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# Enthalpy of mixing of poly(2,6-dimethyl phenylene oxide) and polystyrene

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Various compatibility criteria for polymer-polymer blends are considered and their shortcomings discussed. An unambiguous thermodynamic criteria of compatibility, the enthalpy of mixing  $\Delta H_m$ , is obtained by application of Hess's law to heat-of-solution data for blends and their components. The enthalpy of mixing for PPO/PS blends is determined by utilizing the Hess's-law approach. Consideration is given to the excess glass enthalpy contribution to  $\Delta H_m$ . Consistent with the known compatibility of PPO/PS blends, a small negative  $\Delta H_m$  is found for all blend compositions.

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## I. INTRODUCTION

The development of suitable compatibility criteria for polymer-polymer mixtures has been the subject of recent reviews on polymer miscibility.<sup>1,2</sup> As noted by MacKnight *et al.*,<sup>2</sup> criteria based upon transition behavior or optical clarity are limited by the minimum dispersed phase size detectable with each measurement technique. DSC and dynamic mechanical measurements of blend  $T_g$ 's may yield different results concerning compatibility because each method involves cooperative molecular motions occurring over different domain sizes. Other factors affecting transition or clarity-based criteria are the refractive indices of the respective phases or insufficient separation of blend constituent  $T_g$ 's. An assessment of blend homogeneity therefore requires the use of several procedures together with supplementary information concerning domain size obtained, for example, by electron microscopy.

A direct and unambiguous determination of blend miscibility can be obtained by measuring the blend free energy of mixing,  $\Delta G_m$ . A negative free-energy change is a necessary but not sufficient criterion of compatibility.<sup>3</sup> However, the high viscosities of polymers and their mixtures render experiments with bulk polymers to directly measure any of the terms in the equation

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1)$$

difficult.

The enthalpy of mixing  $\Delta H_m$ , in Eq. (1), is dominant because mixing entropy changes for polymer-polymer systems are generally small. Thus a negative  $\Delta H_m$  may be considered to be sufficient, but not necessary, to yield the negative free-energy change required for miscibility.<sup>3</sup> A negative enthalpy is to be expected in polymer mixtures where specific interactions occur between functional groups. In mixtures of nonpolar polymers the situation is not as well defined. Negative  $\Delta H_m$  values have been reported for nonpolar polymer-solvent mixtures.<sup>4</sup> However,  $\Delta H_m$  became positive as the solvent chain length increased, and Flory and co-workers<sup>5,6</sup> have utilized the equation-of-state method to predict a positive  $\Delta H_m$  in the limit where the solvent attained macromolecular dimensions.

Several methods have been used to obtain  $\Delta H_m$  for

high polymer mixtures: (1) the equation-of-state approach<sup>6,7</sup> as noted above; (2) from cohesive energy densities<sup>8</sup> as seen from the equation

$$\Delta H_m = V_m(\delta_1 - \delta_2)^2\phi_1\phi_2, \quad (2)$$

where  $V_m$  is the volume of the mixture, and  $\delta_i$  and  $\phi_i$  are the solubility parameter and volume fractions of component  $i$ , respectively; (3) from a polymer-polymer interaction parameter  $\chi$ , considered to have the same significance as  $\Delta H_m$ <sup>9-11</sup>; (4) experimentally, by applying Hess's law to heat-of-solution measurements. We note that  $\Delta H_m$  values calculated from Eq. (2) can clearly never be negative. This equation fails to take into account specific functional group interactions, or the negative volume change which occurs during the formation of compatible blends.<sup>8</sup>

The interaction parameter  $\chi$  also is not an adequate substitute for direct determination of  $\Delta H_m$ . Negative  $\chi$  values have been reported<sup>9-11</sup> indicating compatibility in blends where evidence of functional group interactions have recently been found.<sup>12</sup> However,  $\chi$  contains an entropic component and is derived from a simple lattice theory which again does not take into account the mixing volume change that occurs in compatible blends.

The Hess's-law approach for determining  $\Delta H_m$  has been used by several investigators,<sup>13-15</sup> on both amorphous compatible and incompatible blends. Unfortunately, the data on compatible blends<sup>14,15</sup> are ambiguous because no consideration has been given to possibly significant variations in the respective glassy heat contents associated with the thermal histories of the constituents and blend. Hess's law is given by

$$\Delta H_m = a\Delta H_1^s + b\Delta H_2^s - (a+b)\Delta H_{\text{blend}}^s, \quad (3)$$

where  $a\Delta H_1^s$  is the heat of solution of  $a$  moles of blend component 1,  $b\Delta H_2^s$  is the heat of solution of  $b$  moles of blend component 2, and  $(a+b)\Delta H_{\text{blend}}^s$  is the heat of solution of a blend containing  $a+b$  moles of components 1 and 2, respectively. The principal disadvantage of this method is the limited precision attainable;  $\Delta H_m$  is of relatively small magnitude in comparison with the terms on the right-hand side of Eq. (3). The relatively slow dissolution of the polymers and concomitant heat evolution requires the use of a sensitive conduction calorimeter, such as the Tian-Calvet. The latter is capable of detecting enthalpy fluxes of the order of 0.1 mcal/h from milligram-size samples.

TABLE I. Properties of PPO/PS blends.

Wt. fraction		$T_g$ (°C)
PPO	PS	
0	100	105
10	90	104
30	70	126
50	50	145
70	30	163
100	0	218

The Hess's-law approach is utilized in the present study to determine the enthalpy of mixing for the compatible blend, poly(2, 6-dimethyl phenylene oxide)/polystyrene (PPO/PS) and is part of a larger program to determine  $\Delta H_m$  for blends where polymer-polymer interactions are believed to be limited to dispersion forces.

## II. EXPERIMENTAL

### A. Materials

Blends were prepared from PPO ( $M_w = 35\,000$ ) supplied by Dr. Katchman, General Electric Co., Selkirk, N. Y., and PS supplied by Monsanto Co. Both PPO and PS ( $M_w = 270\,000$ ) were purified by dissolving in toluene and reprecipitating from an excess of methanol. The precipitates were carefully dried. Four blend compositions were prepared by freeze-drying 3-wt% benzene solutions of the mixed polymers with the desired composition. Blends were dried *in vacuo* for 72 h. Sheets 0.025 cm thick were formed by compression molding the dried materials at 280°C. The compositions prepared are listed in Table I.

Prior to use, samples cut from the molded sheets were given a precisely determined thermal history in a Perkin-Elmer DSC-II. Thus all samples were heated to 20°C above their respective  $T_g$ 's (see Table I), held at these temperatures for 10 min, and cooled at 10°C/min to room temperature.

### B. Heat-of-solution measurement

Heat-of-solution measurements were carried out in a Tian-Calvet microcalorimeter, with modifications and procedures generally similar to those described by Maron *et al.*<sup>17</sup> Polymer samples were dissolved in *o*-dichlorobenzene at 35°C without agitation. Final polymer solution concentration for the constituents and blends was <0.1%. Agitation was not found necessary to ensure adequate mixing of polymer and solvent. Polymer samples contained in a PTFE-stoppered cuvette were separated from the solvent by a mercury seal until thermal equilibrium was attained. The heat flux resulting from the cuvette-opening procedure was negligible. Heats of solution for pure PPO and PS could be measured with a precision of  $\pm 1\%$  (which is of the order of 10 cal/mol).

The actual  $\Delta H_m$  determinations were carried out with the calorimeter operated in the differential mode, in which one calorimeter cell contained a blend sample, of the order of 8 mg, while the other cell contained the nonblended constituents in the blend composition ratio.

Differential measurement permits the use of higher calorimeter sensitivities and larger samples and cancels the effect of fluctuations in calorimeter operating behavior.

Equation (4), based on Hess's law, relates the net heat flow expressed in terms of an area,  $A_{\text{net}}$ , of the experimental heat flux versus time trace to experimental variables.

$$A_{\text{net}} = \Delta H_{nB}^s \left( \frac{W_{nB}}{R_{nB}} - \frac{W_B}{R_B} \right) - \frac{W_B}{R_B} \Delta H_m, \quad (4)$$

where  $\Delta H_{nB}^s$  is the heat of solution for the nonblended sample,  $W_{nB}$  is the total nonblend sample weight,  $W_B$  is the blend sample weight, and  $R_{nB}$ ,  $R_B$  are calibration constants for respective calorimeter cells. The first term on the right-hand side of Eq. (4) was made negligible by using the appropriate ratio of nonblend to blend sample weights. Thus  $\Delta H_m$  was directly related to  $A_{\text{net}}$ . About six measurements were made for each blend composition.

Heat capacity and  $T_g$  data necessary to calculate the excess glass enthalpy contributed to the measured  $\Delta H_m$  (see Sec. III) were obtained with the DSC-II at a heating rate of 20°C/min.

## III. RESULTS AND DISCUSSION

Enthalpy of mixing values calculated from Eq. (4) and the net heat flux data are shown in Fig. 1. A negative enthalpy of mixing is found at all PPO/PS compositions. The end points corresponding to the pure constituents are necessarily zero in Fig. 1. The substantial error bars are a consequence of the subtraction inherent in Eq. (3). The absolute magnitude of the data scatter (10–20 cal/mol) is similar to that obtained in the heat-of-solution measurements of pure PPO or PS. Thus the acceptable precision of a single  $\Delta H^s$  determination has been carried through into the differential measurements and is now applied to the smaller  $\Delta H_m$  value. Some improvement in the basic precision of this technique may be anticipated.

The  $\Delta H_m$  values shown in Fig. 1 are calculated with

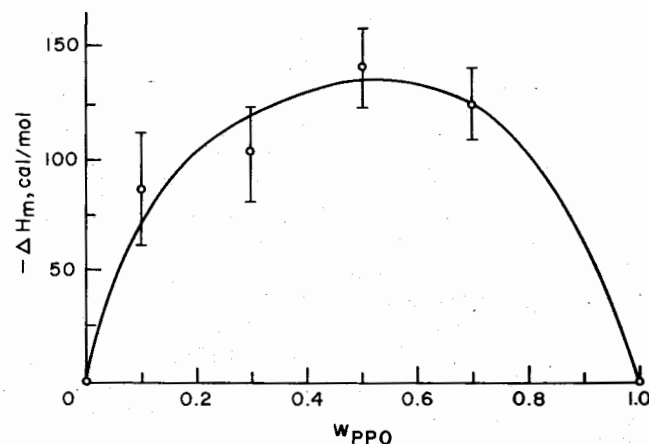


FIG. 1. Enthalpy of mixing data for PPO/PS blends as a function of weight fraction PPO,  $W_{\text{PPO}}$ .

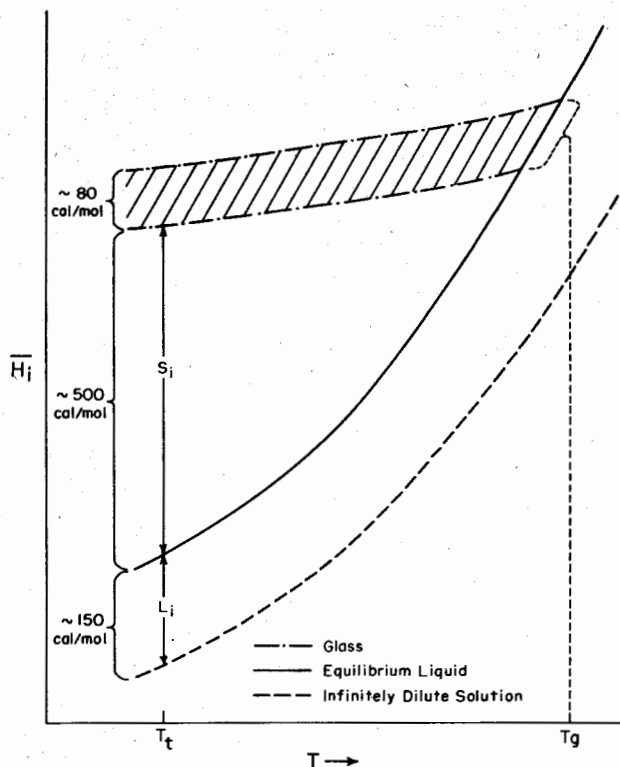


FIG. 2. Relationship between partial molar enthalpies of polymer glass, liquid, and solutions as a function of temperature. Specific data are for PS.

respect to a glassy polymer initial state. More meaningful values calculated with respect to the (extrapolated) liquid polymer initial state are obtained by subtracting the excess enthalpy of the respective polymer glasses. The interrelationships of these terms is shown schematically in terms of the partial molar enthalpy  $H_i$  of the glassy polymer below  $T_g$ , of the equilibrium polymer liquid, and of the polymer in an infinitely dilute solution. Data given in Fig. 2 correspond approximately to PS but qualitatively similar curves apply to PPO and to the respective blends.

Above  $T_g$ , the equilibrium liquid line can be derived from available  $C_p$  data. Liquid enthalpies below  $T_g$  are obtained by integration of the extrapolated  $C_p$  data. As the pure polymer liquid is cooled, the enthalpy will follow the liquid line until  $T_g$  is reached. At this point excess enthalpy is frozen in the glass and the polymer glass enthalpy line is followed at all  $T < T_g$ . An infinite number of glass enthalpy curves corresponding to a spectrum of  $T_g$ 's which depend upon sample thermal history are possible. The particular enthalpy curve of the samples used can be derived from DSC data provided that there is no reorganization in the vicinity of  $T_g$ .

Equation (3) for  $\Delta H_m$  thus can be written in terms of the heats of solution of the hypothetical liquid polymers at the measurement temperature  $T_i$  ( $35^\circ\text{C}$ ):

$$\Delta H_m^L = aL_1 + bL_2 - (a+b)L_{\text{blend}} \quad (5)$$

The polymer samples are, of course, in the glassy state at  $35^\circ\text{C}$  and the measured heat of solution for each component therefore includes two terms,  $L$  and an excess

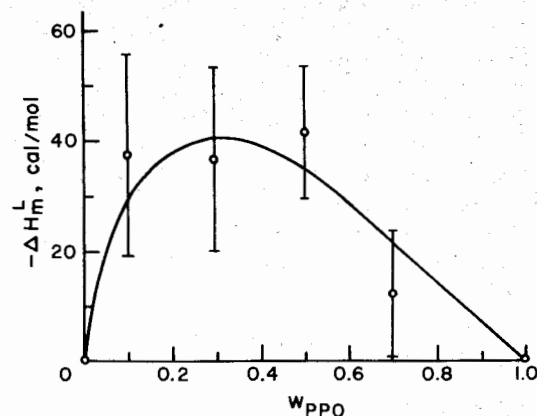


FIG. 3. Enthalpy of mixing as a function of blend composition referred to the liquid state of the constituents.

glass enthalpy  $S$ . Thus, when the differential heat-of-solution experiment is performed, the measured quantities are

$$\begin{aligned} a(L_1 + S_1) + b(L_2 + S_2) - (a+b)(L_{\text{blend}} + S_{\text{blend}}) \\ = \Delta H_m^L + \Delta H_{\text{excess}} \\ = \Delta H_m^L. \end{aligned}$$

The excess enthalpy term is subtracted from the measured  $\Delta H_m$  values shown in Fig. 1 to arrive at the required  $\Delta H_m^L$  values.  $S_i$  values are calculated from the relation

$$S_i = \int_{T_i}^{T_g} C_{p,i}^L(T) dT - \int_{T_i}^{T_g} C_{p,i}^G(T) dT, \quad (6)$$

where  $C_{p,i}^L$  and  $C_{p,i}^G$  are the temperature-dependent heat capacities of the  $i$ th constituent in the (hypothetical) liquid and glassy states, respectively.

$T_g$  values are summarized in Table I;  $C_p$  values were obtained by DSC as noted previously. For each component studied (PPO, PS, and blends), the excess enthalpy  $S_i$  is a major term in the measured heat of solution. As noted for polystyrene in Fig. 2,  $S \approx 500$  cal/mol while  $L \approx 150$  cal/mol.

$\Delta H_m^L$  values for the formation of an equilibrium liquid blend are shown in Fig. 3. The shape of the curve is somewhat changed on subtraction of the  $\Delta H_{\text{excess}}$  terms. The negative  $\Delta H_m^L$  values are, however, consistent with the known compatibility of PPO/PS blends over the entire composition range. Berghmans *et al.*<sup>18</sup> report a zero  $\chi$  value for PPO/PS blends, although it should be noted that  $\chi$  was obtained from melting-point depression data on isotactic polystyrene containing mixtures. This lack of agreement between  $\Delta H_m$  and  $\chi$  is probably due to a combination of the previously mentioned problems inherent in such a comparison and unresolved questions concerning the thermodynamic or kinetic source of the melting-point depression in crystalline blends.<sup>2</sup> It should also be noted that there are expected to be significant differences in  $\Delta H_m^L$  measured at  $35^\circ\text{C}$  and in the vicinity of the  $i$ -PS melting point.

#### IV. CONCLUSIONS

Application of Hess's law to PPO/PS heat-of-solution data produces a small negative  $\Delta H_m$  for all PPO/PS

blend compositions. Such values are consistent with the known compatibility of PPO/PS blends. In addition this is the first time a negative  $\Delta H_m$  has been reported for a compatible blend in which no well-defined functional group interactions of the hydrogen bonding or dipole-dipole type are expected and where consideration has been given to the excess glass enthalpy component of the polymers studied. The negative value of  $\Delta H_m$  is in accordance with evidence for phenyl-group coupling recently presented by Yee<sup>19</sup> and Wellinghoff and Baer.<sup>20</sup> The establishment of a thermodynamic criteria of blend compatibility by extension of the Hess's-law approach to other polymer blends is now under way.

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