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PAIR INTERACTION PARAMETER FOR COMPATIBLE POLY(STYRENE)–POLY(α-METHYLSTYRENE) MIXTURES *

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ABSTRACT

Heats of solution measurements have been performed on sharp fractions of poly(styrene), poly(α-methylstyrene) and their blends to study their compatibility and to quantify the interaction parameter of this system. The results show that the heat of mixing of the two polymers is negative and independent of the temperature at which blends are prepared; this leads to a negative value of the interaction parameter, in keeping with the general behaviour of these mixtures. The effects of the molecular weights is also discussed.

INTRODUCTION

The compatibility of two amorphous polymeric components of a binary mixture is often evaluated on a qualitative basis only, usually by measuring the glass transition temperature of the mixture, as homogeneous systems display a single value for this parameter [1,2].

The quantitative expression of compatibility is correlated with the variation in free energy occurring when crossed contacts are formed between repeating units of mixed polymers [1,2].

The thermodynamic interactions in polymer–polymer systems have been evaluated theoretically by Flory and Huggins (see refs 3 and 4), the interaction parameter χ being estimated either by the Hildebrand solubility-parameter approach or by methods needing the presence of a solvent as a third component of the mixture [1].

The subsequent theories based on the free volume concept developed by Flory and Patterson (see ref. 5) fit some experimental data, but are not easy to handle and require further investigation.

This paper sets out to provide a more reliable evaluation of χ and to separate its enthalpic χ_{12}^{H} and entropic χ_{12}^{S} contributions by calorimetric measurements.

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The relations

$$\Delta_{\mathrm{mix}}G^{\mathrm{E}} = \Delta_{\mathrm{mix}}H^{\mathrm{E}} - T\,\Delta_{\mathrm{mix}}S^{\mathrm{E}} = (v_1 + v_2)B\phi_1\phi_2 \tag{1}$$

$$\Delta_{\mathrm{mix}}H^{\mathrm{E}} = (v_1 + v_2)(B - T\,\delta B/\delta T)\phi_1\phi_2 \tag{2}$$

$$\Delta_{\mathrm{mix}}S^{\mathrm{E}} = -(v_1 + v_2)\ \delta B/\delta T\phi_1\phi_2 \tag{3}$$

$$BV = \chi_{12}RT \tag{4}$$

where v_1, ϕ_1 and v_2, ϕ_2 are the volume and volume fraction of components 1 and 2 in the blend and V is the molar volume of the repeating unit of the polymers (assumed equal to the molar volume of toluene), allow us to derive the values of χ_{12}, χ_{12}^{H} and χ_{12}^{s} when $\Delta_{\mathrm{mix}}H^{\mathrm{E}}$ and its temperature dependence is known.

$\Delta_{\mathrm{mix}}H^{\mathrm{E}}$ obviously cannot be measured by direct mixing of the two polymers. It can be estimated indirectly, with the aid of the Hess law, from measurements of the heats of solution of both 1 : 1 blends and the pure polymers in a common solvent; it follows from Scheme 1 that $\Delta_{\mathrm{mix}}H^{\mathrm{E}}$ can be calculated from the equation

$$\Delta_{\mathrm{mix}}H^{\mathrm{E}} = \Delta_{\mathrm{sol}_1}H + \Delta_{\mathrm{sol}_2}H + \Delta_{\mathrm{mix}_s}H - \Delta_{\mathrm{sol}_3}H \tag{5}$$

$$\begin{tikzcd}
\text{Polymer 1} & + & \text{Polymer 2} \arrow[r, "\Delta_{\mathrm{mix}}H^{\mathrm{E}}"] & \text{Mixture } (1+2) \\
+ & & + & + \\
\text{Solvent S} \arrow[d, "\Delta_{\mathrm{sol}_1}H"] & & \text{Solvent S} \arrow[d, "\Delta_{\mathrm{sol}_2}H"] & \text{Solvent S} \arrow[d, "\Delta_{\mathrm{sol}_3}H"] \\
\text{Solution 1} & + & \text{Solution 2} \arrow[r, "\Delta_{\mathrm{mix}_s}H"'] & \text{Solution } (1+2)
\end{tikzcd}$$

Scheme 1.

This method has received scant attention since the pioneering papers by Struminskii and Slonimskii [6], Ichihara et al. [7] and Zarev et al. [8]. We will apply it to the poly(styrene)–poly(α-methylstyrene) system to obtain χ values as a function of the molecular weight of the components and of the temperature at which blends are prepared.

EXPERIMENTAL

Materials and sample preparation

Table 1 sets out the characteristics of the polymers used. The mass distribution was always very sharp.

TABLE 1

Characteristics of the polymers used in the experiments

Sample	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	Supplier
PS 9	9000	<1.04	Polymer Laboratories
PS 20	20400	<1.07	Polymer Chemical Co.
PS 47	47000	<1.06	Polymer Laboratories
PS 115	115000	<1.04	Polymer Laboratories
PαMS 10	10500	<1.06	Polymer Laboratories
PαMS 53	53000	<1.06	Polymer Laboratories
PαMS 87	87000	<1.06	Polymer Laboratories

Blends corresponding to the weight ratio 1 : 1 were prepared by casting thin films (0.2 mm) from dilute solutions in toluene at 25 ° C. Isothermal evaporations were performed in a flat glass container, starting from 1% solutions, and the process was apparently completed after about seven days. The solvent was completely removed under vacuum at casting temperatures, until constant weight was reached. To avoid the influence of the thermal history on the heat content of the glasses, the homopolymer was also submitted to the same treatment.

Some specimens were prepared at 60 ° C with several evaporation rates.

A commercial toluene of analytical grade was used as solvent without any further purification.

Technique

The technique makes use of a Tian–Calvet microcalorimeter MS70 with a special cell designed to measure heats of solution of polymers [9].

The measurements were performed at 37 ° C. The mixing process reaches completion in about 20 min.

The quoted values of $\Delta_{sol}H$ are an average of at least four measurements. The standard deviation of the calorimetric data from the average is usually about 10% and the accuracy fits the aim of the paper; it can be improved by adding the mercury to the sample holder under vacuum.

RESULTS

The results obtained with films of PS 20 prepared at 60 ° C with several evaporation rates are reported in Table 2. They show that the heat content of a glassy specimen is strongly affected by the preparation conditions; consequently a standard procedure is required in which the equilibrium of the structure is approached at a slow evaporation rate.

TABLE 2

Heats of solutions of PS 20 films prepared at 60 °C with different evaporation rates

Evaporation rate ($cm^3\ h^{-1}$)	$\Delta_{sol}H$ ($J\ g^{-1}$)
0.04	−8.35
0.10	−7.10
0.24	−6.30

TABLE 3

$\Delta_{sol}H$ for homopolymers

Sample	$\Delta_{sol}H$ ($J\ g^{-1}$)	Sample	$\Delta_{sol}H$ ($J\ g^{-1}$)
PS 9	−9.20	PαMS 10	−8.35
PS 20	−8.35	PαMS 53	−12.95
PS 47	−5.00	PαMS 87	−16.30
PS 115	−5.00		

TABLE 4

$\Delta_{sol}H$, $\Delta_{mix}H^E$ and χ_{12} values for different molecular weights of poly(styrene) and poly(α-methylstyrene) blends corresponding to the weight ratio 1 : 1

Sample	M.W. ratio	$\Delta_{sol}H$ ($J\ g^{-1}$)	$\Delta_{mix}H^E$ ($J\ g^{-1}$)	χ_{12}
PS 9/PαMS 10	1.2	−6.70	−2.07	−0.4
PS 9/PαMS 53	5.9	−9.20	−1.87	−0.3
PS 20/PαMS 87	4.3	−9.20	−3.12	−0.5
PS 47/PαMS 53	1.1	−8.55	−0.63	−0.1

The experimental data in Table 3 show that the enthalpy of solution changes with the molecular weight of the homopolymer sample. Poly(styrene) and poly(α-methylstyrene) display opposite trends.

Values of $\Delta_{sol}H$ for some 1 : 1 weight blends are reported in Table 4. The molecular weights of the homopolymers were selected in order to produce blends miscible over the whole composition range; the molecular weight ratio between poly(α-methylstyrene) and poly(styrene) ranges from 1.1 to about 6.

DISCUSSION

As reported in a previous paper [10], measurements on specimens prepared at 25 and 60 °C suggest the conclusion that the entropic contribution to χ is zero; a negative value of χ_{12}, −0.5, was calculated. Consequently experiments were only carried out on specimens prepared at 25 °C with the slowest evaporation rates.

From the experimental data of Tables 3 and 4 and eqn. (5), and assuming $\Delta_{\mathrm{mix}}H \approx 0$, the values of $\Delta_{\mathrm{mix}}H^{\mathrm{E}}$ and χ_{12} shown in Table 4 can be estimated. A negative value of χ_{12} always results, but no general trend with the molecular weight ratio can be detected: the error affecting the χ_{12} values means that this result is possible; nevertheless, it should be noted that the smallest value of χ_{12} is obtained when both the molecular weights are quite large.

According to the Flory–Huggins theory, poly(styrene) and poly(α-methylstyrene) should be compatible over the whole range of composition and temperature.

Our results support the conclusions of Cowie and coworkers [11,12], who extensively studied the poly(styrene)–poly(α-methylstyrene) system and showed that such blends display a range of miscibilities dependent on the molecular weights of the components. Their results were elaborated according to the more recent Flory treatment of polymer–polymer mixtures [5]. The best fit with the experimental data from the phase equilibria would require a negative value of the pair-interaction parameter that could not be obtained experimentally or from the group additivity method.

Application of the Flory–Patterson theory to our data is in progress. Further experiments to explain the dependence of the solubility data on both the preparation conditions and the molecular weight of the polymer are needed.

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