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Light Scattering from Polymer Blend Solutions. 6. Temperature Dependence of Interaction Parameter

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Dilute bromobenzene solutions of polymer blends polystyrene/poly(methyl methacrylate), polystyrene/polyisoprene and polystyrene/polysisobutylene were studied by light scattering under an "optical 0" condition, and the polymer-polymer interaction parameter \( \chi_{12} \) was evaluated as a function of temperature. The segment-segment interaction parameter \( \chi_{12}^0 \) estimated on the basis of the \( \chi_{12} \) and other information was found to decrease with an increase of temperature in all the systems, indicating a USCT behavior in the bulk in the studied temperature range (from about 20°C to about 80°C).

KEY WORDS: Polymer-polymer interaction parameter/Compatibility/Excluded volume effect/UCST/

INTRODUCTION

In previous papers\(^1\text{-}\text{3})\), we have studied dilute solutions of some polymer blends by means of light scattering carried out under the special condition termed "optical 0". This method has proved to allow much more precise determination of the polymer-polymer interaction parameter \( \chi_{12} \)\(^4\) than the classical method.\(^5\) On the basis of this phenomenological parameter and other information, we have estimated the segment–segment interaction parameter \( \chi_{12}^0 \) by the aid of the excluded-volume theory.\(^6\) This "molecular" parameter \( \chi_{12}^0 \) was found to be in fact independent basically of molecular weight, blend composition and solvent, and rather similar in value to the corresponding parameter for the bulk systems (see Ref. 7 for a review).

The purpose of this paper is to study the temperature dependence of the parameters \( \chi_{12} \) and \( \chi_{12}^0 \) for the same systems. Our central interest is to predict through \( \chi_{12}^0 \) the behavior of the dry blends, e.g., upper critical- versus lower critical solution temperature behavior (UCST vs. LCST). We compare results with corresponding data for the bulk systems, whenever such are available.

EXPERIMENTAL

The molecular characteristics of samples of polystyrene (PS), poly(methyl methacrylate) (PMMA), polyisoprene (PIP) and polyisobutylene (PIB) are listed in Table I. All the
Table I Characteristics of Polymer Samples.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Code</th>
<th>$10^{-4}M_{w_{a}}$</th>
<th>$M_{w_{a}}/M_{o}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>PC200&lt;sup&gt;c&lt;/sup&gt;</td>
<td>183 (179)</td>
<td>1.30</td>
</tr>
<tr>
<td>PS</td>
<td>S 50&lt;sup&gt;d&lt;/sup&gt;</td>
<td>51.0 (51.5)</td>
<td>1.03</td>
</tr>
<tr>
<td>PS</td>
<td>F10&lt;sup&gt;e&lt;/sup&gt;</td>
<td>(10.2)</td>
<td>(1.02)</td>
</tr>
<tr>
<td>PMMA</td>
<td>75M&lt;sup&gt;f&lt;/sup&gt;</td>
<td>214</td>
<td>1.35</td>
</tr>
<tr>
<td>PIB</td>
<td>B50&lt;sup&gt;g&lt;/sup&gt;</td>
<td>54.3</td>
<td>1.43</td>
</tr>
<tr>
<td>PIP</td>
<td>113&lt;sup&gt;b&lt;/sup&gt;</td>
<td>(14.3)</td>
<td>(1.04)</td>
</tr>
</tbody>
</table>

a) Determined by light scattering (nominal value is in parentheses).
b) Determined by GPC (nominal value is in parentheses).
c) Pressure Chemicals Co. d) Showa Denko Co.
e) Toyo Soda Co. f) See Ref. 1. g) Fraction of a commercial polymer. h) Polymer Laboratories Co.

samples have a narrow or reasonably narrow distribution in molecular weight (for the sample sources, see the footnotes for Table I). The volume fraction $\phi_i$ and the degree of chain length $m_i$ of polymer i (= 1 or 2) were calculated with

$$\phi_i = \frac{w_i v_i}{w_0 v_0 + w_1 v_1 + w_2 v_2}$$

$$m_i = \frac{M_i}{w_i v_i / V_0}$$

Here $w_i$ is the weight fraction, $v_i$ is the specific volume in the pure state, $M_i$ is the weight-average molecular weight, and $V_0$ is the molar volume of solvent ($i=0$, 1 or 2 with 0 denoting the solvent and thus $m_0=1$). The values of $v_1$ and $v_2$ were assumed to be given by the following relations determined for the liquid polymers:

$$v_1 = 0.9199 + (5.08 + 2.354 \times 10^{-3} t) \times 10^{-4} t$$  \hspace{1cm} (PS)<sup>8</sup>

$$v_2 = 0.9096 + 5.04 \times 10^{-4} t$$  \hspace{1cm} (PMMA)<sup>9</sup>

$$= 1.080 + 6.89 \times 10^{-4} t$$  \hspace{1cm} (PIP)<sup>10</sup>

$$= 1.077 + 6.45 \times 10^{-4} t$$  \hspace{1cm} (PIB)<sup>11</sup>

where $t$ is the temperature in °C

The refractive index increment of the polymers in bromobenzene were determined on a Union Giken differential refractometer Model RM102, Japan. The following relations were found for the temperature range $20^\circ \text{C} \leq t \leq 60^\circ \text{C}$.

$$\frac{dn}{dc} = 0.0399 + 3.10 \times 10^{-4} t$$  \hspace{1cm} (PS)

$$= -0.0599 + 3.33 \times 10^{-4} t$$  \hspace{1cm} (PMMA)

$$= -0.0533 + 2.73 \times 10^{-4} t$$  \hspace{1cm} (PIP)

$$= -0.0823 + 3.80 \times 10^{-4} t$$  \hspace{1cm} (PIB)

where $c$ is polymer concentration in g mL<sup>-1</sup>. These relations are assumed to be valid even for temperatures somewhat higher than $60^\circ \text{C}$, because precise determination of $\frac{dn}{dc}$ was difficult for that temperature range.

Light scattering measurements were made on a Fica light scattering photometer Model 50, France, by using a vertically polarized light of 436 nm. Each solution was composed of
Light Scattering of Polymer Blend Solutions

Table II  Light Scattering Results for PS/PMMA, PS/PIB and PS/PIP in Bromobenzene at Several Temperatures.

<table>
<thead>
<tr>
<th>Polym.-1</th>
<th>Polym.-2</th>
<th>t (°C)</th>
<th>([\eta_1]) (dL g(^{-1}))</th>
<th>([\eta_2]) (dL g(^{-1}))</th>
<th>(\chi_{12})</th>
<th>(\chi_{12}')</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS PC2000</td>
<td>PMMA 75M</td>
<td>15</td>
<td>4.19</td>
<td>2.93</td>
<td>0.0029</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>4.12</td>
<td>3.23</td>
<td>0.0028</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90</td>
<td>4.07</td>
<td>3.43</td>
<td>0.0023</td>
<td>0.030</td>
</tr>
<tr>
<td>PS S50</td>
<td>PIB B50</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td>0.428</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>1.65</td>
<td>1.29</td>
<td>0.0224</td>
<td>0.301</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>1.63</td>
<td>1.54</td>
<td>0.0194</td>
<td>0.226</td>
</tr>
<tr>
<td>PS F10</td>
<td>PIP I13</td>
<td>20</td>
<td>0.48</td>
<td>0.98</td>
<td>0.0189</td>
<td>0.124</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td>0.149</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>0.48</td>
<td>1.03</td>
<td>0.0134</td>
<td>0.077</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90</td>
<td>0.48</td>
<td>1.06</td>
<td>0.0119</td>
<td>0.064</td>
</tr>
</tbody>
</table>

a) Average value from Ref. 6.  b) Average value from Ref. 3.

A PS and one of the other polymers of a similar molecular weight, blended in such a ratio as to meet the optical \(\theta\) condition represented by eq. (3) at each temperature:

\[
\phi_i m_i x_i + \phi_2 m_2 x_2 = 0 \tag{3}
\]

where \(\phi_i = \frac{\partial n}{\partial c_i} = \frac{\partial n}{\partial c_i / \phi_i}\) and \(x_i = \phi_i / \phi\) with \(\phi = \phi_1 + \phi_2\) being the total concentration of polymers.

The intrinsic viscosiety \([\eta]\) of each polymer in bromobenzene was determined at the relevant temperatures. The hydrodynamic expansion factor \(a_\eta\) is evaluated by

\[
a_\eta = \frac{[\eta]}{K_0 M_i^{1/2}} \tag{4}
\]

with values of \(K_0\) (in mLg\(^{-1}\)) of 0.079 for PS, 0.049 for PMMA, 0.097 for PIP and 0.112 for PIB.\(^3\) The temperature dependence of \(K_0\) is small enough to be neglected for the present purpose. Then, \(a_\eta\) is used to evaluate the excluded-volume parameter \(Z\) according to the semiempirical relation\(^3\)

\[
a_\eta = 1 + (7/5) Z \tag{5}
\]

Thus-estimated \(Z\) is used to estimate, on the basis of the theories\(^6\), the mean-square radius \(<S^2>\) and other parameter values necessary for later analysis. Values of \([\eta]\) are listed in Table II.

**RESULTS AND DISCUSSION**

When the condition in eq. (3) is met, the forward scattering intensity \(R_0\) can be represented simply by\(^1\)\(^3\)

\[
K\phi / R_0 = (m_1 x_1)^{-1} + (m_2 x_2)^{-1} - 2 x_{12} \phi + \cdots \tag{6}
\]

where \(K\) is a constant proportional to \((\phi_1 - \phi_2)^2\). Thus the parameter \(\chi_{12}\) is determined from
the initial slope of the $K\phi/R_\theta$ vs. $\phi$ plot without regard to the solvent-polymer interactions.

Figures 1-3 show the plot experimentally obtained. Values of $R_\theta$ were determined by the conventional angular extrapolation method of Zimm. In all cases, the plot gives a well-defined initial slope. Values of $\chi_{12}$ are listed in Table II.

In each system, $\chi_{12}$ is positive and decreases with increasing temperature. From this result, one would expect that compatibility in these systems is improved by raising the temperature. This is presumably correct but not conclusively, because $\chi_{12}$ is merely a phenomenological parameter akin to the excess second virial coefficient $\Delta B^{13}$, which reflects not only the degree of compatibility or incompatibility of the parent polymers but also the excluded volume effect between them. We have discussed this matter in a previous paper, wherein $\chi_{12}$ was given in the form

$$\chi_{12} = (1 - \chi_{11} - \chi_{22} + \chi_{12})h_0(\mathcal{Z}_{12})$$
$$- \frac{1}{2}[(1-2\chi_{11})h_0(\mathcal{Z}_{11})+(1-2\chi_{22})h_0(\mathcal{Z}_{22})]$$

(7)

Here $h_0(\mathcal{Z}_{ij})$ is the function, appearing in the theory of the second virial coefficient$^{14}$, that describes the excluded volume effect between molecules $i$ and $j$ (=1 or 2), and $\chi_{ij}$

Fig. 1. Plot of $K/R_\theta$ vs. $\phi$ for PS/PMMA/bromobenzene solutions under optical $\theta$ conditions.
Fig. 2. Plot of $K_\phi/R_0$ vs. $\phi$ for PS/PIP/bromobenzene solutions under optical $\theta$ conditions.

Fig. 3. Plot of $K_\phi/R_0$ vs. $\phi$ for PS/PIB/bromobenzene solutions under optical $\theta$ conditions.
characterizes the interaction between segments $i$ and $j$ (0, 1 or 2). On the basis of the equations of $Z_{i2}$ and $h_0$ proposed in Ref. 6, eq. 7 can be numerically solved for $\chi_{i2}^0$ provided that values of $\chi_{i2}$, $\chi_{i2}^0$ and $< S_i^2 >$ are known (for the latter two quantities, see the section under Experimental). Values of $\chi_{i2}^0$ thus estimated are given in Table II.

Figure 4 shows $\chi_{i2}^0$ as a function of inverse temperature. In each system, $\chi_{i2}^0$ decreases with increasing temperature, indicating a UCST behavior in the bulk system. In the examined temperature range, the PS/PIB system has the largest $\chi_{i2}^0$ and the largest dependence on temperature, while the PS/PMMA system is the smallest in both respects.

As to PS/PIP, Mori, Hasegawa and Hashimoto$^{15}$ recently studied the X-ray scattering from a dry, disordered PS-PIP block copolymer to determine $\chi_{i2}$ as a function of temperature. Part of their result is indicated by the broken curve in Figure 4, to which our $\chi_{i2}^0$ data are rather close. Benoit et al.$^{16}$ have studied a block copolymer of PS-PMMA type by neutron scattering and suggested a $\chi_{i2}$ value about 0.005 at 160°C. This value seems to be, though not in close agreement, compatible in the order of magnitude with the value about 0.02 expected from our data for that temperature. Koningsveld and Kleintjens$^{17}$ have studied the phase behavior of a low–molecular weight blend of PS/PIB in bulk. They observed strong composition dependence of the interaction parameter $g_{i2}$ in their system. For this reason, comparison of the solution– and the bulk data would make no strict sense. We only note that our $\chi_{i2}^0$ is generally comparable in the order of magnitude with their $g_{i2}$, but that in the light of their result, the temperature dependence of our $\chi_{i2}^0$ seems somewhat unreasonably large.

In conclusion, dilute solutions of a polymer blend provide at least semi–quantitative information on compatibility behavior of the polymers in bulk.

![Fig. 4. Values of $\chi_{i2}^0/V_0$ as a function of inverse temperature: $V_0$ is the molar volume of solvent (or segment) in mL/mol, and the broken curve shows part of the $\chi_{i2}$ data for a dry PS–PIP block copolymer from Ref. 15.](image)
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REFERENCES