Concentration Dependence of Thermodynamic Interaction Parameters in A Polymer-Polymer-Solvent System

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Summary.

The concentration dependence of Thermodynamic Interaction Parameters is reported for the system Polystyrene (PS, $M_{w_3} = 4.4 \cdot 10^5$) – Polybutylmethacrylate (PBMA, $M_{w_2} = 2.7 \cdot 10^5$) – CCl_4.

Introduction.

The only evaluation of thermodynamic interaction parameters between two polymers in a common solvent was performed for critical conditions by Van den Esker[1]. For two polymers in a suitable solvent such data were obtained only for varying concentrations of one of the polymers and constant concentrations of the other[2]. To date, no data exist on the concentration dependence of interaction parameters of two polymers in a common solvent while concentrations of both components are changed. According to Scholte[3] interaction parameters are supposed to be estimated from the angular dependence of scattered light intensities by the polymer mixtures in solution. Scholte derived the equation by describing the scattered light intensity for the mixture of two polymers in a common solvent:

$$R_{\theta\, \theta=0}^{(c)} = \frac{4\pi^2 n^2}{N\lambda^4} \cdot \frac{1}{\rho} \left[\left(\frac{dn}{dw_2}\right)^2 M_{w_2}(1+K_{22}W_3 M_{w_3}) + \left(\frac{dn}{dw_3}\right)W_3 M_{w_3}(1 + K_{11}W_2 M_{w_2}) - 2\left(\frac{dn}{dw_2}\right)\left(\frac{dn}{dw_3}\right)K_{12}W_2 W_3 M_{w_2} M_{w_3} \right] / \left[(1+K_{11}W_2 M_{w_2})(1 + K_{22}W_3 M_{w_3} - K_{12}{}^2 W_2 W_3 M_{w_2} M_{w_3}) \right]$$

(1)

M_{w_2} and M_{w_3} are the molecular masses of PBMA and PS, ρ the mixture density, n the refraction index for the mixture, λ the wave length, dn/dw_i the increments of refraction indices of polymers, w_i their mass fractions in the mixtures, and the parameters K_{ij} are expressed by equations:

$$K_{11} = \frac{1}{M_o} \left[\frac{1}{1-w_2-w_3} + \frac{d^2\psi}{dw_2^2} \right] \tag{2}$$

$$K_{22} = \frac{1}{M_o} \left[\frac{1}{1-w_2-w_3} + \frac{d^2\psi}{dw_3^2} \right] \tag{3}$$

$$K_{12} = \frac{1}{M_o} \left[\frac{1}{1-w_2-w_3} + \frac{d^2\psi}{dw_2 dw_3} \right] \tag{4}$$

$$\psi = w(1-w)g \tag{5}$$

Here, g is the van Laar parameter of thermodynamic interaction and M_o is the molecular mass of a solvent.

Experimental.

The values of parameters K_{ii} are determined from intensities of scattered light by individual polymers at a given concentration in solution, extrapolated to a zero scattering angle by the equation:

$$\left[R_\theta^{(c)} \right]_{\theta=0} = \frac{4\pi^2 n^2}{N\lambda^4} \cdot \frac{1}{\rho_i} \cdot \frac{dn}{dw_i} \cdot \frac{w_i M_{w_i}}{1 + K_{ii} w_i M_i} \tag{6}$$

From Eqs. (2) and (4) the values $\frac{d^2\psi}{dw_2}$ $\frac{d^2\psi}{dw_3}$, and $d^2\psi/dw_2 \cdot dw_3$ and from Eq. (6) values of g may be found. The values for $d^2\psi/dw_i$ may be transformed into corresponding values of interaction parameters between individual polymers and solvent and between solvent and polymer mixture.

To calculate the interaction parameter g_{23} between two polymers in the mixture we have used the following equation:

$$g_{1(23)} = g_{12}w_2 + g_{13}w_3 - g_{12}w_1w_2 - g_{13}w_1w_3 - g_{23}w_2w_3 \tag{7}$$

where g_{1i} and g_{1j} are interaction parameters for the indi-

vidual polymers and solvent, $g_{1(23)}$ is the same parameter
for the polymer mixture and solvent, w_1 and w_i are the mass
fraction of solvent and i-th polymer in mixture.

The experimental methods of light scattering
measurements, solution preparation, and other procedures to
obtain $\left[R_\theta^{(c)}\right]_{\theta,0}$ have been carried at following the description
by Allen et al.[5].

Results and Discussion.

Figure 1 shows the dependence of interaction parameters
g_{23} between two polymers in solution on composition, calcu-
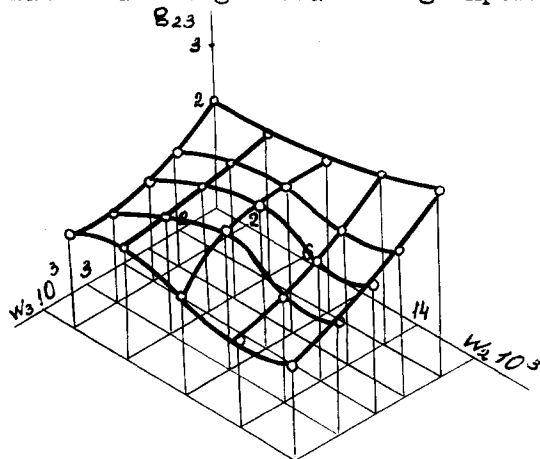lated from light scattering experiments.

Fig. 1. The dependence of
interaction parameters g_{23}
between two polymers in
solution on composition.

The positive values of interaction parameter g_{23} testi-
fies two polymers to be incompatible in a two-phase system,
PS-PBMA[6] stays incompatible in solution as well. That means
that polymer coils do not interpenetrate and do not form any
associates. At the same time the solution of two polymers in
a common solvent is transparent being a thermodynamically
stable system.

The latter statement follows both from negative values
of the thermodynamic interaction parameter between solvent
and mixture of two polymers $(g_{1(23)})$ and from its dependen-
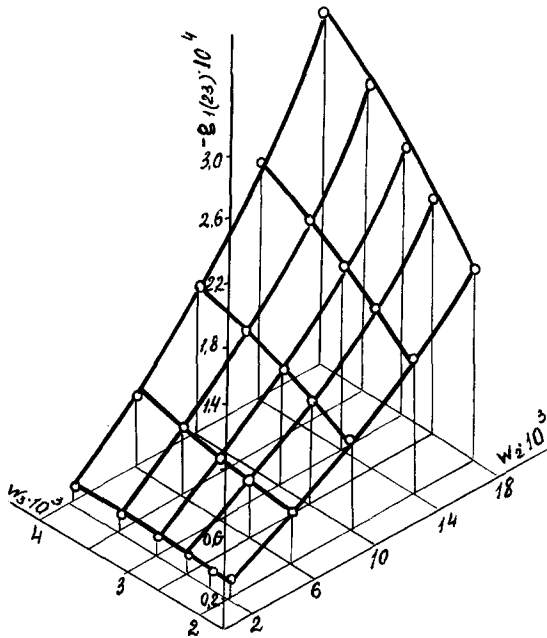ce on mixture composition (Fig. 2).

Fig.2. The dependence of interaction parameters $g_{1(23)}$ between solvent and mixture of two polymers on composition.

It is seen that with small additives as PBMA (w_2) the value $g_{1(23)}$ does not change with increasing concentration of another polymer as PS(w_3) whereas growth of the PBMA fraction at a constant PS concentration leads to a decreasing interaction parameter. Carbon tetrachloride, a good solvent for each polymer[7] preserves the thermodynamic qualities in the mixture; as a result the thermodynamically stable compatible system is formed.

PMR-spectroscopy data on molecular motion in solutions of individual polymers and their mixtures shows[8] that dissolution of the second polymer in the solution of the first one does not change the molecular mobility of each polymer as compared with solutions of individual polymers.

These data in combination with positive values g_{23} allow the conclusion that in solution of a common solvent both polymers preserve their individuality and do not form common entanglement networks.

As follows from Fig. 1, interaction parameters for two polymers in mixture g_{23} in a common solvent practically does not change with growing PBMA concentration at constant

concentrations and vice versa. In any case these values stay positive of all concentration levels. Similar dependence of interaction parameters of polymer mixtures in common solvents was observed [2,5]. Such a picture easily may be explained by component segregation leading to a decreasing number of contact 2-3 between macromolecules.

Thus, the ternary system $PS-PBMA-CCl_4$ exhibits new peculiarities: thermodynamically incompatible polymers PS and PBMA form a thermodynamically stable system in a common solvent where both polymers preserve their individual features and interpenetration of coils does not take place.

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