Thermochimica Acta, 137 (1988) 123-128
Elsevier Science Publishers B.V., Amsterdam - Printed in The Netherlands

EVALUATION OF THE INTERACTION PARAMETER FOR POLY(STYRENE)-POLY(α-METHYLSTYRENE) MIXTURES FROM HEAT OF SOLUTION MEASUREMENTS

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(Received in final revised form May 2, 1988)

ABSTRACT

Heats of solution measurements have been performed on poly(styrene), poly(α-methylstyrene) and their blends to study their compatibility and 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 have been prepared; this leads to a negative value of the interaction parameter in keeping with the general behaviour of these mixtures.

INTRODUCTION

Poly(styrene)-poly(α-methylstyrene) blends have been studied by Krause [1-3], within the framework of the solubility parameter approach, and widely investigated by Cowie [4,5] and Robeson [6].

Cowie has shown [4] that such blends display a range of miscibilities that depends on the molecular weights of the components and the nature of the casting solvent. The effect of the temperature at which they were prepared was not studied.

The thermodynamics of the system were discussed by Cowie [5] on the basis of the more recent Flory treatment of polymer-polymer mixtures [7,8], according to which the non-combinatorial contribution to the free energy of mixing $\Delta_{\text{mix}}G$ is composed of two terms, one derived from the so-called equation of state effects and the other from contact interactions.

0040-6031/88/$03.50

The pair interaction parameter X_{12} of the Flory equation [9,10] has been calculated from the heats of mixing [11] evaluated using either the solubility parameter approach or the experimental values of calorimetric measurements on model molecules: $\Delta_{mix}H$ higher than zero leads to $X_{12}=0.15\ J\ cm^{-3}$ or $X_{12}=4.3\ J\ cm^{-3}$, respectively. A group additivity method [12] has also been considered ($X_{12}=0.7\ J\ cm^{-3}$). Positive values were obtained in all cases, but the best fit with the experimental data from the phase equilibria [4] would require $X_{12} = -0.223\ J\ cm^{-3}$ for specimens cast from toluene.

The aim of our experiments is a more reliable evaluation of $\Delta_{mix}H$ based on the measurements of the heats of solution of both 1:1 blends and the pure polymers in a common solvent; it follows from

$$\begin{tikzcd}
\begin{array}{c}\text{Polymer 1}\\ +\\ \text{Solvent S}\end{array} \arrow[d, "\Delta_{sol_1}H"] & + & \begin{array}{c}\text{Polymer 2}\\ +\\ \text{Solvent S}\end{array} \arrow[d, "\Delta_{sol_2}H"] \arrow[r, "\Delta_{mix}H"] & \begin{array}{c}\text{Mixture (1+2)}\\ +\\ \text{Solvent S}\end{array} \arrow[d, "\Delta_{sol_3}H"] \\
\text{Solution 1} & + & \text{Solution 2} \arrow[r, "\Delta_{mix_S}H"'] & \text{Solution (1+2)}
\end{tikzcd}$$

that $\Delta_{mix}H$ can be calculated from the equation:

$$\Delta_{mix}H = \Delta_{sol_1}H + \Delta_{sol_2}H + \Delta_{mix_S}H - \Delta_{sol_3}H \qquad (1)$$

This method has received scant attention since the pioneering papers by Struminskii and Slonimskii [13-15]. We will apply it to the poly(styrene)-poly(α-methylstyrene) system to obtain the values of the interaction parameter as a function of the molecular weight of the components and the temperatures at which blends are prepared.

EXPERIMENTAL

Materials and samples preparation

Two specimens of poly(styrene), PS, supplied by Polyscience and Pressure Chemical Co., were used; their molecular weights were 2.5×10^5 and 2.04×10^4 respectively; the mass distribution was unknown in the first case and very sharp

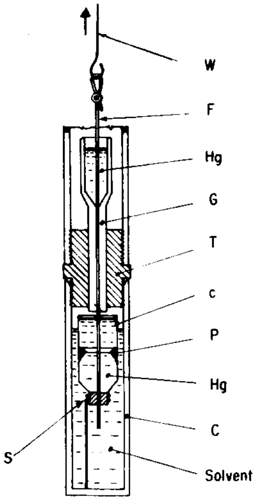

Fig. 1. Cell for calorimetric measurements of heat of solution.

($M_w/M_n<1.06$) in the second. The molecular weight of poly(α-methylstyrene), PαMS, supplied by Polymer Laboratories, was 8.7×10^4 with a narrow mass distribution ($M_w/M_n<1.07$).

Blends corresponding to the weight ratio 1:1 were prepared by casting thin films (0.2 mm) from dilute solutions in toluene at 25 and 60 °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 a vacuum, at casting temperatures, until constant weight was reached. To avoid the influence of the thermal history on the heat content of glasses [14,16,17], the homopolymers were also submitted to the same treatment.

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

Technique

The technique makes use of a Tian-Calvet microcalorimeter mod. MS70 [18]. The special cell designed to measure heats of solution [19] is shown in Fig. 1. C is the standard size cell (ϕ=17 mm and high 80 mm) fitting the interior of the calorimeter and c is a stainless steel second cell, (capacity ~4.5 cm^3), kept in position by the spring clamp S. It contains the polymer P (usually 5+10 mg) and is completely filled with mercury. The bottom of c has a hole (1 mm in diameter), normally closed by a nylon wire F (0.9 mm in diameter); due to the high surface tension, the Hg will not drop down, even though the nylon wire does not provide a tight fit. F comes out through a glass capillary G (1 mm internal diameter), whose end portion is enlarged to create a Hg pool, which, together with the good fit of C against the teflon plug T, makes the cell vapour tight. The solvent (~4.5 cm^3) is placed in C and its level almost reaches the top of c. Once the cell has been introduced into the calorimeter and the heat of friction dissipated, wire W and hence F can be raised about 2 cm from outside. The Hg drops and forces the solvent to rise and fill c. In this way, the solvent comes in contact with the polymer and starts the mixing process with very little thermal disturbance from outside.

Repeated experiments have shown the heat of the falling mercury to be exothermic, as expected.

The measurements have been performed at 37 °C. The mixing processes reach completion in about 20 mins.

RESULTS AND DISCUSSION

Table 1 brings together the experimental data for samples whose molecular weights originate blends miscible over the whole composition range according to Cowie *et al.* [4,5].

The standard deviation of the calorimetric values from the average is about 10% .

Their elaboration is quite easy from the simplest expression for the free energy of mixing based on the Flory-Huggins treatment [20,21]

$$\Delta_{mix}H = (V_1+V_2)\{B - T(\partial B/\partial T)\}\,\Phi_1\Phi_2 \qquad (2)$$

$$\Delta_{mix}S = -(V_1+V_2)(\partial B/\partial T)\,\Phi_1\Phi_2 \qquad (3)$$

$$BV/RT = \chi_{12} \qquad (4)$$

where

V_1, Φ_1 = volume and volume fraction of component 1 in the blend

V_2, Φ_2 = volume and volume fraction of component 2 in the blend

V = molar volume of the repeating unit of the polymers (assumed equal to the molar volume of toluene)

By assuming $\Delta_{mix_S}H = 0$, eqn. (1) allows to estimate the values of $\Delta_{mix}H$:

$\Delta_{mix}H^{25}$=-3.13 J g^{-1} $\qquad$ $\Delta_{mix}H^{60}$=-3.18 J g^{-1}

TABLE 1

Calorimetric data for PS 20/PαMS 87 system.

Sample		$\Delta_{sol}H^{25}$/J g^{-1}	$\Delta_{sol}H^{60}$/J g^{-1}
PS 20	$\Delta_{sol_1}H$	-8.20	-6.35
PαMS 87	$\Delta_{sol_2}H$	-16.55	-11.00
Mixture 1:1	$\Delta_{sol_3}H$	-9.25	-5.50

From eqns. (2) and (4) it follows :

$\partial B/\partial T \cong 0$ $\quad \chi_{12}^{25} = -0.56$ $\quad \chi_{12}^{60} = -0.51$

Negative values of $\Delta_{mix}H$ are in conflict with the positive values reported by Cowie [5]. They give a better reproduction of the phase boundary for toluene cast blends without any further assumption, i.e. entropy of interaction effects. This work is in progress.

Our results at all events support the conclusion that, in general, the entropy of mixing of PS with PαMS is approximately zero; therefore the free energy of mixing and the consequent compatibility between these two polymers is almost determined by $\Delta_{mix}H$. Lastly, the negative values of χ_{12} suggest some form of specific interactions between the components. The behaviour of χ_{12} vs temperature suggests that the system displays a LCST behaviour.

Preliminary results carried out on PS 250 give $\Delta_{sol_1}H^{25} = -10.0$ J g^{-1}, in excellent agreement with the results reported previously [22]. The corresponding heat of solution for the 1:1 mixture ($\Delta_{sol_3}H^{25} = -7.52$ J g^{-1}) leads to $\Delta_{mix}H^{25} = -5.77$ J g^{-1} and $\chi_{12} = -1.05$.

This value is more than twice as large as that the one calculated from PS20/PαMS87 and seems to be too high. One must take into consideration the fact that the molecular weight distribution of the PS sample is unknown, but certainly very large; the meaning of this result is therefore uncertain. According to the calorimetric analysis [23] sharp fractions have to be used; this suggesting that the influence of molecular weight needs to be investigated in depth.

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