The effect of molecular weight and casting solvent on the miscibility of polystyrene–poly(α-methyl styrene) blends

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The glass transition temperatures (T_g) have been measured for blends of polystyrene and poly(α-methyl styrene) in the molecular weight ranges: polystyrene, $2030 < M < 250\,000$, and poly(α-methyl styrene), $17\,000 < M < 250\,000$. The presence of either one T_g or two has been used as a criterion to determine the miscibility of each blend over a range of compositions, and the T_gs were obtained from measurements of the temperature dependence of the heat capacities of the blends. A sinlge T_g was observed over the entire composition range for blends in which the component molecular weights were both less than 70 000 g mol^{-1}, when these were cast from toluene solutions. When propylene oxide solutions were used to prepare the blends, this limit dropped to M=50 000 g mol^{-1}. By using the appearance of two T_gs as an indication that phase separation had taken place, it was possible to establish regions of miscibility and immiscibility as a function of casting solvent and molecular weight for both components. The change in heat capacity at the glass transition was measured and it was found that for miscible blends the heat capacity changes are similar to the calculated values, but for immiscible systems the measured change is smaller than expected.

Keywords Blends; polystyrene; Poly(α-methyl styrene); heat capacity; glass transition temperature; differential scanning calorimeter

INTRODUCTION

The study of polymer blends has assumed an ever-increasing importance in recent years and the resulting research effort has led to the discovery of a number of miscible polymer combinations. Complete miscibility is an unusual property in binary polymer mixtures which normally tend to form phase-separated systems. Much of the work has been of a qualitative nature, however, and variables such as molecular weight and conditions of blend preparation have often been overlooked. The criteria for establishing miscibility are also varied and may not always all be applicable to particular systems

One widely used criterion is the presence of single or multiple glass transitions in the final blend, which has been used to identify miscible and immiscible systems, respectively. This is normally a convenient and reliable guide to the state of the blend and differential scanning calorimetry (d.s.c.) is regularly used to determine the glass transition temperatures T_g, rapidly and accurately.

The dependence of T_g on composition and molecular weight for polymers, copolymers and polymer diluent systems has been discussed by many workers and the techniques used can be conveniently extended to blends[1–9]. In addition, interesting information can be obtained from heat capacity (C_p) data and detailed analyses of the contributions to the heat capacity change, ΔC_p, associated with the glass–rubber transition, have been attempted by several groups[10–13].

It has been reported by Krause[14] that the combination of polystyrene (PS) and poly(α-methyl styrene) (PαMS) is a 'conditionally' compatible system. The same worker has also predicted[15], after examination of the solubility parameters for these two polymers, that (50:50) mixtures should be miscible up to molecular weights of $\sim 10^5$. A brief report[16] suggested that this might be valid but the results are too few to be sufficiently definitive. Robeson *et al.*[17] have also examined two PS–PαMS blends in which the component molecular weights were $> 2.5 \times 10^5$, and the expected two-phase behaviour was observed. As the system exhibits some interesting features it was decided to examine it in greater detail and to determine the effect of (a) component molecular weight and (b) solvent used to cast the blend, on the extent of miscibility.

EXPERIMENTAL

The PS samples were all of narrow molecular weight distribution and were purchased from the Pressure Chemical Co. The PαMS samples were fractions characterized previously[18] with the exception of two ($M_w = 84\,000$ and $17\,000$) which were obtained from Polysciences.

Polymer mixtures were prepared by first dissolving the two components in a common solvent such as toluene, cyclohexane or propylene oxide, and then spreading the solution thinly on a glass plate and allowing the solvent to evaporate at room temperature. This produced a sheet of polymer of approximately 4–16 μm thickness. Samples (10–25 mg)were then scraped into the aluminium pans used for measurement in the differential scanning calorimeter and dried under vacuum at 350K for at least 24 h prior to measurement.

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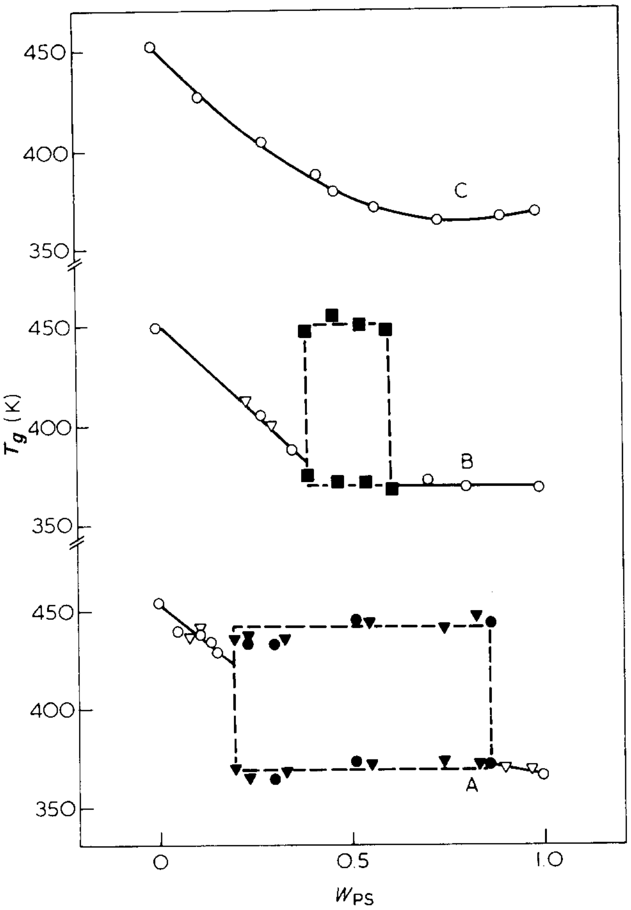

Figure 1 (A) Glass transition temperatures for PS (153 000) and PαMS (156 000) blends of various compositions, expressed as the weight fraction of PS (W_{PS}) in the blend. Blends cast from toluene: showing one T_g (▽) and two T_gs (▼); blends cast from cyclohexane: showing one T_g (○) and two T_gs (●). (B) T_g against W_{PS} for blends of PS (153 000) and PαMS (55 200) cast from cyclohexane (▽); and toluene: one T_g (○) and two T_gs (■). (C) Miscible blends of PS (20 400) and PαMS (90 900) cast from toluene and showing only a single T_g over the whole composition range

The heat capacity was established as a function of temperature for each polymer mixture, using a Perkin–Elmer DSC-2 differential scanning calorimeter. The instrument was equipped with a low-temperature accessory and a scanning autozero to correct for baseline irregularities. Sapphire (34.29 mg) was used as a standard for heat capacity measurements and the temperature scale was calibrated using the melting points of indium, lead and gallium as standards. In order to minimize the effects from sample packing in the pan, and to eliminate any small traces of solvent, the samples were heated to 500K in an inert atmosphere and quenched to room temperature before each measurement. This sample pretreatment has been employed for consistency and did not appear to change the cast structure, as first-run d.s.c. curves were usually similar to those after quenching. Heat capacities were determined over the range 300–500K using dry nitrogen as the atmosphere and with the instrument cold finger immersed in a water–ice mixture.

RESULTS AND DISCUSSION

Molecular weight and solvent effects

The glass transition temperatures T_g were established by locating the temperature at which there was a discontinuity in the C_p–T curve. The miscibility of the system was then assessed by determining whether one or two T_gs were present in blends prepared from PS and PαMS, each of fixed molecular weight but of variable composition with respect to the two components. Examples of this are shown in *Figures 1a, b* and *c* where the effect of both composition and sample molecular weight on the miscibility of the blend is clearly evident. *Figure 1a* shows data for mixtures of PS (153 000) and PαMS (156 000) prepared from toluene and cyclohexane solutions, in which two T_gs are found in the composition range $W_{PS} = 0.2$–0.85, indicating that these mixtures are phase-separated, with only limited miscibility at either end of the composition range. Here W_{PS} is the weight fraction of PS in the blend. It has been suggested that it would be difficult to detect the glass transition of a minor component (<10%) in the blend anyway, so the small miscibility ranges observed here must be interpreted with some caution. The effect of lowering the molecular weight of one component is illustrated in *Figure 1b* for PS (153 000) and PαMS (55 200) toluene-cast blends. There is a narrowing of the miscibility gap to $W_{PS} = 0.3$–0.75 and an extension of the miscible range almost equally at both composition ends. When both component molecular weights are lowered to PS (20 400) and PαMS (90 900), the polymers are miscible over the complete composition range (*Figure 1c*). Again the solvent used to prepare the blends was toluene.

By repeating this procedure for a series of mixtures of different molecular weights, a diagram can be constructed, as shown in *Figure 2*, which defines the miscibility limits of PS–PαMS blends cast from toluene, as a function of molecular weight and blend composition. A parabolic two-phase region can be located at higher molecular weights with a minimum on the tie line joining

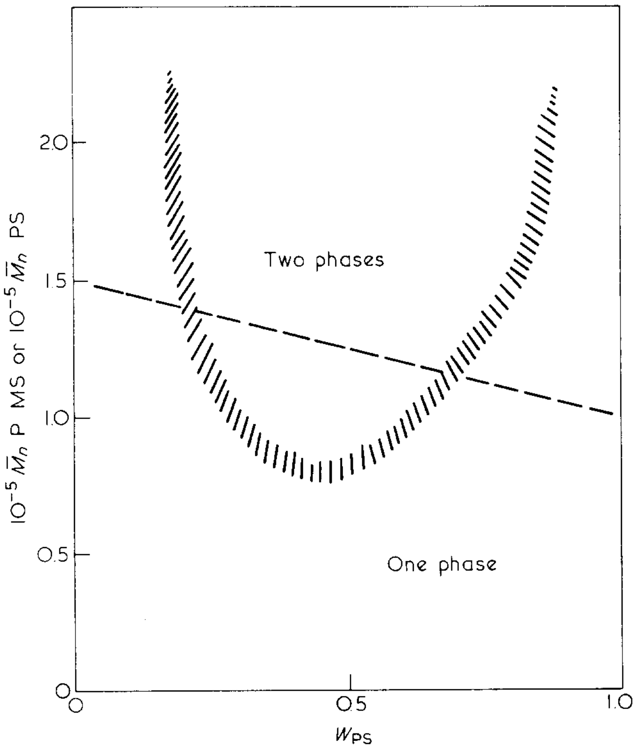

Figure 2 Miscibility gap in blends of PS and PαMS cast from toluene, showing the extent of the one-phase and two-phase regions as a function of component molecular weight and blend composition. The broken line is a tie line between PS (10^5) and PαMS (1.5×10^5) showing the one- and two-phase behaviour to be expected as a function of blend composition

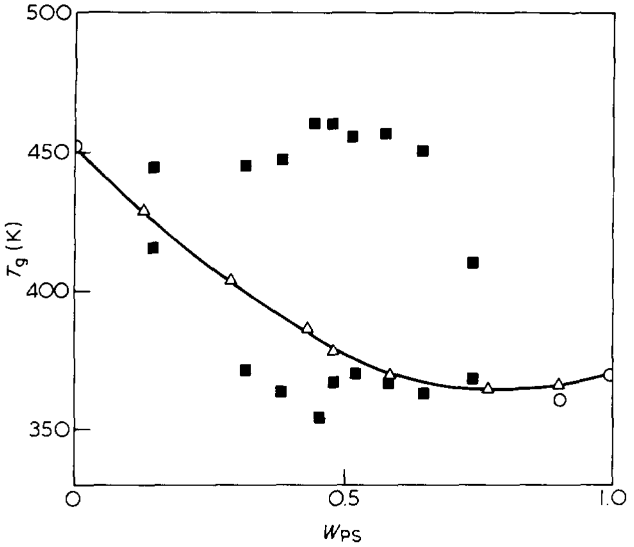

Figure 3 Plot of T_g against W_{PS} for blends of PS (20400) and PαMS (90900) cast from toluene (△) (miscible in all proportions) and propylene oxide (■), showing two T_gs

$M = 75000$ g mol^{-1} for both components. From this diagram one should be able to predict the approximate miscibility range for mixtures of any pair of PS and PαMS samples of known molecular weight, when these blends are cast from toluene solutions at ambient temperature. Thus a tie line drawn between PS (100000) and PαMS (150000) (shown by the broken line in *Figure 2*) indicates that mixtures of these two molecular weights should phase-separate in the composition range $W_{PS} = 0.2$–0.7. Similarly it predicts that if both component molecular weights are less than 75000 g mol^{-1}, then the blends will be miscible in all proportions.

It is difficult to predict the boundaries of this two-phase region with great precision using this method, and so these must be regarded as reasonable guidelines only. It is also likely that variations in sample heterogeneity will also make an exact definition of the phase boundary more difficult. However, the general features are in agreement with the predictions of Krause[15] based on the 'solubility parameter' approach to predicting miscibility in blends, which proposed that molecular weights should exceed 10^5 before two-phase behaviour was observed. The phase boundaries shown in *Figure 2* are more informative and give a better definition of the miscibility gap. Robeson *et al.*[17] found that a (25:75) blend of PS (0.36×10^5) and PαMS (1.65×10^5) showed some evidence of miscibility, whereas a (25:75) blend of PS (2.7×10^5) and PαMS (3.1×10^5) exhibited two-phase behaviour. Reference to *Figure 2* indicates that the first blend is on the border of the one-phase/two-phase region, while the second is clearly in the two-phase region in agreement with their observations.

Miscibility can also be affected by the method of preparation and when blends are prepared from propylene oxide solutions there is a marked extension of the miscibility gap. This contrast in behaviour, caused by the change of casting solvent, is evident on comparing blends of PS (20400) and PαMS (90000) prepared from toluene and propylene oxide for which the data are shown in *Figure 3.*

A single T_g was found in blends cast from toluene, but two appeared when propylene oxide was the casting solvent. In the latter case, the T_gs corresponding to the PαMS domains are lower by 7 to 25K compared with that of pure PαMS, whereas the T_gs for the PS domains are in a narrower range of +5K to −9K compared with the parent polymer. This suggests that there is a slightly greater tendency for the PαMS to be diluted by PS than *vice versa*, but the effect is small. The miscibility gap measured for propylene oxide-cast blends, shown in *Figure 4*, is significantly larger than for toluene-cast blends, and component molecular weight limits for complete miscibility decrease accordingly. Thus when both PS and PαMS have $M < 50000$ miscibility is achieved in all proportions or, as construction of tie lines will show, when blends are prepared from either PS $\leqslant 80000$ and PαMS $\leqslant 10000$, or PS $\leqslant 1500$ and PαMS $\leqslant 60000$, miscibility is again achieved over all compositions.

The influence of casting solvent on blend miscibility has been observed in other systems by Bank *et al.*[19], who found that blends of PS and poly(vinyl methyl ether) are miscible when cast from toluene, benzene or tetrachloroethene, but not when cast from chloroform or dichloromethane. Robard *et al.*[20,21] have suggested that the miscibility of two polymers in a common solvent is influenced by the differences between the individual solvent–polymer interaction parameters χ_{ij}, i.e. $|\Delta\chi| = |\chi_{12} - \chi_{13}|$ where component 1 is solvent and 2,3 represent the polymers. Toluene is an equally good solvent for both PS and PαMS so $|\Delta\chi|$ is small, but while propylene oxide is moderately good for PS it is a poor solvent for PαMS and $|\Delta\chi| \sim 0.09$.[22,23] This differential solvation may explain why the blend miscibility is poorer in propylene oxide than in toluene, and is analogous to the behaviour in some block copolymer systems. Examination of some blends cast from cyclohexane, which is a poor solvent for both polymers at room temperature but where $|\Delta\chi|$ is only ~ 0.005, indicates that the blends are similar to those cast from toluene.

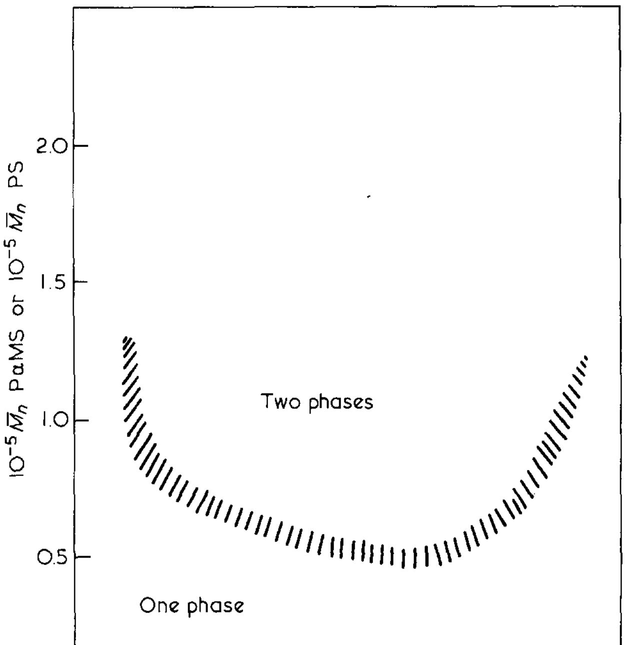

Figure 4 Miscibility gap for blends cast from propylene oxide

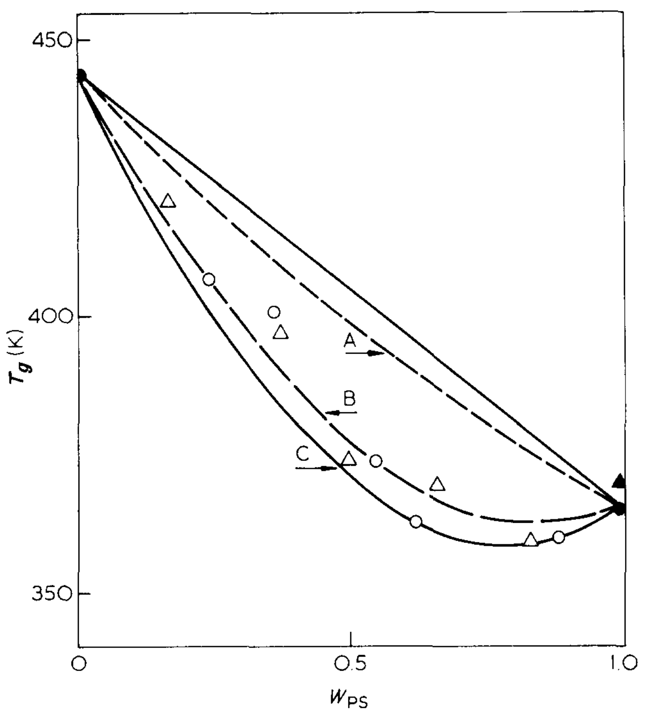

Figure 5 T_g–composition behaviour for miscible blends of PS (10 000) and PαMS (84 000) shown as ○. Also PS (63 000) and PαMS (84 000) shown as △. Curve A is constructed from equation (2). Curves B and C are derived from equation (3) with values of b = 1.45 and 1.65, respectively

T_g–*composition curves*

For those blends which are miscible throughout the composition range and only exhibit one T_g, it is instructive to attempt to predict the trends in T_g with changes in composition. The data for two such blends are shown in *Figure 5*, where the PαMS component was held constant at $M = 84\,000$ and the PS component was varied. There is a general depression of T_g below a linear interpolation line joining the T_g values for the homopolymers, and for blends rich in PS the T_gs actually drop below that for the homopolymer.

Numerous workers have examined the T_g–composition trends in copolymers and the generalized Gordon–Taylor–Wood equation[4]

$$T_g = \frac{T_g^A + (kT_g^B - T_g^A)W_B}{1 + (k-1)W_B} \qquad (1)$$

is widely used, where k is a constant derived from the ratios of the differences in thermal expansion coefficient between the liquid and the glass for each component, and W is the component weight fraction. Application of equation (1) did not result in a particularly good representation of these data and alternative forms were examined.

Couchman and Karasz[7] have derived

$$\ln\left(\frac{T_g}{T_g^A}\right) = \frac{W_B(\Delta C_p)_B \ln(T_g^B/T_g^A)}{W_A(\Delta C_p)_A + W_B(\Delta C_p)_B} \qquad (2)$$

by considering the change in heat capacity $(\Delta C_p)_i$ for component i at its glass transition. Measured values of PS $(\Delta C_p) = 0.07$ cal K^{-1} g^{-1} and PαMS $(\Delta C_p) = 0.06$ cal K^{-1} g^{-1} were used to calculate the broken curve A shown in *Figure 5*, for blends of PS (10 000) and PαMS (84 000). Equation (2) underestimates the depression in T_g over the whole range.

A much better representation of the data is obtained when the equation developed by Jenckel and Heusch[2] for polymer–diluent systems is used. This has the form

$$T_g = W_A T_g^A + W_B T_g^B + W_A W_B b(T_g^A - T_g^B) \qquad (3)$$

where b is an empirical parameter which varies from system to system. Curves which fit the data with reasonable accuracy can be produced for values of $b = 1.45$–1.65 and, while they are not precise over the total composition range, they demonstrate that equation (3) is superior to the other equations for these particular blends.

The effect of solvent on the T_g–composition behaviour of miscible blends was examined and it was found that the depression of T_g in the blends was much greater when toluene was used than for either cyclohexane or propylene oxide which were quite similar in behaviour. While there is some scatter in the data the trends are clearly seen in *Figure 6*. Again one can consider that the $|\Delta\chi|$ effects can explain the differences in toluene and propylene oxide-cast films, where the more intimate mixtures are obtained in the toluene solutions. In cyclohexane solutions $|\Delta\chi|$ is low but now the tendency for tight coils to form in this poor solvent for both polymers results in miscibility which is similar to the propylene oxide-cast blends. This differs from the molecular weight-dependent behaviour and suggests that the level of miscibility in solvent-cast blends will depend not only on the magnitude of the $|\Delta\chi|$ parameter but also on the solvent–polymer interaction parameters which will indicate the extent of coil expansion in a given solvent.

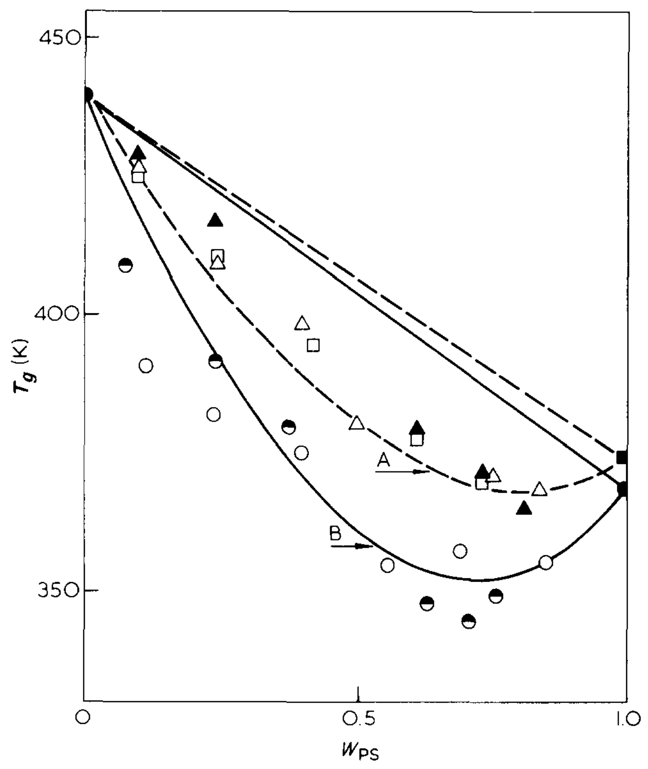

Figure 6 T_g–composition behaviour for (i) blends of PS (17 000) and PαMS (17 000) cast from toluene (○) and propylene oxide (△) and (ii) blends of PS (37 000) and PαMS (17 000) cast from toluene (◒), propylene oxide (▼) and cyclohexane (□). Curves A and B calculated from equation (3)

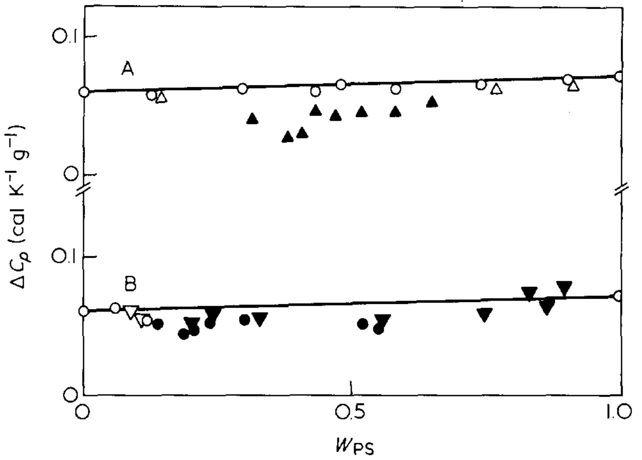

Figure 7 Heat capacity change (ΔC_p) at T_g as a function of blend composition. (A) PS (20 400) and PαMS (90 900) cast from toluene (○) and propylene oxide (△). (B) Blends of PS (153 000) and PαMS (156 000) cast from toluene (○) and cyclohexane (△). Open symbols represent one-phase systems, while filled symbols represent two-phase systems

Heat capacity changes at T_g

From a knowledge of the experimental values of $(\Delta C_p)_i$, the heat capacity change at the glass transition of each component polymer of a blend, it is possible to calculate an expected value for each blend $(\Delta C_p)_{\text{calc}}$ using a simple relation such as

$$(\Delta C_p)_{\text{calc}} = W_A(\Delta C_p)_A + W_B(\Delta C_p)_B \qquad (4)$$

The value obtained can then be compared with the experimental value $(\Delta C_p)_{\text{expt}}$ for both miscible and immiscible systems with one or two T_gs. Any differences observed can then be expressed as an excess value

$$(\Delta C_p)_E = (\Delta C_p)_{\text{expt}} - (\Delta C_p)_{\text{calc}} \qquad (5)$$

or as a ratio $(\Delta C_p)_{\text{expt}}/(\Delta C_p)_{\text{calc}}$.

Representative data are shown in *Figures 7a* and *b*. Here it can be seen that when the system is miscible and exhibits only one T_g, then $(\Delta C_p)_E$ is essentially zero and equation (4) gives a good estimate of the experimental values. When the blends display two T_gs, the value of $(\Delta C_p)_E$ is clearly negative and the summation of the experimental ΔC_p for each transition is always lower than expected. It has been suggested[24] that part of the reduction in the C_p transition height may be due to the size of the dispersed phase, particularly in blends where there is a minor component, and that parts of the minor phase may be too small to detect by d.s.c. There is no real evidence to support this view in our systems as the reduction in ΔC_p usually occurs at both transitions, irrespective of blend composition. A more likely explanation would seem to lie in the possible existence of a diffuse interfacial region[10]. The presence of diffuse interfaces in phase-separated systems has been demonstrated by Letz[25] and it is highly probable that such regions will exist in binary systems which tend towards miscibility, as is the case in the present PS–PαMS system. The change in C_p associated with these regions may often be too small to detect easily and so the total contribution to ΔC_p from each transition will be less than expected. For highly immiscible systems, where phase separation is more complete, the diffuse interfacial volume will be relatively small and $(\Delta C_p)_E$ will be negligible. For phase-separated PS–PαMS blends, $(\Delta C_p)_E$ is negative with an average ratio $(\Delta C_p)_{\text{expt}}/(\Delta C_p)_{\text{calc}} \sim 0.65$, which indicates an extensive diffuse interfacial region between the phases.

One would expect that the interfacial region might decrease as the component molecular weights increase and phase separation becomes more pronounced. This would be reflected in smaller values of $(\Delta C_p)_E$ and some indication of this can be seen in *Figure 7b* where $(\Delta C_p)_{\text{expt}}/(\Delta C_p)_{\text{calc}} > 0.67$, but the data are insufficiently accurate to be conclusive about this effect.

CONCLUSIONS

Blends of PS and PαMS display an interesting range of miscibilities which is a function of component molecular weight and to a lesser extent dependent on the nature of the casting solvent. The miscibility gaps depicted in *Figures 2* and *4* will then represent the behaviour to be expected from blends prepared from toluene and propylene oxide, respectively, at room temperature. They should, therefore, be interpreted only within these limits.

A comparison with melt-blended systems was not attempted because of the thermal instability of PαMS, although some freeze-dried blends were prepared and found to behave in much the same way as the solvent-cast blends. This is being investigated further.

It is also believed that the temperature at which blends are prepared will affect the miscibility of the system and this will be the subject of a forthcoming publication.

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