The thermodynamics of mixing of polystyrene and poly(α-methylstyrene) from a calorimetric viewpoint

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The enthalpy of mixing ($\Delta_M H$) for polystyrene with poly(α-methylstyrene) has been estimated by a semidirect calorimetric method. This involved measuring heats of solution of blends and of mechanical mixtures having the same composition to obtain, by difference, the heat of mixing of the two polymers in their glassy states. By assuming a model for the relaxation of a glass to its corresponding hypothetical liquid state, these were then converted to give a $\Delta_M H$ value for the liquid polymers. A small negative value for the heat of mixing was obtained over part of the composition range, contrary to expectations.

(Keywords: heat of mixing; calorimetry; polystyrene)

Introduction

Mixing, as with all chemical or physical phenomena, is described by an appropriate free energy expression. In the particular case of polymer mixtures, the entropy of mixing ($\Delta_M S$), though positive and therefore favourable to the process, is small and usually insufficient to drive the system to miscibility. Consequently a negative enthalpy of mixing ($\Delta_M H$) is generally required to ensure a stable one-phase blend. It is evident that the energy interactions between different molecular chains will be a key factor in the phase behaviour of high molecular weight materials. If this contribution is positive, polymers will become immiscible at molecular weights higher than some critical value where the unfavourable energetic term offsets the favourable entropic contribution.

According to this simple picture, the more similar are the structures of the polymers to be blended, the better will be the chance of obtaining miscibility. A well-studied system in which the differences between the components are minimal, yet miscibility is limited, is polystyrene (PS) and poly(α-methylstyrene) (PαMS). Although there have been a number of investigations of this system[1–5], some aspects are not completely clear. For instance, there is a molecular weight limit to miscibility (and by implication a positive energy term), but blends do not appear to exhibit reproducible critical solution temperatures (ref. 3 reports changes in the d.s.c. thermograms which are interpreted as phase separation. However, we have been unable to reproduce this behaviour in our laboratories)[6,7]. This is so even when molecular weights are close to the miscibility limit and, moreover, this limit depends on the manner of blending. These discrepancies in the overall picture seem to justify further investigation, not only of the thermodynamic behaviour, but also from the point of view of any theoretical approach.

Recent technical improvements in calorimetry now allow measurements of the heat of mixing of liquid–liquid and liquid–solid systems with considerable precision. However, the high viscosity and low diffusion of polymer melts forbids any direct measurement of the heat developed during mixing. Several attempts[5,8–12] have been made to develop a valid method to overcome this limitation and thus achieve an experimental calorimetric measurement of interactions in polymer blends. Two methods are generally accepted. The first considers the heat of mixing (and therefore the intensity of interactions) of low molecular weight model compounds to be the same as that of polymers having similar repeat units[8–10]. This approach is attractive because of its simplicity, but there are two major shortcomings. Different model compounds for the same polymer give different results, and so the final choice is mainly subjective. It also fails to take account of chain structure effects which play so important a role in all polymer physical properties. The second method, used in this study, involves measurement of the heat of solution of the blend of interest and the heat of solution of a simple mechanical mixture of the two polymers at the same composition. The difference between these quantities directly represents the enthalpy of mixing for the given composition. This approach is a logical simplification of the so-called heat of solution method[5,11,12], which involves the heats of solution of the blend, of polymer 1 and of polymer 2, and the heat of mixing of a solution of polymer 1 with a solution of polymer 2 at the appropriate concentrations.

For polymers, heats of mixing are small compared to heats of solution in a good solvent, thus even an acceptable precision in a large heat of solution value may become inadequate after subtraction of two such large quantities. This implies that the method demands a sensitive calorimeter and multiple measurements on each sample to reduce the experimental uncertainty to a reasonable level. Nonetheless, we believe it provides a more acceptable result, from both theoretical and experimental points of view, than the heats of mixing of model compounds.

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Table 1 Enthalpy differences between polymer glass and hypothetical liquid ($\Delta_R H$) at 333 K, and the values of the coefficients a and b in $C_p = a + bT$, for the blends and pure components

	glass			liquid			
PαMS/PS (w/w)	a ($J\,g^{-1}\,K^{-1} \times 10^3$)	b ($J\,g^{-1}\,K^{-2}$)	ΔT (K)	a ($J\,g^{-1}\,K^{-1} \times 10^3$)	b ($J\,g^{-1}\,K^{-2}$)	ΔT (K)	$\Delta_R H$ ($J\,g^{-1}$)
100/0	−0.06	4.2	320–440	0.92	2.6	465–500	-41.7 ± 1.1
80/20	−0.02	4.2	320–400	0.73	3.1	445–500	-27.8 ± 0.6
50/50	−0.16	4.3	310–385	0.82	2.8	440–480	-26.9 ± 0.6
20/80	−0.13	4.6	310–360	0.72	4.6	415–480	-16.2 ± 0.1
0/100	−0.13	4.1	310–360	0.49	3.1	385–440	-12.4 ± 0.1

Each $\Delta_R H$ value is the average of three or four separate determinations and the errors quoted represent the spread of results obtained. The coefficients a and b are also averages, quoted to two significant figures. ΔT is the experimental temperature range of C_p determination

Experimental

The PS sample ($M_w = 50 \times 10^3$ g mol^{-1}; $M_w/M_n < 1.06$) and the PαMS sample ($M_w = 55 \times 10^3$ g mol^{-1}; $M_w/M_n < 1.06$) were both purchased from Polysciences Inc. Toluene was obtained from Aldrich Chemicals and used as received.

Films of pure polymers and of blends were cast from toluene solutions of a 20% w/v starting concentration under a controlled rate of evaporation (0.04 cm^3 h^{-1}) on a glass surface and finally completely dried under vacuum. Although it is recognized that solvent evaporation is not the best way to blend polymers, this choice was made because of the need to ensure homogeneous glassy samples. Blends at 20/80, 50/50 and 80/20 w/w composition and three mechanical mixtures of the same compositions (using similarly toluene-cast homopolymer samples) were examined in the mixing calorimeter.

Heats of solution were determined with a Setaram C80 differential calorimeter using reversal mixing cells at 333.173 ± 0.001 K. The total amount of sample for each single experiment varied between 5 and 15 mg, while the amount of solvent was fixed at 5.00 cm^3. To avoid secondary effects due to air or to solvent evaporation the empty space in both the lower and upper chambers was completely filled with mercury. Every component of the cell was tightly sealed with Teflon O-rings and stirring during the experiment was provided by the ability of the calorimeter's main body to rotate through 180°.

The process of mixing started with the first rotation, which allowed the solvent to come into contact with the solid sample. The time of stirring thereafter depended on the rate of dissolution, normally for about three-quarters of the time during which the calorimeter registered heat flow. Typically, heat flow exotherms lasted around 1000 s. The final concentration of polymer or mixture (< 1.5% w/v) was chosen to avoid heat of dilution effects. Seven or more measurements on identical samples were normally performed. Results are reported as joules per gram (of blend or of mechanical mixture).

The heat capacities, C_p ($J\,g^{-1}\,K^{-1}$), of PS, of PαMS and of their blends were determined using a Perkin–Elmer DSC-2 scanning calorimeter employing a sapphire sample as reference material. The data both below and above the glass transition were adequately described by the linear relation $C_p = a + bT$, and the coefficients a and b from a least-squares fit are collected in *Table 1* for each of the samples.

Results

Enthalpy correction for glassy mixtures. Because of the relatively high glass transition temperatures (T_g) of both PS and PαMS it is not possible to perform calorimetry at temperatures at which the homopolymers or their blends are in their equilibrium liquid states. The heats of solution obtained in the calorimetric experiments thus refer to polymer (blend or mechanical mixture) glasses, and since a glass is not in conformational thermodynamic equilibrium these data require an enthalpy correction. The enthalpy change, from the non-equilibrium glassy state to the hypothetical equilibrium liquid state below T_g is termed the enthalpy of relaxation ($\Delta_R H$) and is shown in *Figure 1*. The temperature range within which a direct experimental determination of $\Delta_R H$ is possible[13] is itself limited to 30 K or so below T_g and so it is necessary to adopt a theoretical approach to evaluate this correction here.

Several theories[13–16] attempt to describe the thermodynamic phenomena occurring in the glassy state; for the needs of the present work the Petrie–Marshall approach[14] has been chosen on the basis of its simple definition of $\Delta_R H$ at any given temperature below T_g. $\Delta_R H$ is the heat evolved by the glass in reaching the theoretical undercooled liquid state after an infinite time at the chosen temperature. The required calorimetric correction is then made on the assumption that the experimental heat of solution of a polymer glass is equal to the sum of the heat of solution for the sample in the hypothetical liquid state and the value of $\Delta_R H$. The heat of mixing is then given by

$$\Delta_M H = [\Delta_{soln} H(\text{mixture}) - \Delta_R H(\text{mixture})] - [\Delta_{soln} H(\text{blend}) - \Delta_R H(\text{blend})] \qquad (1)$$

$\Delta_R H$ is in turn determined from the measured heat capacities of homopolymer or blend below (g) and above (l) T_g via the expression:

$$\Delta_R H = \int_{T_{exp}}^{T_{ref}} [C_p(\text{l}) - C_p(\text{g})]\, dT \qquad (2)$$

$T_{exp} = 333$ K, and T_{ref} is a chosen reference temperature sufficiently far above T_g (see *Figure 1*). The values of $\Delta_R H$ for the two polymers and for their blends are given in *Table 1*.

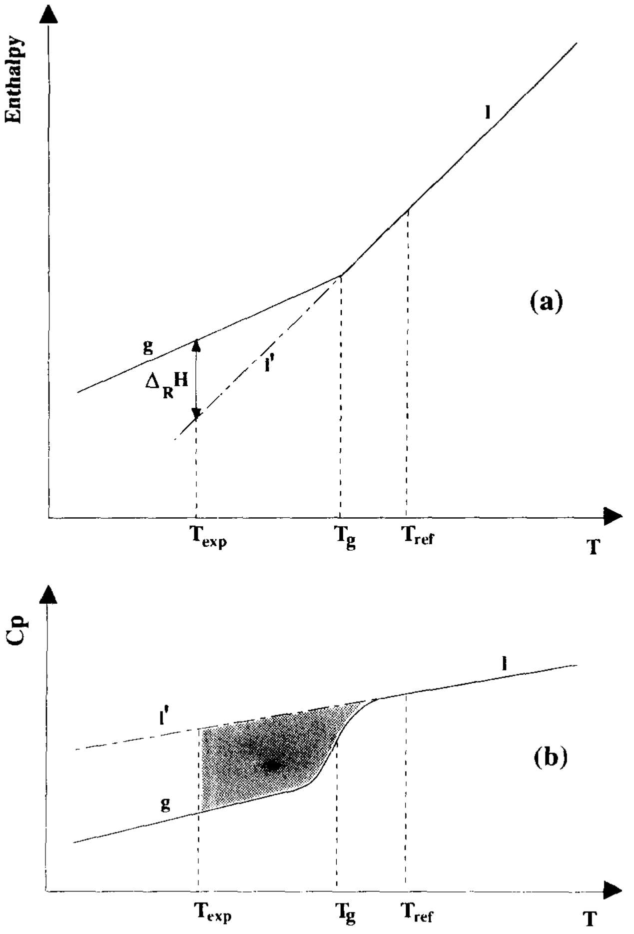

Figure 1 (a) The full line represents enthalpy vs. temperature for a polymer glass (g) and its corresponding liquid (l) above T_g. The extrapolation (– – – –) is the enthalpy of the hypothetical liquid (l') polymer below T_g. $\Delta_R H$ is the change in enthalpy between the glassy state and the hypothetical liquid at any chosen temperature T_{exp}. (b) Heat capacity vs. temperature corresponding to (a). The shaded area is equal to the value of $\Delta_R H$ at T_{exp}. T_{ref} is the limit of integration in equation (1)

Mixing calorimetry. The calorimetric results give the two sets of data shown in *Table 2*: the heats of solution of the blends and the pure components, and the heats of solution of the mechanical mixtures. These latter values, assuming minimal interaction between dissimilar macromolecules in the dissolved state, would be linear composition averages of the heats of solution of the pure components. The fact that this is not the case may indicate that the solutions are not strictly ideal. (The calorimeter solutions, although dilute, may still allow interactions in solution. However, both the blends and mechanical mixtures should be affected equally and any aggregate contribution to $\Delta_M H$ should be minimal. Contributions from mechanical or surface stresses in the solid samples should also be minimal since all were prepared and annealed in a reproducible manner.) Notwithstanding this, the heats of mixing of the hypothetical liquid polymers as a function of blend composition are shown in *Figure 2*; these are obtained from the data in *Table 2* along with the appropriate enthalpy correction. (For the mechanical mixtures, $\Delta_R H$ was taken as the weight fraction average of the pure components.) The error bars in the figure estimate the uncertainty from both the mixing calorimeter and scanning calorimeter data.

Discussion

The heat of mixing for equimolar amounts of the model compounds ethyl benzene and isopropyl benzene[2] is also indicated in *Figure 2.* The order-of-magnitude agreement for the mixing of these two liquids with the current data (using the glass to liquid correction) gives at least a measure of confidence in the method. However, contrary to expectations and (just) within the experimental confidence, $\Delta_M H$ turns out to be negative at low PS concentrations. Such a dependence of the heat of mixing on composition cannot be explained adequately in terms of contact energy interactions alone.

Contact contributions here are certainly positive, around 1 J g^{-1} as evidenced by the model compounds, although somewhat less ($\sim$0.1 J g^{-1}) when estimated by a small molecule-based group contribution such as the Guggenheim Quasi Chemical (GQC) method[17,18]. However, Flory[19,20] and other workers[21,22] have pointed out the limitations in such a simplistic approach and they propose that the overall enthalpy of mixing depends not only on purely chain–chain contact interactions but

Table 2 Heats of solution of mechanical mixtures, pure components and their blends in toluene at 333 K

PαMS/PS (w/w)	Mixture $\Delta_{soln}H$ (J g^{-1})	Blend $\Delta_{soln}H$ (J g^{-1})
100/0	–	−15.5±0.3
80/20	−16.5±0.6	−7.4±0.3
50/50	−9.2±0.2	−8.0±0.2
20/80	−8.5±0.5	−7.4±0.5
0/100	–	−6.8±0.3

The error limits quoted are the standard deviations of each set of determinations

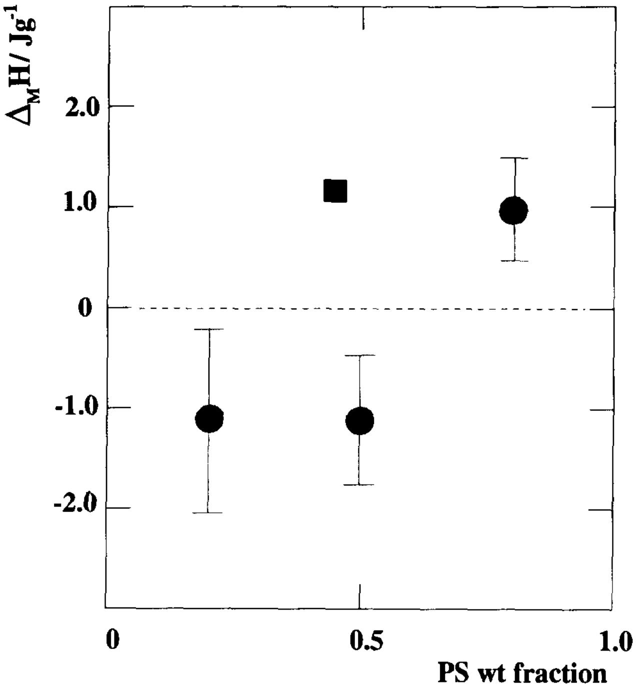

Figure 2 Heat of mixing of polystyrene with poly(α-methylstyrene) as a function of composition. The filled square is the experimental heat of mixing for equimolar amounts of ethyl benzene and isopropyl benzene taken from ref. 2

additionally on a term which takes into account the differences in the liquid structure of the pure components. From this viewpoint, and accepting a need within the present estimate of experimental uncertainty to rationalize the observed enthalpy change in mixtures with an excess of PαMS, the following is proposed.

The concept of breaking down overall molecular contact interactions into various components is well accepted[17,18,23]. In the case of PS and PαMS there are two types, aliphatic (al) and aromatic (arom), and it is supposed that in their mixtures an unfavourable enthalpy term results from the aliphatic–aromatic heterocontacts. The extent of this is proposed to be proportional to the mismatch in fractional surface areas ($\alpha_{al} - \alpha_{arom}$) of the two types[23]. According to Bondi's[24] tabulation of surface areas, for the styrene and the α-methylstyrene repeat units the α_{al} values are 0.27 and 0.39, respectively, and a positive contribution to the enthalpy of mixing should result. Now each homopolymer may also be regarded as an (equilibrium) mixture of contacting aliphatic and aromatic surfaces in which the overall number of internal heterocontacts is minimized, but always with respect to the conformational freedom allowed by chain connectivity. Since the PαMS chain is significantly more rigid than that of PS (the glass transitions differ by ~70 K) the free formation of favourable aliphatic–aliphatic and aromatic–aromatic internal contacts must be restricted. On mixing with PS it is envisaged that these conformational restrictions are somewhat alleviated and the overall effect is of a greater relative number of favourable contacts with a consequent negative enthalpy contribution. (Ref. 1 reports the T_g vs. composition behaviour for PS–PαMS mixtures. The negative deviation from linear ideality is conventionally interpreted as evidence of increased conformational freedom in the mixtures.) It appears, on this argument, that the PαMS structure is able to tolerate the intrusion of PS, with the ultimate effect of an overall lower enthalpy for the blend compared to the pure components. On the other hand, polystyrene does not in its turn benefit in a similar manner from the incorporation of PαMS chains into its internal structure.

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