluorodimethylcarbinol-modified styrene, respectively:



III



IV

Each polystyrene contained only about 2.0–2.7 mol% of the modified unit, to make measurements comparable. The absorption peak identified as that for the self-association of the OH group[1] in the copolymer was used as a reference, and the frequency shifts that result when these samples are blended with PVME are shown in *Table 2*. The magnitudes of these range from a relatively weak response for structure I up to moderately strong for structure IV.

Kwei *et al.*[13] have made quantitative estimates of the strengths of the hydrogen bonding in structure IV polystyrenes with other acceptor molecules, and have proposed that the infra-red frequency shift ($\Delta\nu$) is related to the strength of the H-bond formed in the system. Values of $\Delta\nu$ derived from the spectra are also used here as a guide to H-bonding strength and are listed in *Table 2*. This indicates that in order of increasing H-bond strength the groups are I < II < III < IV. The two PαMS modifications of interest are then at the weaker end, but PαMS II is measurably stronger than PαMS I.

Blend behaviour

One of the most widely studied polymer blends is the binary combination of polystyrene and PVME. Blend miscibility is, however, solvent-dependent, and one-phase blends are obtained when aromatic solvents are used but these are two-phase when films are cast from some chloroalkanes. Blends of PαMS and PVME were prepared from a number of solvents, but only two-phase blends were obtained, irrespective of the method used. Obviously, whatever weak favourable interactions exist that enable one-phase blends of PS and PVME to form, they are overcome by unfavourable interactions when PαMS replaces PS in the blend.

The situation can be changed by introducing hydrogen-bonding sites into the PαMS chain and, as long as the modified units in both PαMS I and PαMS II exceed ~4 mol%, one-phase blends can be prepared, as indicated by the presence of only one T_g for the blend.

Cloud-point curves

Phase separation was observed to occur on heating the blend films, which were clear at room temperature but became opaque at various temperatures above 380 K. The relative effectiveness of the H-bond modification can then be judged on the basis of the thermal stability of the different blends, if it is assumed that the phase separation is caused by the thermal disruption of the

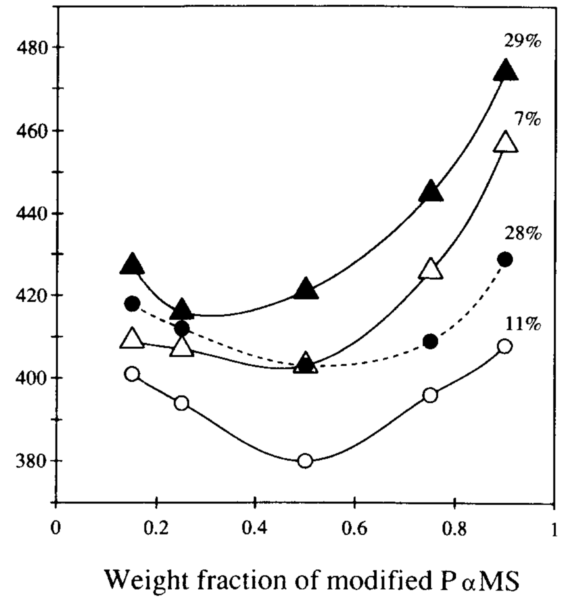


Figure 2 Lower cloud-point curves for blends of PVME with PαMS I: (○) 11 mol% modified units, (●) 28 mol% modified units. Also, PαMS II: (△) 7 mol% modified units, (▲) 29 mol% modified units

hydrogen-bonded structure that is responsible for ensuring a one-phase system. Thus comparison of the lower critical cloud-point (*LCCP*) curve for each blend should be a reflection of the relative effectiveness of the H-bonding in maintaining one-phase systems.

A selection of these cloud-point curves are shown in *Figure 2*, where a comparison can be made between blends of PVME with (a) modified PαMS I containing 11 and 28 mol% H-bonding groups, and (b) PαMS II containing 7 and 29 mol% modified units. The temperatures of the *LCCP* curves, for samples with comparable amounts of the H-bonding groups, are always lower for the weaker PαMS I. This is consistent with the assumption that higher temperatures are needed before thermal agitation of the chains is sufficiently energetic to disrupt the stronger H-bonding in PαMS II blends. The weaker H-bonding sites in PαMS I cannot sustain one-phase behaviour up to higher temperatures unless the concentration of bonding sites is increased. This is also shown in *Figure 2*, where blends of PVME and PαMS I containing 28 mol% of the methylcarbinol group now phase separate in the same temperature region as blends of PαMS II with 7 mol% of the trifluoromethylcarbinol unit. This rise in the temperatures of the *LCCP* curves is observed for an increase in concentration of both types of H-bonding site (see *Figures 3a* and *3b*) and indicates that there is a cooperative effect that strengthens the interactions between the blend components and helps to stabilize the mixtures.

Glass transition temperatures

The glass transition temperatures T_g, measured as a function of the blend composition, are shown in *Figures 4* and *5*. The observed trends in T_g are quite distinctive and require comment. In all cases there is a range of blend composition in which the T_g values recorded for each blend are higher than those expected from the simple rule of mixtures for two homopolymers A and B, which can be expressed as:

$$T_g = w_A T_g^A + w_B T_g^B \qquad (1)$$

where T_g, T_g^A and T_g^B are the glass transition temperatures of the blend, component A and component B, and w_A and w_B are the respective weight fractions of these homopolymers.

The conditions described by equation (1) are only met for blends in which the weight fraction of the modified PαMS is less than 0.4. Above this value the blend T_g values exceed those predicted by equation (1) and a downward concave, curved, dependence is recorded for H-bond-rich systems. Several other examples of this downward concavity of T_g–composition curves have been reported for blends in which specific intermolecular interactions have been found to exist. While the values of T_g recorded for some blends rich in the PαMS component are close to the cloud-point temperatures, there is no apparent interference and a narrow one-phase region does exist above T_g in all cases.

Rodriguez-Parada and Percec[14] observed that, in

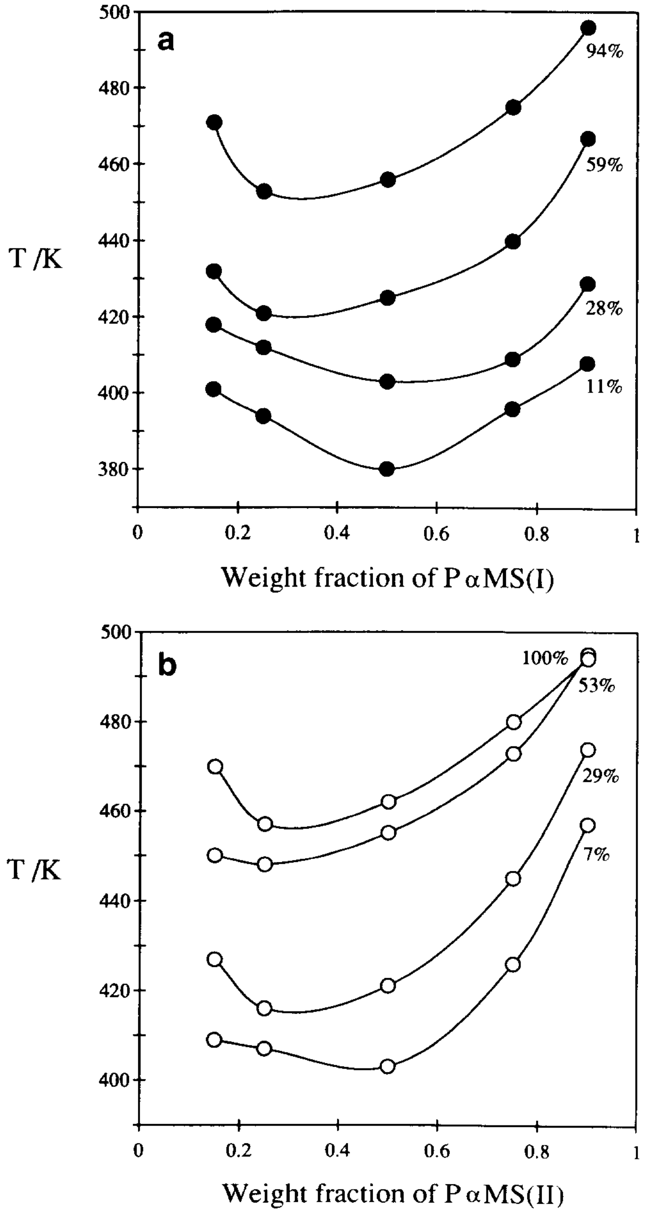


Figure 3 (a) Lower cloud-point curves for PVME/PαMS I blends containing the amount (mol%) of modified units in the PαMS as shown in the figure. (b) Lower cloud-point curves for PVME/PαMS II blends containing the amount (mol%) of modified units in the PαMS as shown in the figure

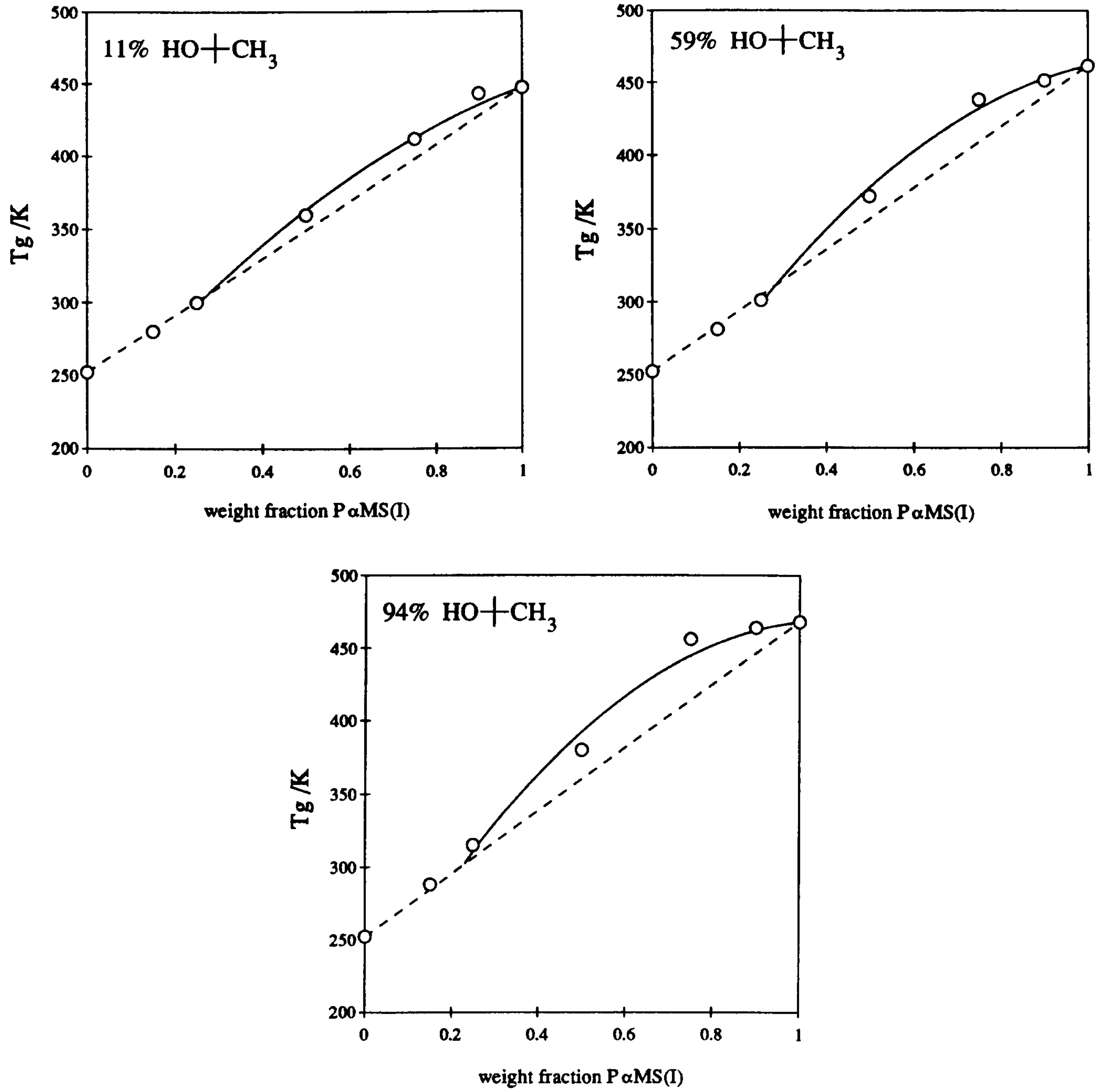


Figure 4 Glass transition temperatures for blends of PVME with PαMS I having the copolymer compositions shown in the diagrams. Broken lines correspond to the rule of mixtures, and the full curves are derived from the Kwei equation

mixtures of poly{2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate} with poly[(*N*-alkylcarbazol-3-yl)methyl methacrylate], where electron donor–acceptor complex formation stimulated the formation of one-phase blends, the T_g–composition curves showed a marked positive deviation from simple additivity. Similar behaviour was reported by Lin *et al.*[15] for polymer pairs comprising poly(vinyl cinnamates) containing different donor–acceptor groups, such as chloro and methoxy units; and by Meftahi and Fréchet[16], who studied the more strongly hydrogen-bonded blends of poly(4-vinylpyridine) and poly(4-hydroxystyrene). More recently, Landry and Teegarden[17] carried out a comprehensive study of polymers containing proton donors of different pK_a blended with polymers containing either nitrogen or carbonyl acceptor groups. In common with the other workers, they observed a pronounced downward concavity of the T_g–composition plots, where the extent of the positive deviations from the simple rule of mixtures reflected the strength of the specific intermolecular interactions operating in the system.

Several empirical equations[18–21] have been proposed that attempt to describe the trend in blend T_g with the composition of the blend. The most versatile of these has proved to be the Kwei equation[22]:

$$T_g = \frac{w_A T_g^A + k w_B T_g^B}{w_A + k w_B} + q w_A w_B \qquad (2)$$

where k and q are adjustable parameters that have been interpreted in terms of different physical quantities. Thus k has been described variously as the ratio of the volume expansion coefficients for the polymer components, and as the ratio of the component heat capacity increments

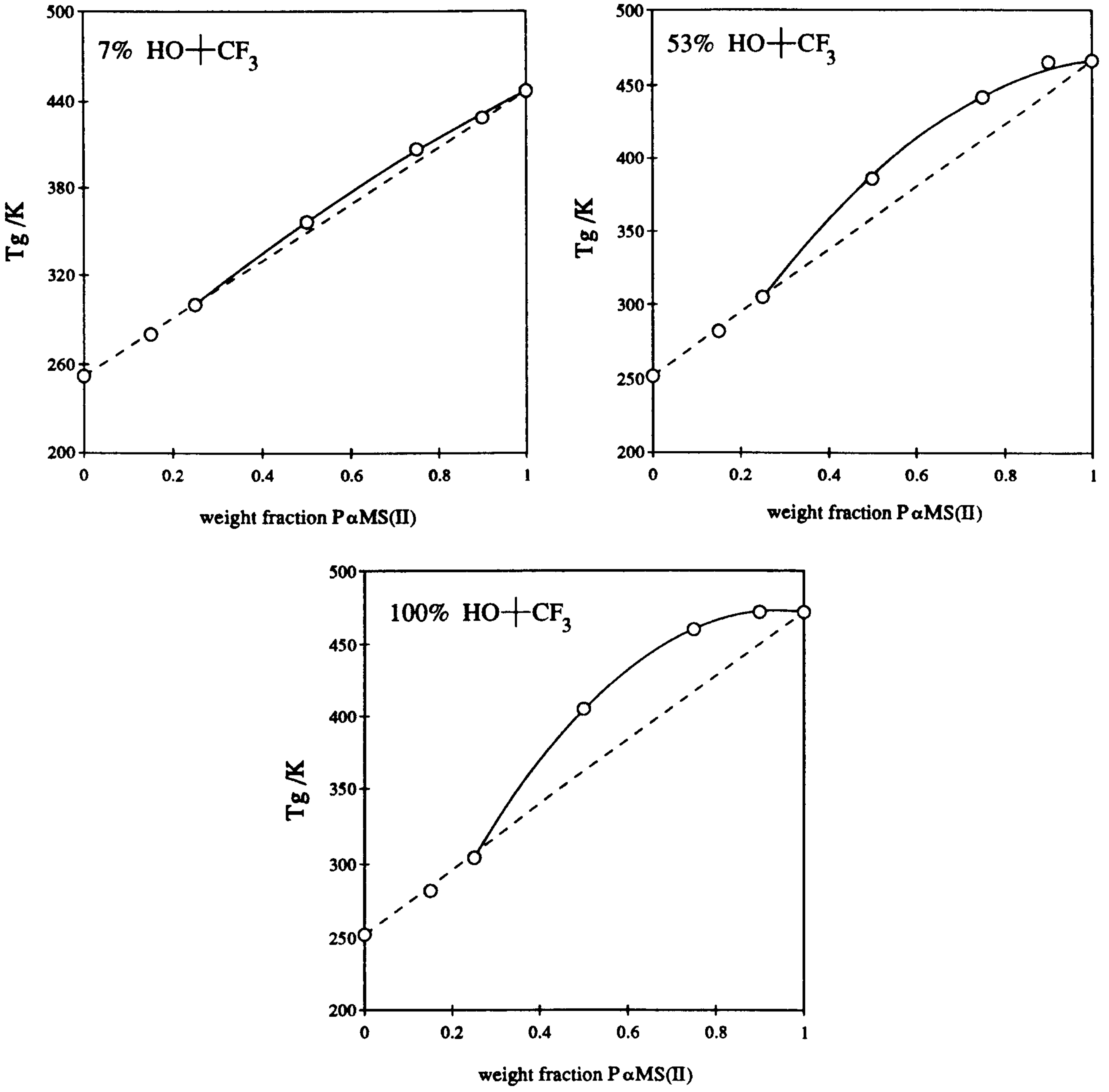


Figure 5 Glass transition temperatures for blends of PVME with PαMS II having the compositions shown in each diagram. The broken lines correspond to the rule of mixtures, and the full curves are calculated using the Kwei equation

at T_g; neither definition is universally applicable and k is usually taken to be an adjustable parameter. Equation (2) is actually an extended Gordon–Taylor equation, with qw_Aw_B as an additional parameter included by Kwei to account for both positive and negative deviations from the weighted average blend T_g calculated from equation (1). The factor q has been used as a measure of the excess stabilization energy of the blend[15] and is regarded as a qualitative estimate of the strength of the specific intermolecular interactions. Couchman[23] has expressed the q parameter as the ratio $\Delta\varepsilon/\Delta C_p$, where $\Delta\varepsilon$ is the difference between segmental interaction energies in the liquid and glassy states, and ΔC_p is the heat capacity increment. This reflects the energetic nature of this parameter, but the use of q is still largely as a fitting parameter; thus a positive value, caused by H-bonding in the blend, leads to T_g values that are higher than the weighted average, and the larger the value of q, the stronger the specific interactions between the blend components.

Because the data displayed in *Figures 4* and *5* appear to be divided into two regions, equation (2) can only describe the blends rich in the H-bond donor group copolymers with a single set of k and q values, while the remaining data follow equation (1). Indeed, there is the suggestion of a cusp or discontinuity for the T_g values for blends of PαMS with high concentrations of the modified units in the chain. Cusps in T_g–composition curves have been reported for polymer–plasticizer mixtures[24–26], and in some polymer blends when the difference between the component T_g values exceeds 50 K[27,28]. However, the shapes of the T_g–composition curves in these cases are in the opposite sense to those recorded here, with a concave upwards section

Table 3 Values of the parameter q derived using the Kwei equation with $k = 1$

PαMS I (mol% modification)	q	PαMS II (mol% modification)	q
11	122	7	62
59	197	53	242
94	232	100	354

originating from the lower T_g component merging into a linear dependence for blends rich in the higher T_g component. This can be pictured as requiring a 180° rotation of the data in *Figures 4* and *5* to duplicate the trends observed in blends of poly(caprolactone) with several chlorinated polymers studied by Aubin and Prud'homme[28]. These authors interpreted their data using the suggestion by Kovacs[29] that the free volume of the high-T_g component approached zero at the critical temperature corresponding to the cusp point. The Kovacs hypothesis does not seem to be appropriate in this case, and we prefer to regard this relatively abrupt change of behaviour as a transition from a tightly bound H-bonded network structure, with restricted chain mobility and reduced free volume, for the blends rich in PαMS I and II, to a less organized mixture of the two polymers where the H-bonding no longer dominates the chain packing and the blends obey the simple rule of mixtures. As the positive deviations of T_g occur in mixtures rich in the H-bond donor group and in blends of PαMS with high concentrations of the modified unit, there may also be an element of self-association taking place, which will alter the characteristics of the blend. In other blend systems involving PαMS I and PαMS II components, which will be reported in a later publication, these positive T_g–composition trends are equally pronounced, but instead of a cusp show either an asymmetric or a symmetric positive deviation over the whole composition range. Thus, the cusp may be an exaggerated form of the asymmetrical behaviour.

A partial analysis of the data can be made using the Kwei equation, by fitting it to the concave section of the T_g–composition curve as shown in *Figures 4* and *5*. The values of q, for $k = 1$, are listed in *Table 3*, and show a general increase, in line with the number of possible H-bonding sites in the blends.

Clearly these values should only be used as a rough guide to the level of secondary specific intermolecular interactions in each system, but the observed trends are consistent with other data. Thus, internally, for the same H-bonding group q increases with the number of bonding sites in the PαMS copolymers in both series studied. Similarly, the value of q is generally larger for the trifluoromethylcarbinol-substituted PαMS than for the methylcarbinol-modified polymers, when there are comparable levels of group substitution. This is in agreement with the measured relative strengths of the H bonds in the copolymers.

CONCLUSIONS

Poly(α-methylstyrene) can be modified by incorporating potential hydrogen-bonding groups of differing strength in the phenyl ring. These are donor sites, and subsequent blending of the copolymers formed with a polymer with an acceptor group, in this case poly(vinyl methyl ether), leads to the formation of one-phase blends when the extent of modification exceeds 4 mol%. The stability of these blends, estimated by measuring the lower critical cloud-point temperatures, shows that one-phase blends are maintained up to and in excess of 380 K, and that the temperature at which phase separation occurs is a function of the type and number of hydrogen-bond donor groups in the PαMS samples. The formation of these specific bonding sites in the polymer blend is also reflected in the T_g values recorded, which were usually higher than expected if the simple rule of mixtures was used to estimate the blend T_g. This can be treated in a qualitative way using the Kwei equation to describe part of the T_g–composition behaviour, usually in blends rich in the modified PαMS.

ACKNOWLEDGEMENT

The authors wish to thank Dr R. Ferguson for assistance in the program writing subsequently used for computer data analysis.

REFERENCES

1 Pearce, E. M., Kwei, T. K. and Min, B. Y. *J. Macromol. Sci., Chem. (A)* 1984, **21**, 1181

2 Eisenberg, A., Smith, P. and Zhou, Z.-L. *Polym. Eng. Sci.* 1982, **22**, 1117

3 Pugh, C. and Percec, V. *Macromolecules* 1986, **19**, 65

4 Ting, S. P., Pearce, E. M. and Kwei, T. K. *J. Polym. Sci., Polym. Lett. Edn* 1980, **18**, 201

5 Ting, S. P., Bulkin, B. J., Pearce, E. M. and Kwei, T. K. *J. Polym. Sci., Polym. Chem. Edn* 1981, **19**, 1451

6 Kim, H. I., Pearce, E. M. and Kwei, T. K. *Macromolecules* 1989, **22**, 3374

7 Wang, L. F., Pearce, E. M. and Kwei, T. K. *J. Polym. Sci. (B) Polym. Phys.* 1991, **29**, 619

8 Saeki, S., Cowie, J. M. G. and McEwen, I. J. *Polymer* 1983, **24**, 60

9 Cowie, J. M. G. and McEwen, I. J. *Polymer* 1985, **26**, 1662

10 Kenyon, W. O. and Waugh, G. P. *J. Polym. Sci.* 1958, **32**, 83

11 Coleman, M. M., Graf, J. F. and Painter, P. C. 'Specific Interactions and the Miscibility of Polymer Blends', Technomic, Basel, 1991

12 Cowie, J. M. G. and Reilly, A. A. N. submitted for publication

13 Kwei, T. K., Pearce, E. M., Ren, F. and Chen, J. P. *J. Polym. Sci. (B) Polym. Phys.* 1986, **24**, 1597

14 Rodriguez-Parada, J. M. and Percec, V. *Macromolecules* 1986, **19**, 55

15 Lin, A. A., Kwei, T. K. and Reiser, A. *Macromolecules* 1989, **22**, 4112

16 Meftahi, M. V. and Fréchet, J. M. *Polymer* 1988, **29**, 477

17 Landry, C. J. T. and Teegarden, D. M. *Macromolecules* 1991, **24**, 4310

18 Gordon, M. and Taylor, J. S. *J. Appl. Chem.* 1952, **2**, 493

19 Jenckel, F. and Heusch, R. *Kolloid Z.* 1953, **30**, 89

20 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **1**, 123

21 Couchman, P. R. and Karasz, F. E. *Macromolecules* 1978, **11**, 117

22 Kwei, T. K. *J. Polym. Sci., Polym. Lett. Edn* 1984, **22**, 307

23 Couchman, P. R. *Macromolecules* 1991, **24**, 5772

24 Roy, S. K., Brown, G. R. and St Pierre, L. E. *Int. J. Polym. Mater.* 1983, **10**, 13

25 Fried, J. R., Lai, S.-Y., Kleiner, L. W. and Wheeler, M. E. *J. Appl. Polym. Sci.* 1982, **27**, 2869

26 Pezzin, G., Omacini, A. and Zilio-Grandi, F. *Chem. Ind. (Milan)* 1968, **50**, 309

27 Nandi, A. K., Mandal, B. M., Bhattacharyya, S. N. and Roy, S. K. *Polym. Commun.* 1986, **27**, 151

28 Aubin, M. and Prud'homme, R. E. *Macromolecules* 1988, **21**, 2945

29 Kovacs, A. J. *Adv. Polym. Sci.* 1963, **3**, 394