NOTE

The Concentration Dependence of the Polymer–Solvent Interaction Parameter for Polystyrene– Methylcyclohexane System

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The molecular weight fractionation of polymers by the solubility difference has been extensively studied by Kamide and his coworkers,[1] based on the Gibbs theory and the modified Flory–Huggins dilute polymer solution theory. According to their study, for the multicomponent polymer–single solvent system, the following quantities are influenced significantly by the concentration dependence of the polymer-solvent interaction parameter χ; the average molecular weights, the molecular weight distributions, and the volume fractions of polymers existing in both the polymer-lean and polymer-rich phases, and the volume ratio of both phases. In these investigations, the concentration dependence of the χ parameter is approximately expressed by eq 1,[2]

$$\chi = \chi_0 (1 + p v_p) \qquad (1)$$

where χ_0 is a temperature-dependent, but concentration-independent parameter, v_p, the volume fraction of the polymer and the parameter p represents the concentration dependence of χ.

Kamide et al. have carried out the phase-separation and fractionation experiments for polystyrene (PS)–cyclohexane (CH),[3] PS–methylcyclohexane (MCH),[3–6] poly(α-methylstyrene) (PαMS) –CH,[7] polyethylene–cyclohexanone[8] systems. (For example, the molecular weight distribution (MWD) and the volume fraction of the polymers dissolving in the two phases, the partition coefficient and the volume ratio of the polymer-lean to the polymer-rich

phase.) The results obtained by actual fractionation were found to agree with the theoretical prediction provided p was taken as 0.6 for PS–CH and 0.7 for the PS–MCH and PαMS–CH systems. The value estimated for the PS–CH system in phase-separation is in good agreement with those determined by osmotic pressure, isothermal distillation, vapor pressure, critical misibility, and ultracentrifuge techniques.[6] The lack of reliable experimental data on p obtained by other methods independent of phase-separation for the PS–MCH system occasioned the present study, in which an attempt is made to measure the χ parameter by the high pressure membrane osmometry (HPMO).

HPMO is known to be an excellent method for determining χ in moderately concentrated solutions of polymers. In this case, the χ-parameter can be deduced from the experimental osmotic pressure π data by using the following relation given in the Flory–Huggins theory,

$$\frac{\pi \bar{V}_1}{RT} = -\left\{ \ln(1 - v_p) + \left(1 - \frac{1}{X}\right) v_p + \chi v_p^2 \right\} \qquad (2)$$

where $\bar{V}_1$ is the partial molar volume of solvent, R the gas constant, T absolute temperature, and X the polymer to solvent molar ratio.

An anionic polystyrene sample, of the weight-average molecular weight $M_w = 1.1 \times 10^5$ and of the ratio of the weight- to the number-average molecular weight M_w/M_n less than 1.06, manufactured by

Pressure Chemical Co., U.S.A., was used as the sample. Reagent-grade methylcyclohexane was distilled immediately prior to use. The osmotic pressures of the solutions of PS in MCH were measured at 72.00°C in a concentration range of about 4—33 wt%. The details of the osmometer used are described in the literature.[9] Sartorius Membranefilter SM 115 was used as a semipermeable membrane. The concentration of the solution was determined by the evaporation of known amounts of solution used for the osmometry, to dryness and weighing of the residual polymer.

The values of the χ-parameter were obtained by means of eq 2 with the observed osmotic pressure and the polymer volume fraction. The values of v_p, π, and χ are given in Table I. Reference to Figure 1 shows that the χ-parameter plotted against v_p with

Table I. Osmotic pressure π and χ-parameter for a polystyrene $(M_w = 1.1 \times 10^5)$ in methylcyclohexane at 72°C

v_p	$\dfrac{\pi}{\text{mmHg}}$	χ
0.0442	11.5	0.511
0.0849	24.2	0.529
0.1270	44.5	0.546
0.1285	48.3	0.546
0.1355	49.0	0.550
0.1651	79.0	0.561
0.1678	71.5	0.564
0.1692	75.0	0.565
0.1740	85.0	0.566
0.2806	310.5	0.615
0.3246	504.5	0.637
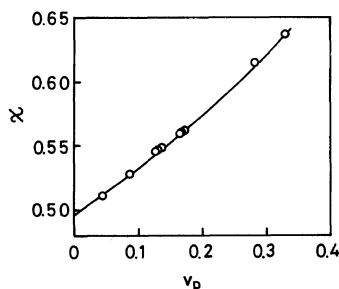
Figure 1. Plots of the χ-parameter against the polymer volume fraction v_p. Open circles represent the experimental values and the full line represents eq 3.

open circle can be reasonably represented by a full line, given by

$$\chi = 0.494 + 0.386 v_p + 0.163 v_p^2$$
$$= 0.494(1 + 0.781 v_p + 0.329 v_p^2) \qquad (3)$$

Comparison of eq 3 with eq 1 yields $p = 0.78$.

Koningsveld and Kleintjens[10] expressed the pair interaction parameter, g, in a closed form:

$$g = \alpha + \beta_0/(1 - \gamma v_p) \qquad (4)$$

where α, β_0, and γ are phenomenological parameters. Recently, Dobashi et al.[11] obtained $\alpha = 0.1091$, $\beta_0 = 0.8646$, and $\gamma = 0.2481$ for PS–MCH system at 72°C through observation of the cloud points.

The parameter p in eq 1 can be expressed in terms of the phenomenological parameter α, β_0, and γ in eq 4 in the form

$$p = 2\beta_0\gamma - (1 - \gamma)/(\alpha + \beta_0 - \beta_0\gamma) \qquad (5)$$

Then, we obtain $p = 0.60$ at 72°C from Dobashi et al.'s data.[11]

In summary, p was found to be 0.7 by phase separation,[4] 0.78 by osmotic pressure and 0.6 by the cloud point method.[11] These values are fairly close to each other, if the difference of the measuring method and of the theoretical background are taken into account. We thus conclude that the additional experiments reported here again confirms the validity of the modern fractionation theory, based principally on a modified Flory–Huggins solution theory and the Gibbs phase rule.

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