Polymer Bulletin 9, 563-569 (1983)

Polymer Bulletin

Interaction Between Components of Polymer Blends by Scattering

G. Hadziioannou[1], J. Gilmer[2] and R.S. Stein*[2]

[1] IBM Research Labs, 5600 Cottle Road, San Jose, CA 95193, USA

[2] Polymer Research Institute, University of Massachusetts, Amherst, MA 01003, USA

Summary

The Flory interaction coefficient χ_{AB} of binary polymer blends of high concentration may be determined from the study of light, x-ray, or neutron scattering at q=0. Neutron scattering measurements are particularly effective for these measurements since scattering intensity may be enhanced through deuteration of one component.

Scattering Measurements at Low Concentration

The scattering of radiation by an isotropic condensed two-phase system arises from fluctuations in density and concentration. The concentration fluctuations were described by Einstein[1,2] as

$$R_c = K \frac{RTc_B}{(\partial\pi_A/\partial c_B)_T} \tag{1}$$

where R_c is the concentration fluctuation contribution to the Rayleigh factor at q=0 [$q=(4\pi/\lambda)\sin(\theta/2)$ where λ is the wavelength of the radiation and θ the angle between the scattered and incident ray]. The Rayleigh factor† is defined as

$$R = \frac{I_s p^2}{I_o V_s} \tag{2}$$

where I_s and I_o are the scattered and incident intensities, p is the sample-to-detector distance and V_s is the scattering volume. c_B is the concentration of phase B and π_A is the osmotic pressure between phase A in solution and in pure phase A.‡

*To whom correspondence should be sent.

†The Rayleigh factor has dimensions of cm^{-1} and is identical with the differential scattering cross-section ($\partial\Sigma/\partial\Omega$) conventionally used by neutron scatterers.

‡The result should be symmetrical in the choice of labelling phases A and B and is not dependent on which is arbitrarily designated as the solvent.

The equation was originally derived by Debye[3] for light scattering for which

$$K = K_L = \frac{2\pi^2 n^2}{N_o \lambda_o^4} n^2 \left(\frac{\partial n}{\partial c_A}\right)^2_{T,P} \tag{3}$$

where n is the refractive index of the solution, N_o is Avagadro's number, and λ_o the wavelength of light in vacuum. However, the equation is also valid for x-ray scattering for which[4]

$$K = K_X = N_o i_e \left(\frac{\partial \rho^e}{\partial c_B}\right)^2 = \frac{N_o i_e}{\rho_B^2} (\rho_A{}^e - \rho_B{}^e)^2 \tag{4}$$

where i_e is the Thomson scattering factor for a single electron $[(e^2/m_e c_o{}^2)^2$ where e and m_e are the electronic charge and mass and c_o is the velocity of light], ρ^e, $\rho_A{}^e$ and $\rho_B{}^e$ are the electron densities (in moles electrons/cm^3) of the solution, components A and B, respectively, and ρ_B is the gravimetric density of phase B.

For the coherent contribution to neutron scattering[5]

$$K = K_N = (N_o/m_B{}^{*2}) \; (a_A{}^* - a_B{}^*)^2 \tag{5}$$

where $m_B{}^*$ is the mass per mole of lattice cells of component B and $a_A{}^*$ and $a_B{}^*$ are the scattering lengths per lattice cell. Note that these are given by

$$m_B{}^* = m_B \; (v_o/v_B) \tag{6}$$

$$a_A{}^* = a_A \; (v_o/v_A) \tag{7}$$

and

$$a_B{}^* = a_B \; (v_o/v_B) \tag{8}$$

where m_B is the molecular weight of the monomer unit of B and v_A, v_B, and v_o are the volumes of the monomer units of A and B and of the lattice cell, respectively, while a_A and a_B are the scattering lengths per monomer unit of the two components. Note that K_N is independent of v_o, a reasonable result since v_o is dependent upon the arbitrary choice of the lattice. Alternatively, K_N may be expressed in terms of molecular parameters as

$$K_N = (N_o/m_B{}^2) \; [a_A(\frac{v_B}{v_A}) - a_B]^2 \tag{9}$$

Debye[3] used the virial expansion for the osmotic pressure for dilute solution in solvent (A) giving

$$\pi_A = RT \; [\frac{c_B}{M_B} + A_2 c_B{}^2 + \ldots] \tag{10}$$

where M_B is the average molecular weight of component B and A_2 is the second virial coefficient. Substitution of (10) in (1) leads to the familiar Zimm equation[6] for q=0

$$\frac{Kc_B}{R_c} = \frac{1}{M_B} + 2A_2c_B \tag{11}$$

permitting the experimental determination of M_B and A_2 from measurements of R_c at q=0 as a function of c_B in dilute solution. This equation serves as the basis for the determination of polymer molecular weights by light scattering.

Kirste et al.[7] have extended this approach to the neutron scattering of polymer blends and obtained molecular weights and second virial coefficients for dilute blends. The second virial coefficient is related to the Flory interaction parameter χ_{AB} in monomeric solvents through the relationship for a low molecular weight solvent A[8]

$$A_2 = (1/2 - \chi_{AB})/\rho_B{}^2V_A \tag{12}$$

where ρ_B is the (gravimetric) density of component B and V_A is the molar volume of the solvent. [It is assumed that the monomer volume equals the lattice cell volume ($v_A = v_o$).] More generally, for a polymeric solvent[9],

$$A_2 = (1/2 - y_A\chi_{AB})/\rho_B{}^2V_A) \tag{13}$$

where y_A is the number of lattice cells occupied by a molecule of component A. That is

$$y_A = V_A/(N_o v_o) \tag{14}$$

This is related to the degree of polymerization of component A, z_A, by

$$z_A = M_A/m_A = y_A(v_o/v_A) \tag{15}$$

where M_A and m_A are the polymer and monomer molecular weights of component A. It is noted that χ_{AB} is the interaction parameter per lattice cell so that the interaction parameter per molecule of A is $y_A\chi_{AB}$. Using this definition, the dependence of χ_{AB} upon M_A is minimized.

Kirste et al.[10] showed that negative χ_{AB} values (corresponding to negative heats of mixing) characterized miscible blends, whereas immiscibility was associated with χ_{AB} becoming positive. However, their analysis was restricted to dilute blends. There is much evidence[11-14] that χ_{AB} is concentration dependent in blends, so that their characterization of blend miscibility is only applicable to systems in which one component is present at low concentration. The extension to high concentration requires means for determination of χ_{AB} under these conditions.

Extension to High Concentration

Debye and Bueche[15] showed that Eq. (1) may be extended to high concentration through use of the Flory-Huggins equation for osmotic pressure[8] which is for solution in monomeric solvent A

$$\pi_A = -\frac{RT}{V_A}[\ln \phi_A + (1 - \frac{1}{y_B})\ \phi_B + \chi_{AB}\phi_B{}^2] \tag{16}$$

where ϕ_A and ϕ_B are the volume fractions of components A and B. This led to a prediction of the variation of $\mathcal{R}_c$ with concentration exhibiting a maximum at a concentration related to V_B/V_A (and not dependent upon χ_{AB}). The method never became popular for molecular weight measurement, partly because of the difficulty of clarifying concentrated solutions to render them suitable for light scattering measurements.

This approach, however, is a good one for the description of the neutron scattering from polymer blends, especially if the scattering intensity is enhanced through increasing ($a_A^* - a_B^*$) by using a deuterated species for one of the blend components. Under these conditions, the contribution of the polymer to $\mathcal{R}_c$ is much greater than that arising from small amounts of impurities. Also, for a polymer blend, V_B/V_A is often of the order of unity so that the scattering maximum occurs at appreciable concentrations rather than at very low concentrations as with a monomeric solvent.

For polymeric solvents, Eq. (16) may be generalized as

$$\pi_A = -\frac{RT}{V_A}\left[\ln \phi_A + \left(1 - \frac{y_A}{y_B}\right) \phi_B + y_A \chi_{AB} \phi_B^2\right] \tag{17}$$

Substitution of (17) in (1) and rearranging gives

$$\frac{K m_B^{*2}}{\mathcal{R}_c v_o N_o} = \frac{1}{y_A \phi_A} + \frac{1}{y_B \phi_B} - 2\chi_{AB} \tag{18}$$

or

$$\frac{K m_B^2}{\mathcal{R}_c v_B N_o} = \frac{1}{z_A\left(\frac{v_A}{v_B}\right)\phi_A} + \frac{1}{z_B \phi_B} - 2\chi_{AB}\left(\frac{v_B}{v_o}\right) \tag{19}$$

Thus a measurement of $\mathcal{R}_c$ for known z_A and z_B permits the determination of χ_{AB}. This approach is equivalent to that used by Wendorff[11] for the determination of χ_{AB} for the poly(vinylidene fluoride)/poly(methyl methacrylate) blends from the concentration fluctuation contribution to small angle x-ray scattering. (Note that Wendorff's interaction parameter is equivalent to our $y_A \chi_{AB}$.) A somewhat similar proposal has been made by Russell.[12]

It is noted that for neutron scattering using Eq. (5) for K_N, Eq. (18) becomes

$$\frac{(a_A^* - a_B^*)^2}{\mathcal{R}_c v_o} = \frac{1}{y_a \phi_A} + \frac{1}{y_B \phi_B} - 2\chi_{AB} \tag{20}$$

This equation is expressed completely in terms of lattice parameters and is symmetrical in A and B. In terms of molecular parameters, it becomes

$$\frac{\left[a_A\left(\frac{v_B}{v_A}\right) - a_B\right]^2}{\mathcal{R}_c v_B} = \frac{1}{z_a \phi_A\left(\frac{v_A}{v_B}\right)} + \frac{1}{z_B \phi_B} - 2\chi_{AB}\left(\frac{v_B}{v_o}\right) \tag{21}$$

The term $\chi_{AB}(v_B/v_o)$ represents the interaction coefficient per monomer unit of component B.

If one utilizes the equation for the coherent neutron scattering from a two component incompressible system[16-20]

$$R_c = (a_A^* - a_B^*)^2 S_{AA}(q) \tag{22}$$

where $S_{AA}(q)$ is the interference function between A units given by

$$S_{AA} = N_A y_A^2 \,[P_A(q) + N_A Q_{AA}(q)] \tag{23}$$

where N_A is the number of molecules of component A per unit volume, $P_A(q)$ is the intramolecular interference function within A molecules and $Q_{AA}(q)$ is the intermolecular interference function between A units on different molecules, by substituting (22) in (20) one obtains

$$\frac{1}{v_o S_{AA}} = \frac{1}{y_A \phi_A} + \frac{1}{y_B \phi_B} - 2\chi_{AB} \tag{24}$$

which is the same as

$$\frac{1}{y_A \phi_A [P_A(q) + N_A Q_A(q)]} = \frac{1}{y_A \phi_A} + \frac{1}{y_B \phi_B} - 2\chi_{AB} \tag{25}$$

This is equivalent to the deGennes result[21] using the random phase approximation for the case of q=0.

Use of Three Component Systems

The application of these equations is related to measurements on concentrated binary solutions. In such cases, it is not possible to independently measure the molecular weight or radius of gyration of a component of the blend. However, this may be done using three component scattering theory[18,20] where one species, A, is partially deuterated (D and H) to mole fraction x and the other, B, is not.[22-25] In this case, scattering theory gives

$$\begin{aligned} R_c(q) &= x(1 - x)\,(a_D^* - a_H^*)^2\, N_A y_A^2 P_A(q) \\ &+ (\overline{a_A^*} - a_B^*)^2\, N_A y_A^2 [P_A(q) + N_A Q_{AA}(q)] \end{aligned} \tag{26}$$

Since $v_D = v_H$, this equation is equivalent to

$$\begin{aligned} R_c(q) &= x(1 - x)\,(a_D - a_H)^2\, N_A z_A^2 P_A(q) \\ &+ [\overline{a_A} - a_B(\tfrac{v_A}{v_B})]^2\, N_A z_A^2 [P_A(q) + N_A Q_{AA}(q)] \end{aligned} \tag{27}$$

where $\overline{a_A}$ is the average scattering length for component A given by

$$\overline{a_A} = x a_D + (1 - x) a_H \tag{28}$$

Here a_D and a_H are the scattering lengths of deuterated and hydrogenous species of A, N_A is the total number of molecules per cm^3 of both species of A having degree of polymerization z_A (assuming $z_A=z_D=z_H$). Differences in interaction between H and B and D and B are neglected, so it is assumed that $P_A=P_H=P_D$ and $Q_{AA}=Q_{HH}=Q_{DD}=Q_{HD}$.

By measuring $R_c(q)$ as a function of x at constant N_A, Eq. (27) may be resolved into contributions from the two terms.[17,20,22-25] The variation of the first term with q characterizes the q dependence of $P_A(q)$ which yields the radius of gyration, $(R_g)_A$, of A through

$$P_A(q) = 1 - \frac{1}{3}(R_g)_A{}^2q^2 + \ldots \tag{29}$$

while the magnitude of the first term at q=0 characterizes z_A related to the molecular weight of A. The second term of Eq. (27) permits the determination of the denominator of the left side of Eq. (25), so if z_B is known, χ_{AB} may be calculated.

This approach has been used in our laboratory for the study of blends of polystyrene with poly(vinyl methyl ether) and poly(vinylidene fluoride) with poly(methyl methacrylate) which will be described in a forthcoming publication.[26] Values of χ_{AB} obtained[23,24] are consistent with those obtained by other techniques.[11-13]

Acknowledgments

The authors appreciate suggestions and discussions with Prof. H. Benoit, Dr. Julia Higgins, Prof. W.H. Stockmeyer, and Dr. Gerrit ten Brinke in the development of this approach. The support of these studies by grants from the National Science Foundation and the IBM Corporation is appreciated.

References

1. EINSTEIN, A., Ann. Physik, 33, 1275 (1910).
2. LANDAU, L.D. and LIFSHITZ, E.M., Statistical Mechanics, New York, McGraw-Hill, 1962.
3. DEBYE, P., J. Appl. Phys., 15, 338 (1944).
4. GLATTER, O. and KRATKY, O., Small Angle X-Ray Scattering, New York, Academic Press, 1982, Chapt. 12.
5. KIRSTE, R.G., et al., Polymer, 16, 120 (1975).
6. DOTY, P., et al., J. Phys. Chem., 12, 144 (1944); 13, 159 (1945).
7. KRUSE, W.A., et. al., Makromol. Chem., 177, 1145 (1976).
8. FLORY, P.J., J. Chem. Phys., 10, 51 (1942).
9. SCOTT, R.L., J. Chem. Phys., 17, 279 (1949).
10. JELENIC, J., et al., private communication of results to be published in Macromol. Chem., 183, (1982).
11. WENDORFF, J.H., J. Polym. Sci., Polym. Letters Ed., 18, 439 (1980).
12. RUSSELL, T., Ph.D. Dissertation, University of Massachusetts, Amherst, MA, 1979, p. 157.
13. MORRA, B.S. and STEIN, R.S., J. Polym. Sci., Polym. Phys. Ed., 20, 2243 (1982).
14. KWEI, T.K., et al., Macromolecules, 7, 667 (1974).
15. DEBYE, P. and BUECHE, A., J. Chem. Phys., 18, 1423 (1950).
16. WILLIAMS, C.E., et al., J. Polym. Sci., Polym. Letters Ed., 17, 379 (1979).

17. AKASU, A.Z.,et al., J. Polym. Sci., Polym. Phys. Ed., 18, 863 (1980).
18. BENOIT, H., et al., Makromol. Chem., Suppl. 4, 85 (1981).
19. LIEBLER, L. and BENOIT, H., Polymer, 22, 195 (1981).
20. PICOT, C. in Static and Dynamic Properties of the Polymer State, Ed. by PETHRICK, R.A. and RICHARDS, R.W., Dortrecht, Holland, Reidel, 1982, pp. 127-172.
21. DE GENNES, P.G., Scaling Concepts in Polymer Physics, Ithaca, Cornell Univeristy Press, 1979, p. 109.
22. HIGGINS, J.H., Presentation at NATO Advanced Study Institute, Glasgow, Sept. 6-18, 1981.
23. STEIN, R.S., Presentation at IUPAC Macromolecular Symposium, Amherst, July 12-16, 1982.
24. STEIN, R.S., et al., Presentation at SPE NATEC SYMPOSIUM, Bal Harbour, FL, Oct. 25-27, 1982.
25. WARNER, M., Chain Distributions and Interaction Parameters in Deuterated Polymer Blends, Report RL-82-058, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0OX, UK, Sept., 1982.
26. HADZIIOANNOU, G. and STEIN, R.S., submitted for publication.

Accepted January 24, 1983

K