Light Scattering from Polymer-Polymer-Solvent Ternary Systems. A Simple and Reliable Method for Estimating the Interactions between Unlike Polymers

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There have been several interesting studies on light scattering from polymer 1-polymer 2-solvent ternary systems.[1-6] Stockmayer and Stanley[1] have measured the light scattering from the ternary solution in which both of the polymers have large refractive index increments (of the same sign) to evaluate the interactions between the unlike polymers in the dilute limit of polymer concentrations. Such an approach, however, has not been followed in many later studies. Instead, the solvent has been, in most cases,[2-6] chosen to give a nearly zero refractive index increment for one of the polymers so that the scattering from the other polymer has been selectively observed. An apparent reason for this may be that it is not necessarily easy for the former type of experiments to provide a precise estimate of the excess function ΔB_{12} of interest, since it usually is quite small compared to B_{11} and B_{22}.[1] Here

$$\Delta B_{12} = B_{12} - (B_{11} + B_{22})/2 \qquad (1)$$

and B_{ij} is a virial coefficient defined by the osmotic pressure expansion

$$\pi/(RT) = \sum_i c_i M_i^{-1} + \sum_i \sum_j B_{ij} c_i c_j + \ldots \qquad (2)$$

with c_i and M_i being the concentration and molecular weight, respectively, of polymer i.

The purpose of this report is to draw attention to the capability of scattering methods to provide values of ΔB_{12} with enhanced accuracy if measurements are made under the special condition as described below.

The (forward) reduced scattered light intensity R_0 from a multicomponent system is given by [1,7,8]

$$R_0/K^* = \sum_i \nu_i^2 M_i c_i - 2\sum_i \sum_j \nu_i \nu_j M_i M_j B_{ij} c_i c_j + \ldots \qquad (3)$$

where the summations extend over all solute molecules; ν_i is the refractive index increment of molecule i, and K^* is the light scattering constant (exclusive of the refractive index increment factor). For a ternary system with monodisperse polymers 1 and 2 and a solvent, eq 3 with eq 1 becomes

$$R_0/(K^*c) = \nu_1^2 x_1 M_1 + \nu_2^2 x_2 M_2 - 2c[(\nu_1 x_1 M_1 + \nu_2 x_2 M_2) \times (\nu_1 x_1 M_1 B_{11} + \nu_2 x_2 M_2 B_{22}) + 2\nu_1 \nu_2 x_1 x_2 M_1 M_2 \Delta B_{12}] + \ldots \qquad (4)$$

$$c = c_1 + c_2 \qquad (5)$$

$$x_i = c_i/c \qquad (i = 1 \text{ or } 2) \qquad (6)$$

Then, if the condition

$$\nu_1 x_1 M_1 = -\nu_2 x_2 M_2 \qquad (7)$$

is met, we have

$$\nu_1^2 K^* c/R_0 = [x_1 M_1 (1 + \gamma)]^{-1} - (4\Delta B_{12} c)/(1 + \gamma)^2 + \ldots \qquad (8)$$

$$\gamma = (x_1 M_1)/(x_2 M_2) \qquad (9)$$

We note that the second term in eq 8 includes nothing but ΔB_{12} and the independently determinable parameter γ. Thus, measurements made satisfying eq 7 should provide a most reliable value of ΔB_{12}.

Within the framework of the Flory-Huggins theory,[9] ΔB_{12} is proportional to the interaction parameter χ_{12} between unlike polymer segments, if the specific volumes v_1 and v_2 of the polymers are identical. Since this is not generally the case, the above equations should be modified in order to determine χ_{12} according to the present principle. The second virial coefficient B_{ij} is related to the Flory-Huggins parameters χ_{si} and χ_{ij} by[1]

$$B_{ij} = (1 - \chi_{si} - \chi_{sj} + \chi_{ij})(v_i v_j)/(2v_s) \qquad (\chi_{ii} \equiv 0) \qquad (10)$$

where v_s is the specific volume of solvent. Accordingly, eq 3 with eq 10 gives eq 11 and 12, if the condition in eq 13 is met.

$$\nu_1^2 K^* c/R_0 = [x_1 M_1 (1 + \gamma')]^{-1} - (2v_1^2 \chi_{12} c)/[v_s (1 + \gamma')^2] + \ldots \qquad (11)$$

$$\gamma' = (x_1 M_1 v_1^2)/(x_2 M_2 v_2^2) \qquad (12)$$

$$\nu_1 x_1 M_1 v_1 = -\nu_2 x_2 M_2 v_2 \qquad (13)$$

In the above arguments, the polymers have been assumed to be monodisperse. Ternary systems with polydisperse polymers 1 and 2 cannot be similarly treated, since B_{ij} is known to be molecular weight dependent. However, the molecular weight dependence being usually small, B_{ij} may be regarded as constant, as a first approximation valid for polymers having not-too-broad molecular weight distributions. In this context, it may be easily shown from eq 3 that M_1 and M_2 appearing in eq 4, 7-9, and 11-13 should be replaced by the weight-average molecular weights $M_{1,\mathrm{w}}$ and $M_{2,\mathrm{w}}$, respectively.

We have pointed out that if light scattering measurements are made under the specified conditions, the apparent second virial coefficient obtained from the conventional Zimm plot becomes directly proportional to $-\Delta B_{12}$ or $-\chi_{12}$. As a matter of fact, it will not be a very difficult problem to experimentally realize the condition in eq 7 or 13. The first thing to do will be to find a solvent in which ν_1 is roughly equal to *minus* ν_2. For most pairs of polymers whose refractive indices differ sufficiently from each other, such solvents will be found without too much effort. Then, exact adjustment of ν_i to eq 7 or 13 may be done by a suitable choice of temperature, since ν_i depends on temperature in an appreciably sensitive manner in most cases.[10] For polystyrene (PS)-poly(methyl methacrylate) (PMMA) and PS-polyisoprene (or polybutadiene) systems, solvents such as bromobenzene,[10] chlorobenzene, and dichlorobenzene,[10] will be suitable for this purpose. A preliminary light scattering result made for a PS-PMMA-bromobenzene system shows that the present method is promising not only in quickly indicating whether the polymer pair is compatible or not, viz., $\chi_{12} \leq 0$ or > 0, but in providing a plausible value of χ_{12}.

Finally, we would like to comment that small-angle neutron scattering has the advantage, over light or X-scattering, that for any system to be tested, the neutron-scattering contrast factors corresponding to ν_i could be easily manipulated by deuterating one of the polymers and also a part of the solvent molecules.[12]

References and Notes

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Communications to the Editor

Concerning the Paper by J. J. Gonzáles and K. W. Kehr on "Distribution of Reacted Sequences in Homopolymers"

The paper by González and Kehr[1] considers the derivation of kinetic equations for the probabilities of reacted-unit sequences in the products of functional-group reactions proceeding with neighboring-group effects; i.e., it concerns the theory of macromolecular reactivity. Many American, German, and Russian scientists have worked for many years in the field of the theory of macromolecular reactions. Unfortunately, González and Kehr have ignored many results of these studies.

For example, in the introduction to their paper, González and Kehr mention that it is considerably easier to describe the distribution of unreacted units than that of reacted units, as there exists the independence of finding any sequences to both sides of the diad AA. Here the authors refer only to their own papers of 1974–1977, although this fact was proved much earlier by many authors (ref 2, 3, 4, and 5).

Moreover, eq 1 of González and Kehr

$$q_l(t) = q_2(t) \exp\{-k(l-2)t\} \tag{1}$$

is immediately derived from the well-known equation of McQuarrie[2]

$$P(\mathrm{A}_j) = e^{-jk_0t} \exp\left\{2(k_0 - k_1)\left[t - \frac{1 - e^{-k_0t}}{k_0}\right]\right\} \tag{2}$$

which is valid for all $j \geq 2$, and therefore

$$P(\mathrm{A}_l) = P(\mathrm{A}_2) \exp\{-(l-2)k_0t\}$$

As $P(\mathrm{BA}_lB)$ (in the McQuarrie's denotion) is identical with q_l (in the González and Kehr denotion)

$$\begin{aligned} q_l = P(\mathrm{BA}_l\mathrm{B}) = P(\mathrm{A}_l) - 2P(\mathrm{A}_{l+1}) + P(\mathrm{A}_{l+2}) = \\ P(\mathrm{A}_2)e^{-(l-2)k_0t} - 2P(\mathrm{A}_2)e^{-(l-1)k_0t} + P(\mathrm{A}_2)e^{-lk_0t} = \\ e^{-(l-2)k_0t}[P(\mathrm{A}_2) - 2P(\mathrm{A}_3) + P(\mathrm{A}_4)] = P(\mathrm{BA}_2\mathrm{B})e^{-(l-2)k_0t} \end{aligned} \tag{3}$$

which is identical with eq 1 ($k = k_0$).

In part II González and Kehr introduce the assumption about the uniform distribution of reacted and unreacted sequences. It should be pointed out that for the first time this hypothesis was proposed by Klesper in 1971[4] (González and Kehr do not refer to this paper) and its validity was confirmed by Monte-Carlo calculations. On this assumption, González and Kehr derive the kinetic equations for the probabilities of reacted sequences. Here they exactly repeat the consideration earlier proposed and published by Platé, Litmanovich, Noah, et al.[6-9] in 1971–1974. Unfortunately, in this case González and Kehr again do not give the corresponding references. The final results obtained by González and Kehr are identical with those published earlier.[6-8] Taking into consideration the above-mentioned facts, the affirmation of the authors[1] ". . . to our knowledge nobody has yet been able to find the distribution of sequences of reacted units" seems rather surprising.

The only difference in the approach of González and Kehr consists in adoption of four rate constants instead of the usual three rate constants for reactions with neighboring-group effects: k_0, k_1, and k_2 (corresponding to the number of reacted neighbors). The constants of González and Kehr are $k = k_0$, $k(c) = k_2$, and two different constants $k(a)$ and $k(\tilde{a})$ for the substitution of functional groups with the reacted neighbors on the left and on the right of the unit under consideration. One can easily show by letting $k(a) = k(\tilde{a}) = k_1$ that eq 8 of González and Kehr is identical with eq 32 of ref 7. As $r_1(t) = P(\mathrm{ABA})$, $q_1(t)$

$$\mathrm{d}r_1(t)/\mathrm{d}t = -2kcr_1(t)q_1(t)/\rho(t) - k(a + \tilde{a})r_1(t)[1 - q_1(t)/\rho(t)] + k\sum_{m=3}^{\infty}(m-2)q_m(t)$$

$= P(\mathrm{BAB})$, and $\rho(t) = P(\mathrm{AB})$, and with the aid of the relationships between the probabilities of j clusters and j tuplets derived by McQuarrie,[2]

$$\sum_{m=3}^{\infty}(m-2)q_m(t) = P(\mathrm{A}_3) \tag{4}$$

eq 8 of González and Kehr can be transformed into

$$\mathrm{d}P(\mathrm{ABA})/\mathrm{d}t = -2k_2P(\mathrm{ABA})P(\mathrm{BAB})/P(\mathrm{AB}) - 2k_1P(\mathrm{ABA})\left[1 - \frac{P(\mathrm{BAB})}{P(\mathrm{AB})}\right] + k_0P(\mathrm{A}_3) \tag{5}$$

and with

$$P(\mathrm{AB}) - P(\mathrm{BAB}) = P(\mathrm{A}_2\mathrm{B}) \tag{6}$$

$$\mathrm{d}P(\mathrm{ABA})/\mathrm{d}t = k_0P(\mathrm{A}_3) - 2P(\mathrm{ABA})\frac{k_2P(\mathrm{BAB}) + k_1P(\mathrm{A}_2\mathrm{B})}{P(\mathrm{AB})} \tag{7}$$

which exactly coincides with eq 32 of ref 8.

By the same pathway, eq 9 of González and Kehr can be transformed into eq 36 of ref 8:

$$\begin{aligned} \mathrm{d}r_l/\mathrm{d}t = \mathrm{d}P(\mathrm{AB}_l\mathrm{A})/\mathrm{d}t = \\ -2k_2P(\mathrm{AB}_l\mathrm{A})P(\mathrm{BAB})/P(\mathrm{AB}) - 2k_1P(\mathrm{AB}_l\mathrm{A}) \times \\ [1 - P(\mathrm{BAB})/P(\mathrm{AB})] + \\ k_2P(\mathrm{BAB})\{\sum_{n=1}^{l-2}P(\mathrm{AB}_n\mathrm{A})P(\mathrm{AB}_{l-n-1}\mathrm{A})\}/P(\mathrm{AB})^2 + \\ 2k_1[1 - P(\mathrm{BAB})/P(\mathrm{AB})]P(\mathrm{AB}_{l-1}\mathrm{A}) \end{aligned} \tag{8}$$

Taking relationship 6 into account, one can obtain

0024-9297/79/2212-1230$01.00/0