

HEATS OF POLYMER MIXING

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Abstract - Properties of compatible multicomponent polymer systems can be studied quantitatively only if their fundamental thermodynamic parameters can be established. Thus measurements of mixing enthalpies in such polymer-polymer pairs is of interest in arriving at criteria for compatibility. Direct determinations are awkward, but the required parameters can be obtained from differential heat of solution measurements. The metastability of polymer blends in phase separated regions below their glass transition temperatures provides additional insight when calorimetric measures are performed below T_g . These factors are illustrated with examples of compatible, near-compatible and incompatible binary mixtures containing poly(2,6-dimethyl phenylene oxide) and polystyrene or halogenated derivatives of polystyrene.

INTRODUCTION

A quantitative understanding of the properties of compatible polymer systems - polymer blends - requires a determination of phase boundaries and of the thermodynamics (and kinetics) of the mixing process. This understanding has come about only quite recently and only in a few cases. The difficulties encountered include (1) the comparative rarity of the occurrence of miscible binary polymer systems, (2) the difficulty of establishing thermodynamic equilibrium at temperatures approaching the glass transition of the blend, and (3) the sensitivity of compatibility to effects of molecular weight (and presumably molecular weight distribution) and to changes in chemical structures of either or both of the prospective constituents, (1,2).

Several polymer-polymer blends are known to be compatible over only limited regions of the temperature-composition plane, (3). A two phase, incompatible, regime may be present at all temperatures for a given composition (usually around equal volume fractions of the constituents) or there may occur a lower critical solution temperature (LCST). Because of the difficulty in attaining equilibrium already referred to it is normally necessary for the LCST to be located some tens of degrees above the T_g for a definitive determination. It is also possible that a second, upper consolute point g (a UCST) is present in certain cases, though again direct observation of the critical temperature and associated phase boundary lying at or below T_g is not possible, (4). The research reported below describes a technique for overcoming this difficulty; in several systems evidence for the existence of a UCST has been obtained. The upper portion of Fig. 1 illustrates schematically a typical situation. It should be noted that the comparatively slow kinetics of phase separation and rehomogenization can be taken advantage of in the determination of phase boundaries in polymer-polymer systems. In establishing such a boundary it is usually not practical or desirable to attain the macroscopic phase separation or layering typically observed in low molecular systems. Instead the determination of either one or two phase states for a particular composition-temperature locus is correlated with the observation of, respectively, a single or double glass transition. It is clear that this criterion may be somewhat compromised by a lack of understanding of the relation of domain size to glass transition manifestations, (5).

The determination of the phase boundary or boundaries represents only a portion of the thermodynamic information required to characterize a polymer blend. A complete definition requires a knowledge of the free energy of mixing ΔG_m as a function of composition and temperature (from which data, of course, the phase boundary may be obtained). For binary polymer systems where each constituent is of high molecular weight it is anticipated that the entropic contribution ΔS_m to ΔG_m will be orders of magnitude smaller than in low molecular weight mixtures (though non-configurational contributions to ΔS_m itself may be significant) and that the enthalpic term ΔH_m will therefore be dominant, $m(1)$.

Experimental determinations of ΔH_m for polymer mixtures have been rare, reflecting the difficulty of such measurements. Direct measurement would appear to be unfeasible; two indirect approaches have been attempted. In the first, ΔH_m for low molecular analogies (or if possible oligomers) of the respective polymers have been measured by conventional means

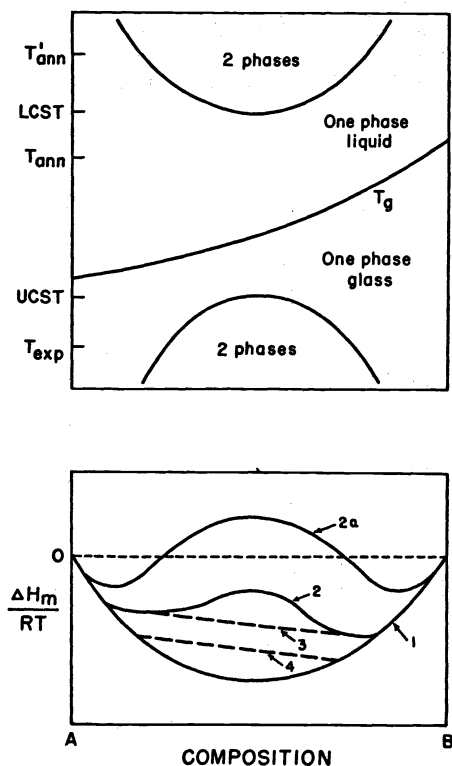
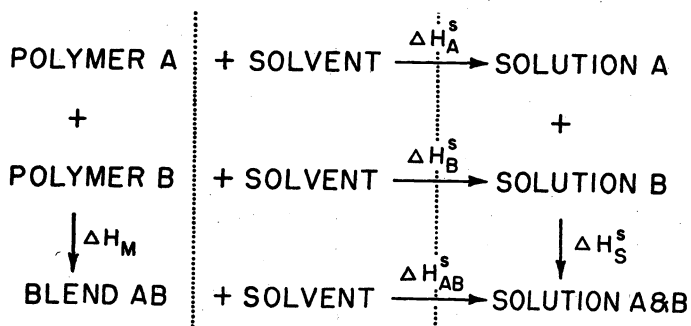


Fig. 1: (Upper): Schematic of binary amorphous polymer blend displaying two consolute points. T_{ann} and T_{exp} refer to annealing and experimental dissolution temperatures used in this study; (lower): Schematic of reduced mixing enthalpies $\Delta H_m/RT$ for systems of decreasing compatibility in the order 1,2,2a. The dashed lines 3 and 4 represent anticipated measured ΔH_m for equilibrium situations; for certain cases of metastability (see text) ΔH_m 's following curves 2 or 2a are found.

and the results applied to the polymer blend, (6). This method of course neglects molecular weight and/or configurational effects on ΔH_m and further, as is shown below, foregoes an advantage to be gained by using the metastability of polymer-polymer blends. In the second indirect technique, the heats of solution of the blend and of its constituents in a suitable solvent are measured, and ΔH_m calculated from the appropriate Hess' Law cycle, (Fig. 2) (7,8).



$$\Delta H_A^s + \Delta H_B^s + \Delta H_S^s = \Delta H_M + \Delta H_{AB}^s$$

$$\Delta H_M = a\Delta H_A^s + b\Delta H_B^s - \Delta H_{AB}^s$$

Fig. 2: Hess' Law scheme used to calculate ΔH_m from constituent and blend heats of solution. Note that ΔH_S^s is negligible provided that solutions are sufficiently dilute.

This method suffers from experimental problems of attaining adequate precision. The respective heats of solution are often substantial compared with ΔH ; this problem is aggravated by the fact that if measurements are performed below T_g , a sizable correction to obtain ΔH for the liquid standard state is required, see Fig. 93. As a result of these problems the interpretation of some earlier measurements in this area may be in doubt.

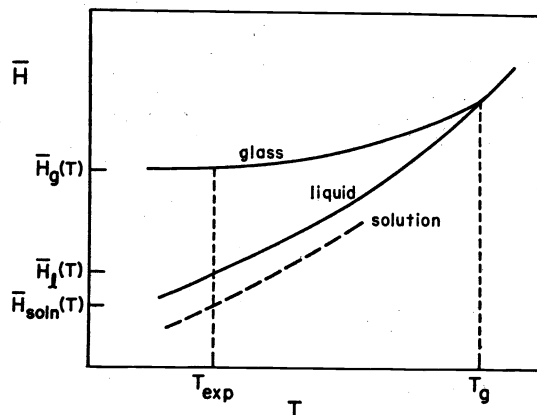


Fig. 3: Schematic of partial molar enthalpies of a polymer in the glassy, supercooled liquid, and solution states.

Polymers

The polymer systems employed in this study are based on poly(2,6-dimethyl phenylene oxide) (PPO) and halogen substituted polystyrenes (PS) or related copolymers. PPO and PS itself form a blend that appears to be compatible over all accessible domains in the phase diagram. Derivatives of PS are less compatible. Thus poly(4-chlorostyrene), for example, is totally incompatible with PPO. Therefore when increasing amounts of P4C1S are incorporated in a random copolymer with PS a transition from compatible to incompatible behavior is observed. A more detailed analysis demonstrates the appearance of an LCST, which, for this system, decreases from about 320° to 200°C as the mole fraction of 4C1S in the PS-P4C1S copolymer is increased from 0.57 to 0.75, (9,11).

A more complex situation is encountered when copolymers of 4-chlorostyrene and 2-chlorostyrene with PPO are investigated. In this case a "compatibility window" is observed; again the boundary separating one and two phase regimes represents the locus of a series of LCST's for mixtures of PPO with the respective copolymers.

PS and P2C1S are themselves compatible over certain ranges of composition and temperature, (10). In this case the location and size of the one phase regime is known to be a strong function of the molecular weight of the PS as shown by our studies in the 1×10^4 to 5×10^4 dalton interval.

Experimental

The synthesis and characterization of the polymers used in this study are described elsewhere, (12). The heats of solution of given blends and their respective constituents in 1,2 dichlorobenzene (less than 1% final solutions) were measured in a modified Tian-Calvet microcalorimeter. Blends were prepared by freeze drying solutions of the constituents followed by annealing at a specific temperature substantially above T_g , chosen to avoid (in most cases) temperatures at which incipient phase separation would occur. The heats of dissolution of the homogeneous samples were then measured either at 34.8° or 67.6°C. Typically six or more measurements of the identical samples were performed. An overall accuracy of

+ 1-2 joules/g in ΔH , was thereby obtained. Ancillary measurements of T_g 's and heat capacities (C_p) of polymers, copolymers and blends were carried out using a Perkin-Elmer DSC-2.

Results and Discussion

We consider first the simplest case, that of PPO/PS blends. The relevant thermal quantities are shown in Fig. 4. The primary measurement was the heat of solution, ΔH_s . At the temp-

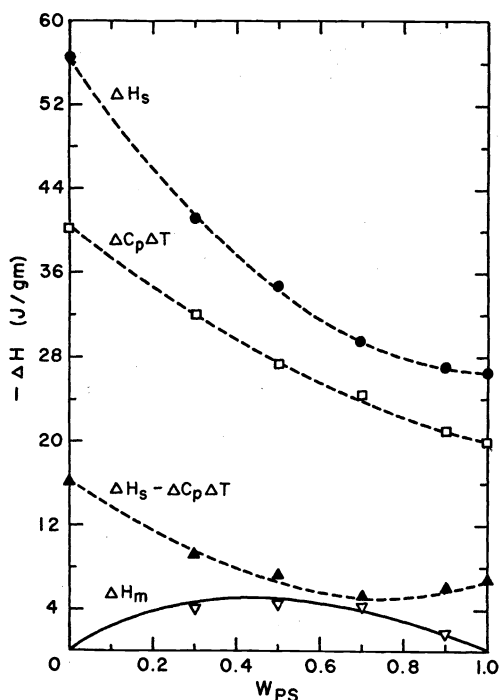


Fig. 4: Thermal quantities used in determining ΔH_m for PPO/PS blends, see text.

erature of solubilization, T_g^x , of 34.8°C, both homopolymers and their blends were below their respective T_g 's and thus a correction term $\Delta C_p \Delta T$ was required to reduce the data to the liquid standard state. ΔC_p is the change in heat capacity of the samples at their T_g 's while ΔT is the difference $T_g^x - T_g^g$. It developed that because of cancellation of higher terms this first order approximation to the glass-liquid enthalpy sufficed. The solid line in Fig. 4 represents the desired quantity ΔH_m , (13). For this system the heat of mixing is negative and (in comparison with "less compatible" systems to be discussed later) fairly large in the mid-composition ranges. It should be noted that a negative ΔH_m in itself does not imply total miscibility [see, for example, curve 2 in Fig. 1 (lower)].^m

A second application of the technique is shown in Fig. 5. In this case the blend constituents were PS, and copolymers of 4-fluorostyrene (4-FIS) and 2-fluorostyrene. Because of the proximity of the T_g 's of PS and these copolymers of any composition it was not possible to test compatibility^g in this system by the usual T_g measurements. ΔH_m measurements for all copolymer compositions (and for 50/50 weight percent blends) were effectively zero. This result is interpreted as indicating incompatibility in this system, subject to the reservation (see below) that a region of limited miscibility close to T_g may occur.

The system PS/P2C1S revealed some cases in which, for the first time, positive ΔH_m 's were measured, Fig. 6. This, of course, is normally only possible where a concomitant^m positive $T\Delta S_m$ term yields an overall negative ΔG_m . In high molecular weight binary polymer blends, the entropic contribution is considered very small; thus a positive ΔH_m would be a contradiction of this analysis. An alternative explanation is the following^m. Although the blends as prepared were compatible (as revealed in ancillary T_g measurements) it is possible that at the temperature of dissolution the equilibrium state^g corresponded to phase separation. This would normally be concealed, of course, by the metastability of the homogeneously prepared blend below its T_g . The appearance of a positive ΔH_m at the experimental dissolution temperature of 34.8°C, ^g is thus indicative of a two phase regime in this temperature region. Since it is also known that a single phase regime is present below about 200°C., at least

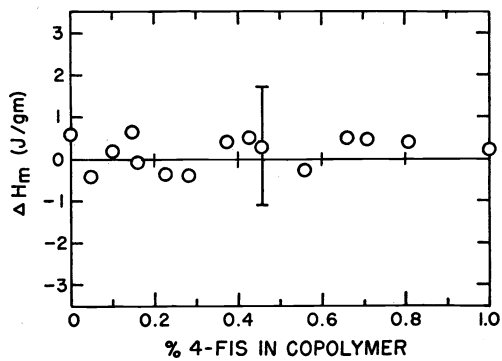


Fig. 5: Heats of mixing for blends of PS with copolymers of 4- and 2-fluorostyrene of indicated mole fraction compositions. The data refer to the ΔH_m for blends containing equal weights of PS and the respective copolymer.

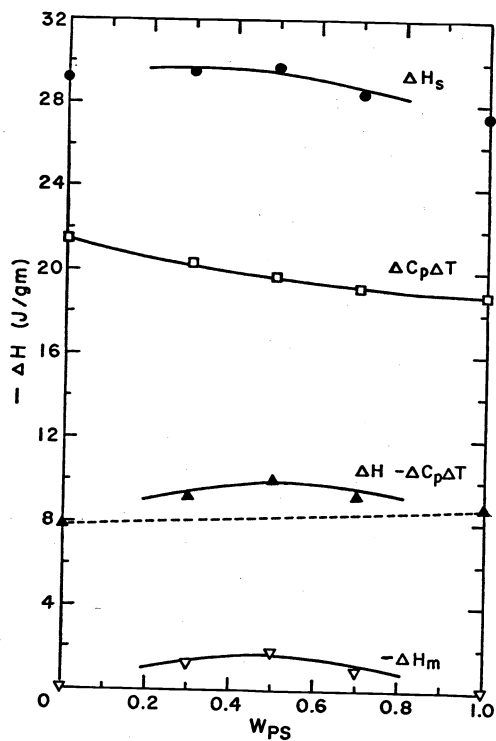


Fig. 6: ΔH_m and related thermal quantities for PS (50,000 daltons)/P2C1S blends.

to the vicinity of T_g ($\sim 120^\circ\text{C}$.), it follows that an UCST should occur at sub- T_g temperatures, (10).

A confirmation of this analysis was obtained through further studies of the PS/P2C1S system using a lower molecular weight PS (20,400 daltons). The lower molecular weight PS would be

expected to form a more compatible system with P2C1S. This was shown to be the case from the ΔH_m results, Fig. 7. Again all blends used were compatible at the annealing tempera-

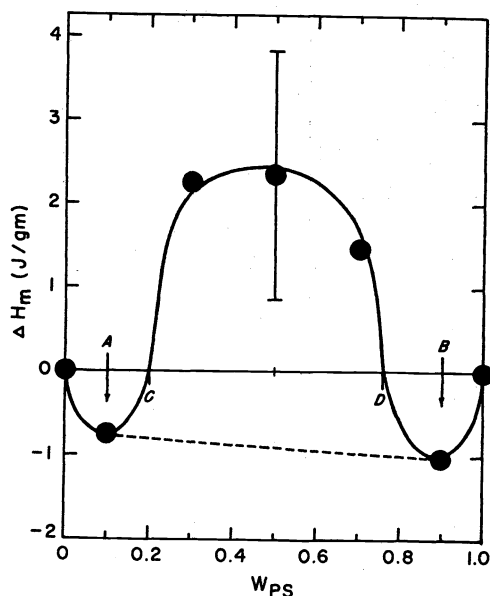


Fig. 7: ΔH_m for PS (20,000 daltons)/P2C1S blends. AB and CD represent loci of the binodal and spinodal boundaries respectively.

tures. However a positive ΔH_m was observed for blends containing between approximately 20 and 75 weight percent PS. A slightly negative ΔH_m was found at extreme compositions. This would indicate a somewhat narrowed two phase regime (compared with the 50,000 dalton blends). The exact locations of the binodal and spinodal can in principle be mapped out when equivalent data for other dissolution temperatures becomes available.

Finally a more complicated case is shown in Fig. 8 in which the polymer components used (in 50/50 weight percent blends) are PPO and copolymers of 4- and 2-fluorostyrene. As noted, this system shows a compatibility window extending (at -35°C .) from about 10 to 55 mole percent of 4-fluorostyrene, (11). The rather complicated behavior seen in Fig. 8 is then explained as follows (see Fig. 9). For copolymers containing less than 10 or more than 55 mole percent of the para-substituted isomer, initial incompatibility at annealing and at dissolution temperatures (T_{ann} , T_{ex} respectively) is observed and thus ΔH_m is again effectively zero. Approaching the nominal boundary of the compatibility window the two phase region is as schematically indicated in panel B of Fig. 9 with the appearance of a negative ΔH_m in the corresponding mixing enthalpy diagram. Further within the compatibility window, panel C, a situation analogous to the PS/P2C1S system, above, is encountered. At the center of the compatibility window the extent of the separated two phase domains are reduced (panel D, Fig. 9) and a tendency towards a negative ΔH_m is observed. The situation is then mirrored on the other side of the compatibility maximum.

The above analysis obviously suggests the possibility of confirmatory measurements involving various combinations of T_{ann} and T_{ex} . Unfortunately these are compromised by the inherent measurement errors in ΔH_m . As Fig. 8 indicates additional measurements at 67.6°C . were carried out, but the results were statistically indistinguishable from those carried out at the lower dissolution temperature.

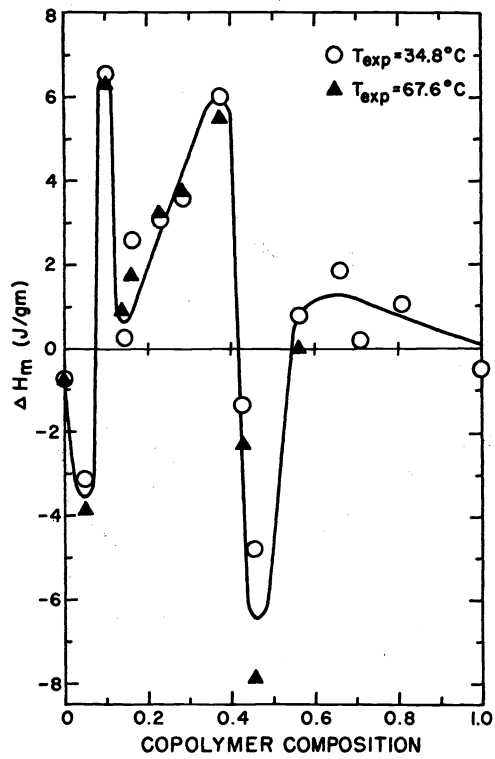


Fig. 8: ΔH_m for PPO with copolymers of 4- and 2-fluorostyrene (50/50 weight percent blends).

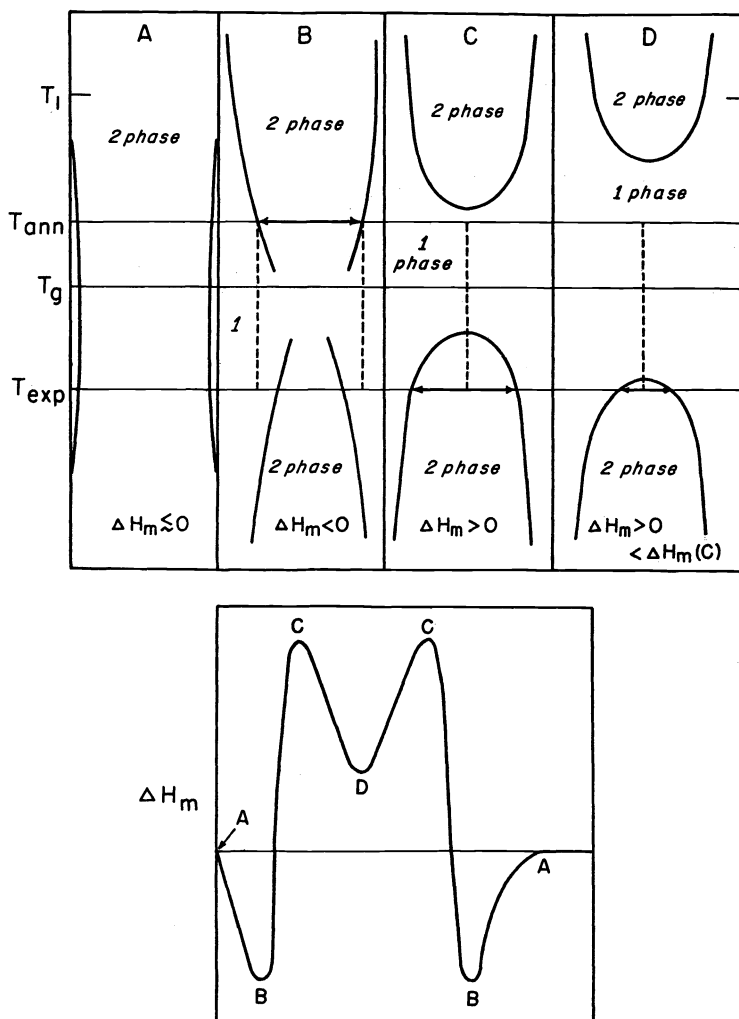


Fig. 9: (Upper): Schematic of phase diagrams for amorphous binary blends of differing miscibilities; (lower): schematic of corresponding ΔH_m 's assuming metastable homogeneous blends below T_g (shown composition independent in this simplified representation).

Conclusion

Heat of mixing measurements represent a powerful tool for the quantitative investigation of polymer compatibility. In the present study they have revealed a wealth of detail regarding phase behavior in selected systems which is inaccessible by other techniques. If it were possible to increase the precision of such determinations by an order of magnitude it would be feasible not only to determine phase boundaries above and below T_g in detail, but also to calculate, by Gibbs-Helmholtz integration, ΔG_m itself, and thereby test current theories of polymer-polymer interaction.

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