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On Polymer Mixture Thermodynamics†

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The object of this note is to draw attention to an important relationship which exists between certain parameters in two different considerations of the entropy change involved in the mixing of two polymers. On one hand, we extend Silberberg's treatment of polymer solutions[2] which yields the original Flory–Huggins[3,4] entropy of mixing expression upon the introduction of a simplifying assumption. Second, we consider Huggins' recent refinement of the theory which deals with entropy changes involved in the variation of the immediate surroundings of a polymer segment when the composition of the solution is changed.[5–7]

Extending Silberberg's treatment to a mixture of two polymolecular homopolymers 1 and 2 we can write for the total number of configurations Ω_{1+2}:

$$\Omega_{1+2} = \frac{\left(\sum_i N_{1i}m_{1i} + \sum_j N_{2j}m_{2j}\right)!}{\prod_i (N_{1i}!) \prod_j (N_{2j}!)} \times \prod_i (V_{1i}^*(\phi_1)/V)^{N_{1i}(m_{1i}-1)} \prod_j (V_{2j}^*(\phi_2)/V)^{N_{2j}(m_{2j}-1)} \quad (1)$$

where N_{1i} and N_{2j} are the numbers of molecules of species i in polymer 1 and species j in polymer 2. The relative chain lengths m_{1i} and m_{2j} are measured in arbitrary units; with polymer solutions the size of the solvent molecules usually serves as a yard stick. The "parametric" volume V^* was introduced by Silberberg to correct for the gross overestimation of the number of configurations involved in the term containing the factorials. Once the first segment of a polymer chain is placed somewhere in the total volume V, the volume available to any of the next $(m - 1)$ segments is restricted to a parametric volume V^* surrounding the preceding segment. Silberberg shows that assuming V^* to be independent of the composition of the mixture leads to an entropy of mixing expression identical with the original Flory–Huggins equation.[2]

We prefer to retain a possible concentration dependence and derive the free enthalpy (Gibbs free energy) of mixing ΔG_ϕ per mole of polymer segments in the usual way, adding to the entropy terms a Van Laar-type heat of mixing, $g\phi_1\phi_2$:

$$\Delta G_\phi/RT = \sum_i \phi_{1i}m_{1i}^{-1}\ln\phi_{1i} + \sum_j \phi_{2j}m_{2j}^{-1}\ln\phi_{2j} + g\phi_1\phi_2 - \sum_i \phi_{1i}(1 - m_{1i}^{-1})\ln\tau_{1i} - \sum_j \phi_{2j}(1 - m_{2j}^{-1})\ln\tau_{2j} \quad (2)$$

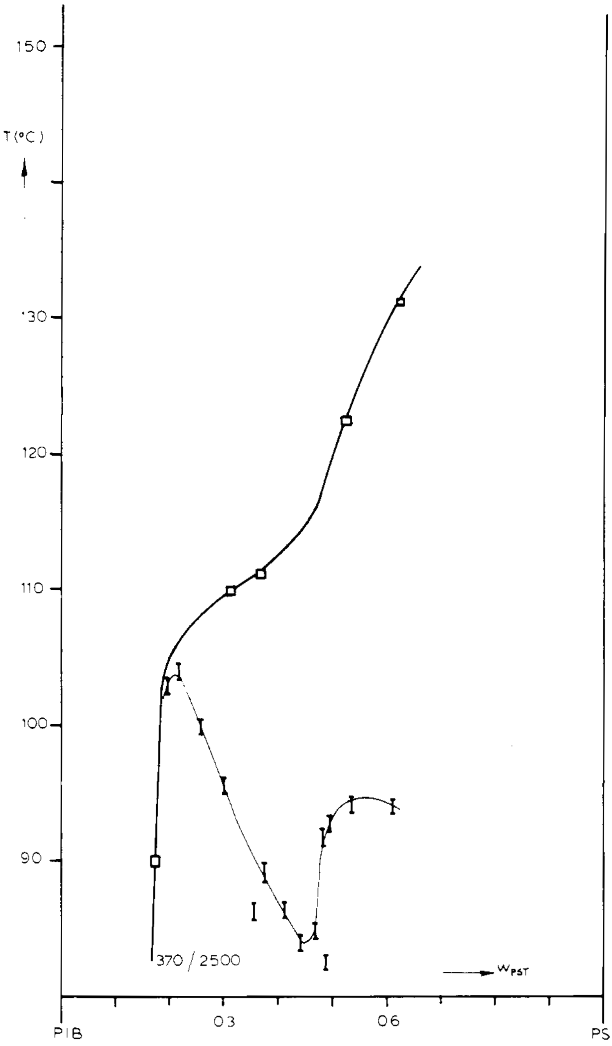

Figure 1. Cloud-point curve (□) and spinodal (by pulse induced critical scattering[14,15]) (**I**) for a polyisobutylene/polystyrene system (molecular weights indicated); $w_{\rm pst}$ is the weight fraction of polystyrene.

where ϕ denotes a volume fraction ($\Sigma_l\phi_{kl} = \phi_k$, the volume fraction of whole polymer k), τ_{kl} stands for $V_{kl}^*(\phi_k)/V_{kl}^*(1)$, and RT has its usual meaning. Silberberg's simplifying assumption ($\tau_{kl} = 1$) reduces eq 2 to the original Flory–Huggins expression for a mixture of two polymolecular polymers (the first three terms on the rhs).

For reasons outlined below it seems useful to compare eq 2 with Huggins' more recent expressions[5–7] in which he, like Flory et al.,[8–10] introduces the interacting surfaces of the segments. It is thus possible to allow for a disparity between the interacting surfaces (volumes) of segments 1 and 2. This considerably relaxes the rigidity of the original lattice model (one and the same coordination number for both types of segment), and, i.e., appears to accommodate the experimentally well-known concentration dependence of the interaction parameter g.[11] Huggins' considerations[5,6] lead to an expression for g which, for random mixing, reads

$$g = \beta\,[1 - (1 - \rho)\phi_2]^{-1} = \beta Q^{-1} \quad (3)$$

Here, $\rho = (\sigma_2/\sigma_1)/(v_2/v_1)$, with σ_k and v_k the contact area and molecular volume, respectively, of the segments of polymer k, and $\beta = \sigma_2\Delta\epsilon/2RT$, with $\Delta\epsilon$ = the interchange energy (cf. ref 5 and 6). Equation 3 is used below for relating g to T when

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† Dedicated to Dr. Maurice L. Huggins on the occasion of his 80th birthday.

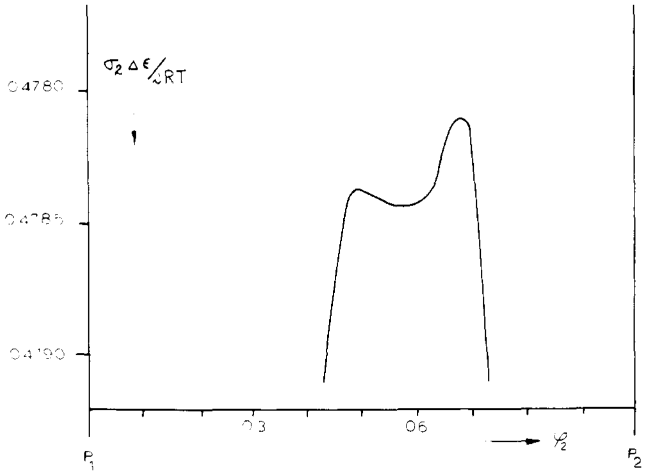

Figure 2. Spinodal calculated with Huggins' eq 4 for $m_1 = 7.2$ and $m_2 = 45$; $k_1 = -0.69$, $k_2 = +0.91$, $\rho = 0.8$.

comparing measured and calculated limits of thermodynamic stability.

Huggins further amends the combinatory entropy of mixing (the first two terms on the rhs of eq 2) by making allowance for the influence of the immediate surroundings of a segment on its average randomness of orientation with respect to the preceding segment in the chain molecule. Setting the average allowed number of orientations of the segment equal to ν^0 when it is at infinite dilution in the second polymer, and correcting it to a value $\nu^0(1 - k_S)$ for a segment in the undiluted polymer, he calculates two "orientational" contributions to the entropy of mixing. Inserting these terms into the full ΔG_ϕ expression, one obtains

$$\Delta G_\phi/RT = \sum_i \phi_{1i} m_{1i}{}^{-1} \ln \phi_{1i} + \sum_j \phi_{2j} m_{2j}{}^{-1} \ln \phi_{2j} + g\phi_1\phi_2 - \phi_1 \ln (1 + k_1 \rho \phi_2 Q^{-1}) - \phi_2 \ln (1 + k_2 \phi_1 Q^{-1}) \quad (4)$$

Two parameters k_{S1} and k_{S2}, related to k_1 and k_2 by $k_{Si} = k_i/(1 + k_i)$, were treated by Huggins in a rather intuitive way and had so far to be considered as empirical parameters. Recently, it was found that the formulation of ΔG according to eq 4 is very useful in the description of peculiarly shaped spinodals in some liquid oligomer/polymer mixtures.[12,13] An example of this work is given in Figure 1 which shows the spinodal of such a system determined with Gordon et al.'s pulse induced critical scattering method.[14,15]

At least qualitatively, the obvious bimodality of the spinodal appeared to be well within the scope of eq 4. To calculate such shapes, negative and positive values had to be assigned to k_1 and k_2 (Figure 2), and this seems to make physical sense, in view of the flexibilities of polyisobutylene and polystyrene chains and their mutual influence.[12,13]

We now come to the objective of this note and suggest that further development of a theoretical basis for Huggins' k_S parameters might be supported by a comparison of Silberberg's and Huggins' formulations of the free enthalpy of mixing. To clarify this point we simplify the relevant terms in eq 2, neglecting m^{-1} with respect to 1 and assuming τ to be independent of chain length. The comparison of eq 2 and 4 then suggests

$$\tau_1 = V_1{}^*(\phi_1)/V_1{}^*(1) \equiv 1 + k_1 \rho \phi_2 Q^{-1} \quad (5a)$$

and

$$\tau_2 = V_2{}^*(\phi_2)/V_2{}^*(1) \equiv 1 + k_2 \phi_1 Q^{-1} \quad (5b)$$

Silberberg conceives the parametric volumes to be identical or at least closely related to the coil volumes.[16] Adopting this picture we must expect a negative value of k_1 to involve a decrease in coil size of polymer 1 with decrease in concentration. In the dilute-solution limit of polymer 1 in polymer 2 ($\phi_1 = 0$, $\phi_2 = 1$) we have $\tau_1 = 1 + k_1$, whereas bulk polymer 1 ($\phi_1 = 1$, $\phi_2 = 0$) is characterized by $\tau_1 = 1$. Conversely, with respect to polymer 2: $\phi_2 = 0$, $\phi_1 = 1$ gives $\tau_2 = 1 + k_2$ (for a dilute solution of 2 in 1), and $\phi_2 = 1$, $\phi_1 = 0$ gives $\tau_2 = 1$ (for bulk polymer 2).

As far as bulk polymers are concerned we note that eq 5a and 5b give meaningful results. Recent neutron scattering measurements[17] point to the coils having unperturbed dimensions in the amorphous bulk state ($\tau = 1$); eq 5 are consistent with that feature. At the other end of the concentration scale we have less foothold. A negative value of k_1 suggests $\tau_1 < 1$ at infinite dilution of polymer 1, i.e., coil contraction with respect to the unperturbed bulk dimension.

We are aware of only one reported value in the literature that may lend some support to the latter conclusion. The coil size of polymethylstyrene dissolved in deuterated poly(methyl methacrylate) appears to be very small and points to a collapse of the molecules.[18] The negative second virial coefficient further indicates the possible relevance of this example to the present analysis, but we cannot be sure until coil-dimension data on systems with two-peaked spinodals become available. In the present framework one would then expect the coils of polymer 2 to be expanded in dilute solutions in polymer 1 ($k_2 > 0$). We do not know of any experimental evidence for this at the moment.

Although the present interpretation placed on τ_1 and τ_2 is empirical in nature, the presence of these parameters in the expression for ΔG_ϕ does allow the effects of changes in configurational behavior on mixing to be accounted for, and the possibilities of more fundamental interpretations of τ_1 and τ_2 are currently being investigated.

References and Notes

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Polymer Chain Stiffness Parameter, σ, and Cross-Sectional Area per Chain

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Privalko and Lipatov[1–6] have been concerned recently with correlation of various physical properties with the chain