related virtual structure factor $S_\chi(q)$, and also the basic time constant τ_R (eq 12) have to be considered as time-dependent. Another possible reason is the increase of T_g with increasing volume fraction of the brominated component. As a consequence, the kinetics could get progressively slower during unmixing. It appears difficult, to discriminate between the different effects on the basis of the presented results alone.

Relaxation times can only be derived for the T-jump 170 → 132 C from Figure 7. The values obtained are shown in Figure 10. They are compared to a theoretical curve following from eq 12. The parameters used in order to adjust the theoretical curve to the measured data were $\tau_R = 4.7 \times 10^3$ s and $\chi/\chi_s = 1.15$. The curve provides a reasonable fit to the measured data. The deviation at low wave vectors could be due to errors introduced by hole scattering.

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft (SFB41) is gratefully acknowledged.

References and Notes

(1) Gilmer, J.; Goldstein, N.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2219.

(2) Hashimoto, T.; Kumaki, J.; Kawai, H. *Macromolecules* **1983**, *16*, 641.

(3) Snyder, H. C.; Meakin, P.; Reich, S. *Macromolecules* **1983**, *16*, 757.

(4) Cahn, I. W. *Trans. Metall. Soc. AIME* **1968**, *242*, 166. Hilliard, J. E. In *Phase Transformations*; Anderson, H. L., Ed.; American Society for Metals: Metals Park, OH, 1970.

(5) de Gennes, P.-G. *J. Chem. Phys.* **1980**, *72*, 4756.

(6) Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.

(7) Strobl, G. R. *Macromolecules* **1985**, *18*, 558.

(8) Strobl, G. R.; Bendler, J. T.; Kambour, R. P.; Shultz, A. R. *Macromolecules* **1986**, *19*, 2683.

(9) Wilhelm, T.; Hoffman, R.; Fuhrmann, J. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 81.

(10) Wendorff, J. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 439.

(11) Herkt-Maetzky, C.; Schelten, J. *Phys. Rev. Lett.* **1983**, *51*, 896.

(12) Shibayama, M.; Yang, H.; Stein, R. S.; Han, C. *Macromolecules* **1985**, *18*, 2179.

(13) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University: Ithaca, NY, 1979; Chapter IV.

(14) Strobl, G. R. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1970**, *26*, 367.

Light Scattering from Polymer Blend Solutions. 4. Data Analysis for Asymmetrical Dilute Systems

Takeshi Fukuda,* Minoru Nagata, and Hiroshi Inagaki

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan.
Received June 19, 1986

ABSTRACT: The second virial coefficient B_{12} between unlike polymers 1 and 2 is assumed to be, as suggested by the Flory–Krigbaum theory, of the form $B_{12} = \text{const} \times h_0(\bar{Z}_{12})$, where h_0 is the same function as for the coefficient between like polymers. The argument $\bar{Z}_{12}$ is determined so as to be consistent with the first-order perturbation theory of B_{12}. Thus-determined $\bar{Z}_{12}$ is largely different, especially for highly asymmetrical systems, from the corresponding argument of the Flory–Krigbaum function, which is virtually the only theory available to date to describe ternary solutions of chemically different polymers. Also, the modified Kurata–Yamakawa function is adopted for h_0. As to mixtures of homologous polymers differing in molecular weight, this treatment gives numerical results generally close to those given by the Padé approximant due to Tanaka and Šolc. On the basis of this B_{12} function, a simple procedure is proposed to analyze light scattering data for the "net" interaction parameter $\chi_{12}°$ between unlike polymers. It is applied to experimental data for ternary solutions of varying degrees of asymmetry to give the most satisfactory results thus far obtained.

Introduction

In previous papers dealing with light scattering from two polymers dissolved in an optical Θ solvent,[1-3] it has been established that the Flory–Huggins[4] (FH) interaction parameter χ_{12} between unlike polymers is generally a function of chain length, concentration, and solvent power (see note 5 for the definition of the χ parameters). Thus, χ_{12} in a ternary solution is merely an apparent quantity and cannot be used for, e.g., quantitatively predicting the miscibility of the polymers in the bulk or in the presence of a solvent at a given fraction. However, if adequate solution data are available, it should be possible, at least in principle, to convert χ_{12} into a more quantitative piece of information on the polymer–polymer interaction.

As to infinitely dilute solution, the problem is directly concerned with the description of the second virial coefficient B_{12} between different polymers.[6] For homologous monodisperse polymers, fairly successful theories of the second virial coefficient are available to date.[7] Thus, if the ternary solution considered is symmetrical with respect to the two polymers, viz., the same size and the same affinity for the solvent, those theories may be applied for the mentioned purpose. This approach has been taken to analyze the χ_{12} data for some reasonably symmetrical systems.[1,3] On the other hand, there as yet seem to be no adequate theories applicable to asymmetrical systems, and this imposes a severe constraint not only on the application of the proposed particular light scattering technique[1-3,8] but also on solution approaches in general for determining polymer–polymer interactions.

In this paper, we propose a simple treatment based on the perturbation theory on B_{12} combined with an already-established closed-form expression for the second virial coefficient for homologous monodisperse systems. The expression for B_{12} or χ_{12} resulting from this treatment is entirely different, especially for highly asymmetrical systems, from that due to Flory and Krigbaum,[10] which is virtually the only theory thus far available to describe ternary systems composed of chemically different polymers. On the basis of this B_{12} function, a simple procedure will be proposed to analyze ternary-solution light scattering data for the "net" interaction parameter $\chi_{12}°$ which is considered to characterize the interaction between the given polymer pair. The validity of this procedure will be confirmed against experimental data for ternary systems of varying degrees of asymmetry. The previously proposed approximate method of analysis[1] will be shown to be valid for those particular systems.[1-3]

Theoretical Section

The FH parameters χ_{0i} and χ_{12} for the infinitely dilute solution[5] are related to the second virial coefficients B_{ii} between like polymers and B_{12} between unlike polymers by[9]

$$B_{ii} = (v_i^2/2V_0)(1 - 2\chi_{0i}), \qquad i = 1 \text{ or } 2 \tag{1}$$

$$B_{12} = (v_1 v_2/2V_0)(1 - \chi_{01} - \chi_{02} + \chi_{12}) \tag{2}$$

where the subscript 0 denotes the solvent, v_i is the specific volume of the (pure) polymer,[2] and V_0 is the molar volume of the solvent. The two-parameter theoretical expressions for these coefficients are[7]

$$B_{ii} = (N_A n_i^2 \beta_{ii}/2M_i^2)h_{ii} \tag{3}$$

$$B_{12} = (N_A n_1 n_2 \beta_{12}/2M_1M_2)h_{12} \tag{4}$$

where N_A is the Avogadro number, n_i is the number of segments, M_i is the molecular weight, β_{ij} is the binary cluster integral between segments i and j, and h_{ij} is the factor in question, representing the excluded volume effect between polymers i and j ($i, j = 1$ or 2).

If we define parameters $\chi_{0i}°$ and $\chi_{12}°$ by

$$N_A\beta_{ii} = V_0(1 - 2\chi_{0i}°) \tag{5}$$

$$N_A\beta_{12} = V_0(1 - \chi_{01}° - \chi_{02}° + \chi_{12}°) \tag{6}$$

and identify the statistical segments with the lattice-theoretical segments[2], i.e., $n_i = m_i$, with $m_i = v_iM_i/V_0$, then from eq 1–6 we have

$$1 - 2\chi_{0i} = (1 - 2\chi_{0i}°)h_{ii} \tag{7}$$

$$1 - \chi_{01} - \chi_{02} + \chi_{12} = (1 - \chi_{01}° - \chi_{02}° + \chi_{12}°)h_{12} \tag{8}$$

Thus, χ_{12} is expressed by

$$\chi_{12} = (1 - \chi_{01}° - \chi_{02}° + \chi_{12}°)h_{12} - (1/2)[(1 - 2\chi_{01}°)h_{11} + (1 - 2\chi_{02}°)h_{22}] \tag{9}$$

Our problem is evaluating $\chi_{12}°$ for given values of χ_{12} and other observable parameters. This requires the aid of theories.

It is known[7] that h_{ii} is a function of a single argument $\bar{Z}_i$, the excluded volume parameter Z_i divided by the cubic expansion factor α_i^3:

$$h_{ii} = h_0(\bar{Z}_i) \tag{10}$$

According to the FH notations, $\bar{Z}_i$ is given by

$$\bar{Z}_i = N_A^{-1}(4\pi\langle S_i^2\rangle)^{-3/2}m_i^2V_0(1 - 2\chi_{0i}°) \tag{11}$$

where $\langle S_i^2\rangle$ is the mean-square radius of gyration of polymer i. A number of theoretical expressions for h_0 can be found in the literature.[7]

As to homologous polymers differing only in chain length, there also exist expressions for h_{12},[10-13] among which only that of Flory and Krigbaum (FK)[10a] is directly applicable to systems composed of chemically different polymers. According to FK, h_{12} is given by the same function h_0 as for identical polymers

$$h_{12} = h_0(\bar{Z}_{12}) \tag{12}$$

with[10c]

$$h_0(X) = (5.73X)^{-1} \ln (1 + 5.73X) \qquad \text{(FKOm)} \tag{13}$$

where the new parameter $\bar{Z}_{12}$ may be given by

$$\bar{Z}_{12} = N_A^{-1}[2\pi(\langle S_1^2\rangle + \langle S_2^2\rangle)]^{-3/2}m_1m_2V_0(1 - \chi_{01}° - \chi_{02}° + \chi_{12}°) \tag{14}$$

By using eq 11, we can rewrite eq 14 as

$$\bar{Z}_{12} = 2^{1/2}(\sigma + \sigma^{-1})^{-3/2}(\epsilon\sigma^{-3/2}\bar{Z}_1 + \epsilon^{-1}\sigma^{3/2}\bar{Z}_2)(1 + \kappa) \tag{15}$$

$$\epsilon = m_2/m_1 \tag{16}$$

$$\sigma = (\langle S_2^2\rangle/\langle S_1^2\rangle)^{1/2} \tag{17}$$

$$\kappa = \chi_{12}°/(1 - \chi_{01}° - \chi_{02}°) \tag{18}$$

Thus $\bar{Z}_{12}$ and hence h_{12} are a function of five independent variables, $\bar{Z}_1$, $\bar{Z}_2$, ϵ, σ, and κ. For homologous polymers, two variables, e.g., $\bar{Z}_1$ and ϵ, suffice to define h_{12}.

As described later, this FK theory is rather unsatisfactory when applied to the PS/PMMA system. It has been shown[7] that eq 13 as applied to homologous monodisperse systems is less satisfactory than some other theories.[7] Therefore, one way to have an improved expression for h_{12} may be to use a more successful h_0 function in place of eq 13 but with the argument $\bar{Z}_{12}$ as given by FK, i.e., eq 15. However, this did not prove to be an essential improvement.

Here we propose another treatment. We still assume h_{12} to be a function of a *single* argument $\bar{Z}_{12}$. This argument is determined as follows: In the special case in which the two polymers are identical, $\bar{Z}_{12} = \bar{Z}_i$ and $h_{12} = h_{ii}$, and thus the function h_{12} must be given by the same function h_0 as for identical polymers and expanded as[7]

$$h_{12} = h_0(\bar{Z}_{12}) = 1 - 2.865\bar{Z}_{12} + ... \tag{19}$$

On the other hand, we carry out the perturbation calculations[7] on B_{12} between two Gaussian chains with segment numbers m_1 and m_2, segment lengths b_1 and b_2, respectively, and an interaction β_{12} between unlike segments. The result gives

$$h_{12} = 1 - (3/2\pi)^{3/2}(32/15)(m_1m_2\beta_{12}/r_1^4r_2^4) \times [r_1^5 + r_2^5 + (5r_1^2r_2^2/2)(r_1 + r_2) - (r_1^2 + r_2^2)^{5/2}] + ... \tag{20}$$

where $r_i^2 = m_ib_i^2$. We take account of the non-Gaussian nature of real chains by adopting the conventional approximation of uniform expansion, thus equating r_i^2 to the mean-square radius in the perturbed state multiplied by six:

$$r_i^2 = 6\langle S_i^2\rangle, \qquad i = 1 \text{ or } 2 \tag{21}$$

Comparison of eq 19 and 20 gives

$$\bar{Z}_{12} = 0.3723[\sigma^{5/2} + \sigma^{-5/2} - (\sigma + \sigma^{-1})^{5/2} + (5/2) \times (\sigma^{1/2} + \sigma^{-1/2})](\epsilon\sigma^{-3/2}\bar{Z}_1 + \epsilon^{-1}\sigma^{3/2}\bar{Z}_2)(1 + \kappa) \tag{22}$$

The double-contact term for homologous polymers previously obtained[12] is readily recovered from eq 19 with eq 22, if the parameters are appropriately reinterpreted (e.g., $b_1 = b_2$ and $\kappa = 0$). Equation 22 differs from the FK equation 15 in the first factor, including numerics, composed of σ only. The difference between the two equations can be very large, when σ is different from unity. Generally, eq 15 approaches zero much more rapidly than eq 22, as σ or σ^{-1} becomes larger than unity.

We now make some quantitative comparison of the theories, taking the case with homologous polymers, i.e., $\chi_{12}° = 0$ and $\chi_{01}° = \chi_{02}°$. On the basis of eq 9, we calculate χ_{12} between two polymers differing in length, using the combination of eq 22 and the Kurata–Yamakawa h_0 function[14] as recently revised by Tanaka and Šolc[11] along with the Yamakawa–Tanaka equation[15] for α (method 1):

$$h_0(X) = (2.193)^{-1}[1 - (1 + 3.537X)^{-0.620}] \qquad \text{(KYm)} \tag{23}$$

$$\alpha_i^2 = 0.541 + 0.459(1 + 6.94Z_i)^{0.46} \qquad \text{(YT)} \tag{24}$$

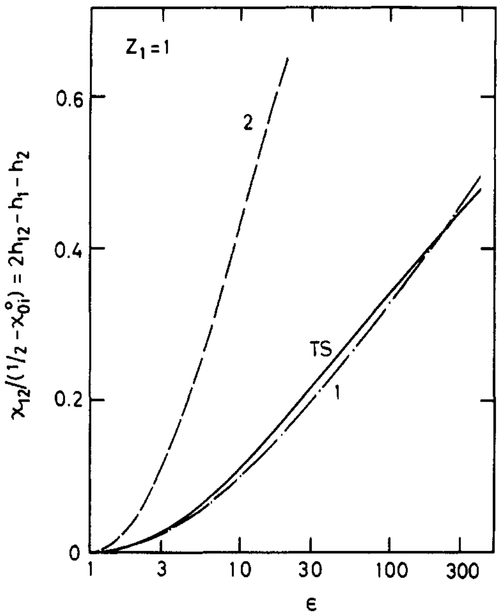

Figure 1. Plot of $\chi_{12}/[(1/2) - \chi_{0i}^\circ]$ vs. chain length ratio ϵ for a blend of homologous monodisperse polymers ($\chi_{12}^\circ = 0$) with $Z_1 = 1$: curve 1 is due to method 1 (eq 26 with eq 22, 23, and 24), curve 2 is due to method 2 (eq 26 with eq 13, 15, and 25), and curve TS is due to Tanaka and Šolc.[11]

Similarly, we calculate χ_{12} using the combination of eq 13 and 15 along with the modified Flory equation[4,10c] for α (method 2):

$$\alpha_i^5 - \alpha_i^3 = 1.276 Z_i \qquad \text{(Fm)} \qquad (25)$$

We also evaluate the Tanaka–Šolc (TS) Padé approximant of h_{12} for homologous polymers,[11] which satisfies the perturbation expansion up to the triple-contact term. In Figure 1, values of χ_{12} obtained by the three methods are shown as a function of chain length ratio ϵ (≥ 1, for we let the shorter chain be polymer 1). We have shown in the figure only the case with $Z_1 = 1$, but results are nearly insensitive to Z_1. The ordinate scale is χ_{12} divided by $(1/2) - \chi_{0i}^\circ$, equal to $2h_{12} - h_{11} - h_{22}$, so that it is independent of χ_{0i}°. We also note that the TS definition[11] for χ_{12} is opposite in sign to that of FH[4] and hence to ours.[2] The figure shows that all the theories predict χ_{12} to be positive, if $\epsilon > 1$ and $(1/2) - \chi_{0i}^\circ > 1$, becoming larger and larger with increasing ϵ. However, numerical differences among the theories are enormous. Method 1 predicts much smaller χ_{12} than method 2 and, notably, gives nearly the same results as the TS theory in the practically interesting range of ϵ. The difference in χ_{12} between methods 1 and 2 comes mainly from the difference in $\bar{Z}_{12}$ rather than in h_0. As already implied, eq 15 decreases with increasing ϵ much more rapidly, hence giving larger h_{12} and χ_{12} than eq 22 does.

In homologous polymer systems, the magnitude of this "ghost" χ_{12}, ghost because $\chi_{12}^\circ = 0$, is relevant to the controversy regarding the appearance of a maximum of the second virial coefficient upon varying the mixing ratio of two monodisperse polymers differing in size.[11,13] In this connection, it is suggested that direct measurements of χ_{12} by, e.g., neutron scattering which makes the combined use of the deuterium-labeling and optical Θ techniques may prove to be a powerful test of theories. In heteropolymer systems, this effect of size difference superposes on the contribution from generally nonzero χ_{12}°, and thus the evaluation of χ_{12}° depends largely on the precision of the theory to be employed. This is especially so when the size difference is large, the chain lengths are large, and the solvent power is strong for the polymers. This, in turn, points out favorable experimental conditions for determining χ_{12}°, i.e., similar sizes, short chains, and poor solvents.

Discussion

We now test the two combinations of theories designated methods 1 and 2 against experimental data for polystyrene (PS)/poly(methyl methacrylate) (PMMA) blends in bromobenzene[1] and in mixtures of 1,4-dioxane and 1-bromonaphthalene.[3] One may expect that good theories will give a value of χ_{12}° independent of chain lengths m_i, chain length ratio ϵ, radius ratio σ, and solvent powers χ_{0i}°. According to previous results,[1-3,16] the PS/PMMA pair is characterized by a fairly small value of χ_{12}° and suitable for such a test, since, when χ_{12}° is small, the aforementioned effect of size difference makes a relatively large contribution to χ_{12}, and thus the role of theories becomes relatively important. Our problem now is to solve for χ_{12}° the following equation, which is equivalent to eq 9:

$$\chi_{12} = (1 - \chi_{01}^\circ - \chi_{02}^\circ + \chi_{12}^\circ) h_0(\bar{Z}_{12}) - (1/2)[(1 - 2\chi_{01}^\circ) h_0(\bar{Z}_1) + (1 - 2\chi_{02}^\circ) h_0(\bar{Z}_2)] \qquad (26)$$

This requires, in addition to values of χ_{12}, some knowledge about the respective binary solutions.

We estimate the value of $\langle S^2 \rangle$ of each polymer according to the previously proposed scheme.[3] It is based on the semiempirical relation between the hydrodynamic expansion factor α_η and Z:[16]

$$\alpha_\eta^4 = 1 + (7/5) Z \qquad (27)$$

where $\alpha_\eta^3 = [\eta]/[\eta]_0$, with the intrinsic viscosity $[\eta]_0$ in the Θ state calculated with[17]

$$[\eta]_0 = K_0 M_w^{1/2} \qquad (28)$$

$$K_0 = 0.079 \text{ mL/g} \quad \text{(PS)}$$
$$= 0.049 \text{ mL/g} \quad \text{(PMMA)}$$

The unperturbed mean-square radius is also calculated with

$$[\eta]_0 = 6^{3/2} \Phi_0 \langle S^2 \rangle_0^{3/2} / M_w \qquad (29)$$

assuming Φ_0 to be 2.5×10^{23} (cgs) in all cases.[18] The value of Z from eq 27 is substituted in the YT equation 24 to obtain the expansion factor α and then $\langle S^2 \rangle$ ($= \alpha^2 \langle S^2 \rangle_0$). Table I lists the value of $[\eta]$ of each polymer and its $\langle S^2 \rangle^{1/2}$ value estimated in this manner. We have determined $\langle S^2 \rangle$ of some high molecular weight samples by light scattering, for which the calculated values closely agree (Table I). For this reason, we may regard the calculated values as being independent of the particular theories employed for their evaluation.

On the basis of the values of χ_{12} determined by the optical Θ method (Table II) and the calculated values of $\langle S^2 \rangle$ and $\langle S^2 \rangle_0$, we obtain all the parameter values necessary to solve eq 26 by either method 1 or method 2. We solved eq 26 for χ_{12}° in an iterative manner using a microcomputer. Results are given in Table II. Apparently, method 1 gives more uniform values of χ_{12}° than method 2 does. For the two systems in which ϵ is as large as 2.4 and 3.7, respectively, the values of χ_{12}° due to method 2 are negative, whereas those due to method 1 are positive and similar in magnitude to those for other more symmetrical systems. These even qualitatively different results stem mainly from the difference in the expression for $\bar{Z}_{12}$. As already noted, eq 15 and 22 are different from each other only in the dependence on σ. This implies that asymmetry of ternary systems is better characterized by

Table I
Molecular Characteristics of Polymer Samples (30 °C)

sample	$10^{-4}M_w$	M_w/M_n	solvent[a]	$[\eta]$, dL/g	$\langle S^2\rangle_w^{1/2}$,[b] Å	χ_{0i}[c]
PS PC200	242	1.30	BB		714 (694)	0.472 (0.474)
PS PC200′	179	1.30	DO/BN	4.02	583	
PS F80	77.5	1.01	BB	2.24	366 (368)	0.466 (0.466)
			DO/BN	2.06	358	
PS S50	51.5	1.03	DO/BN	1.46	281	
PS 49H	28.3	1.10	BB		204	
PS 39H	2.45	1.27	BB		51.5	
PMMA 75M	214	1.35	BB		587 (588)	0.473 (0.475)
			DO/BN	2.95	555	
PMMA 80M	111	1.22	DO/BN	1.73	378	
PMMA 78M	62.7	1.45	BB	1.33	286 (292)	0.467 (0.463)
PMMA 40M	44.1	1.44	DO/BN	0.91	227	
PMMA 31M	21.1	1.27	BB		152	0.461 (0.454)
PMMA 91M	2.45	1.04	BB		44.8	

[a] BB = bromobenzene; DO/BN = a mixture of 1,4-dioxane/1-bromonaphthalene (51/49 by volume). [b] Calculated with eq 27–29 and 24. Values in parentheses were measured[1] and corrected for polydispersity according to $\langle S^2\rangle_z/\langle S^2\rangle_w = (1 + 2p)/(1 + p)$, with $p = M_w/M_n - 1$. [c] Calculated with eq 27–29, 24, 11, and 7. Values in parentheses were measured.[1]

Table II
Values of χ_{12} and $\chi_{12}°$ for PS/PMMA Blends (30 °C)

blend						$\chi_{12}°$ [c]		
PS (1)	PMMA (2)	ϵ[a]	solvent	σ	χ_{12}[b]	method 1	method 2	method 3
PC200	75M	0.78	BB	0.82	0.0026	0.034	0.012	0.034
F80	78M	0.71	BB	0.78	0.0030	0.025	0.005	0.027
49H	31M	0.66	BB	0.75	0.0040	0.023	0.004	0.026
39H	91M	0.88	BB	0.88	0.0117	0.041	0.033	0.039
PC200′	75M	1.05	DO/BN	0.95	0.0023	0.030	0.020	0.025
F80	80M	1.26	DO/BN	1.06	0.0025	0.027	0.019	0.024
S50	40M	0.76	DO/BN	0.81	0.0033	0.023	0.010	0.021
F80	75M	2.44	DO/BN	1.55	0.0033	0.031	−0.009	0.031
S50	75M	3.67	DO/BN	1.98	0.0037	0.019	−0.039	0.032

[a] $\epsilon = (M_{w2}v_2)/(M_{w1}v_1)$, with $v_1 = 0.935$ and $v_2 = 0.825$ mL/g (cf. ref 1). [b] From ref 1 and 3. [c] Value for a solvent molar volume about 106 mL: calculated with the $\langle S^2\rangle$ value from Table I and the $\langle S^2\rangle_0$ value from eq 28 and 29 using eq 11, 22, 23, 24, and 26 (method 1), eq 11, 13, 15, 25, and 26 (method 2), or eq 11, 23, 24, 30, and 31 (method 3).

σ rather than ϵ. In Figure 2, the values of $\chi_{12}°$ due to methods 1 and 2 are respectively plotted as a function of σ. In both cases, the data points seem to form a single curve, as expected. Those due to method 2 rapidly decrease with increasing σ, clearly indicating the failure of the theory. On the other hand, the $\chi_{12}°$ values due to method 1 show no clear trend with σ in the examined range, lying in the range $\chi_{12}° = 0.028 \pm 0.006$. Considering the small magnitude of $\chi_{12}°$, the scatter of the points should be ascribed to experimental errors, and it can be concluded that method 1 describes asymmetric ternary solutions with sufficient accuracy at least for $\sigma < 2$. Its validity for $\sigma > 2$ is not clear at this time, and it should not be applied to such systems. However, it is clear that the limit of applicability is enlarged when we deal with systems with larger $\chi_{12}°$.

For a perfectly symmetrical system with a small $\chi_{12}°$, we write $\chi_{01}° = \chi_{02}° = \chi_{0i}°$, $\bar{Z}_1 = \bar{Z}_2 = \bar{Z}$, and $\bar{Z}_{12} = \bar{Z}(1 + \kappa)$, with $\kappa = \chi_{12}°/(1 - 2\chi_{0i}°) \ll 1$. Then eq 26 is transformed simply to (see note 19)

$$\chi_{12} = \chi_{12}°[\mathrm{d}\Psi(\bar{Z})/\mathrm{d}\bar{Z}] \qquad (30)$$

where $\Psi(\bar{Z}) = \bar{Z}h_0(\bar{Z})$ is the interpenetration function. We previously analyzed the above PS/PMMA data according to eq 30. Since $\bar{Z}_1$ and $\bar{Z}_2$ were not precisely equal to each other, we assumed $\bar{Z}$ to be given by

$$\bar{Z} = (\bar{Z}_1\bar{Z}_2)^{1/2} \qquad (31)$$

In Table II are also listed values of $\chi_{12}°$ computed according to this scheme by the combined use of the KYm equation for h_0 and the YT equation for α (method 3). These values are slightly different from those previously given,[1,3] since the previous values are based on the original KY equation.[14] Generally, the values due to method 3 are very close to those due to method 1 in the examined range of σ. This confirms that eq 30 with eq 31 is a valid approximation for reasonably symmetrical systems with a *small* $\chi_{12}°$.

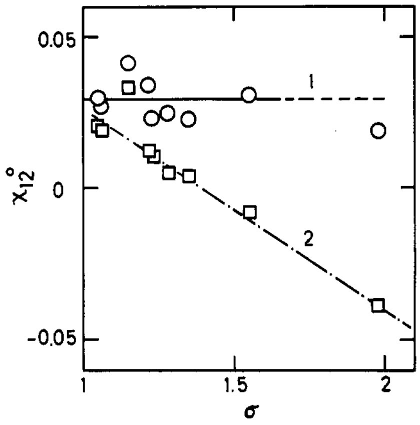

Figure 2. Plot of $\chi_{12}°$ vs. σ (or σ^{-1} if $\sigma < 1$) for PS/PMMA blends (30 °C) estimated with light scattering data according to method 1 (circles) and method 2 (squares). See Table II and the footnotes.

In summary, we have established a procedure for evaluating the "net" interaction parameter $\chi_{12}°$ between unlike polymer segments. It is based on eq 26 with eq 22 for $\bar{Z}_{12}$ and eq 23 for h_0. This procedure seems reliable at least for $\sigma < 2$. In order to evaluate other necessary parameters such as Z_i, $\chi_{0i}°$, and $\langle S_i^2\rangle$, the simple method based on eq 27–29 and 24 can be used, but the validity of such an approximate method should be checked by direct measurements. Insofar as the present examples are concerned, this method reproduces experimental values of both $\langle S_i^2 \rangle$ and χ_{0i} with high precision (see Table I) and should be of practical value. For a reasonably symmetrical system with a small $\chi_{12}°$, eq 30 with eq 23 and 31 may be used instead of eq 26 with eq 22 and 23.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research, the Ministry of Education, Japan (Grant-in-Aid 59550613).

Registry No. PS, 9003-53-6; PMMA, 9011-14-7.

References and Notes

(1) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1984**, *17*, 548.

(2) Fukuda, T.; Nagata, M.; Inagaki, H. *Macromolecules* **1986**, *19*, 1411.

(3) Nagata, M.; Fukuda, T.; Inagaki, H. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 127.

(4) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.

(5) Equation 12 in ref 2 defines the χ parameters appearing in our light scattering work. Since, in this paper, we are concerned only with infinitely dilute solutions, eq 14 (instead of eq 12) in ref 2 may be regarded as the defining equation for them. In terms of the g_{ij} functions (e.g.: Koningsveld, R.; Chermin, H. A. G.; Gordon, M. *Proc. R. Soc. London, A* **1970**, *319*, 331; see also eq 1 in ref 2), the χ_{ij}'s for infinitely dilute solution are given by[2]

$$\chi_{0i} = g_{0i} - (\partial g_{0i}/\partial\phi)_{\phi=0} \quad (i = 1 \text{ or } 2)$$

$$\chi_{12} = g_{12}$$

(6) Krigbaum, W. R.; Flory, P. J. *J. Chem. Phys.* **1952**, *20*, 873.

(7) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.

(8) Klotz, S.; Cantow, H.-J.; Kögler, G. *Polym. Bull. (Berlin)* **1985**, *14*, 143.

(9) Stockmayer, W. H.; Stanley, H. E. *J. Chem. Phys.* **1950**, *18*, 153.

(10) (a) Flory, P. J.; Krigbaum, W. R. *J. Chem. Phys.* **1950**, *18*, 1086. (b) Orofino, T. A.; Flory, P. J. *J. Chem. Phys.* **1957**, *26*, 1067. (c) Stockmayer, W. H. *Makromol. Chem.* **1960**, *35*, 54.

(11) Tanaka, G.; Šolc, K. *Macromolecules* **1982**, *15*, 791.

(12) Yamakawa, H.; Kurata, M. *J. Chem. Phys.* **1960**, *32*, 1852.

(13) Noda, I.; Kitano, T.; Nagasawa, M. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1129.

(14) (a) Kurata, M.; Fukatsu, M.; Sotobayashi, H.; Yamakawa, H. *J. Chem. Phys.* **1964**, *41*, 139. (b) Yamakawa, H. *J. Chem. Phys.* **1968**, *48*, 2103.

(15) Yamakawa, H.; Tanaka, G. *J. Chem. Phys.* **1967**, *47*, 3991.

(16) Fukuda, T.; Inagaki, H. *Pure Appl. Chem.* **1983**, *55*, 1541.

(17) Fukuda, T., unpublished experiments.

(18) A value recommended for polymers with reasonably narrow distribution in molecular weight (cf.: Kurata, M., et al. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Academic: New York, 1975; Chapter IV.)

(19) Since eq 30 has been claimed to be incorrect by some people,[20] we add some words to justify it. In the mentioned symmetrical case with a small $\chi_{12}°$, eq 26 reads

$$\chi_{12} = (1 - 2\chi_{0i}°)(1 + \kappa)h_0(\bar{Z}_{12}) - (1 - 2\chi_{0i}°)h_0(\bar{Z}) \quad \text{(R1)}$$

with $h_0(\bar{Z}_{12}) = h_0(\bar{Z} + \kappa\bar{Z})$ being expanded around $\chi_{12}° = 0$ or $\kappa\bar{Z} = 0$ as

$$h_0(\bar{Z}_{12}) = h_0(\bar{Z}) + \kappa\bar{Z}[\mathrm{d}h_0(\bar{Z})/\mathrm{d}\bar{Z}] + ... \quad \text{(R2)}$$

Inserting eq R2 in eq R1 and neglecting higher terms in κ, we have

$$\chi_{12} = \kappa(1 - 2\chi_{0i}°)[h_0 + \bar{Z}(\mathrm{d}h_0/\mathrm{d}\bar{Z})] = \chi_{12}°[\mathrm{d}(\bar{Z}h_0)/\mathrm{d}\bar{Z}] \quad \text{(R3)}$$

which is identical with eq 30. See ref 1 for a more simple description.

(20) Su, A. C.; Fried, J. R. *Macromolecules* **1986**, *19*, 1417.

Investigation of Transition Phenomena of Polymers in Dilute Solutions by Gel Permeation Chromatography

Constantinos Tsitsilianis and Anastasios Dondos*

Department of Chemical Engineering, University of Patras, 26110 Patras, Greece.

Received May 9, 1986

ABSTRACT: Gel permeation chromatography (GPC) has been used as a new technique for the study of temperature-induced polymer transitions in dilute solutions. Using a GPC apparatus with controlled temperature, we have studied the transition of polystyrene in solution in the binary solvent mixture benzene–methanol (74:26 v/v) and the transition of the triblock copolymer poly(methyl methacrylate)–polystyrene–poly(methyl methacrylate) in solution in tetrahydrofuran. The GPC method has corroborated our previous findings on transition phenomena of polymers observed near Θ conditions.

Introduction

In recent years many papers have appeared dealing with the transition phenomena of macromolecular chains in dilute solutions. Some of these are reported as helix–coil transitions, mainly found for biopolymers and wormlike polymers.[1-5] Another type of transition is reported as conformational[6-28] and is related to an order–disorder transition of the side groups of the macromolecular chains. In the case of block and graft copolymers the transtion phenomena are related to the segregated and nonsegregated conformations of these copolymers.[29-40]

Recently, we observed a new type of transition closely related to Θ conditions.[41-43] More precisely, this transition appeared just above the Θ conditions and was observed either by changing the temperature of the solution when the polymer is dissolved in a single solvent or by chainging the solvent composition at constant temperature when the polymer is dissolved in a binary solvent mixture. This transition seems to be related to an abrupt augmentation of the mobility of the chain backbone affecting mainly the short-range interactions. The phenomenon has also been observed by Nishio et al.;[44] using photon correlation spectroscopy they found strong fluctuation in the chain density in the same temperature range.

All the above transition phenomena have been studied by a variety of experimental techniques. Some of these techniques, e.g., IR spectroscopy,[5,7,39] UV spectroscopy,[6,40] ultrasonic relaxation,[21] and quasi-elastic neutron scattering,[28] are concerned with local changes in the macromolecular chain. There are other techniques, e.g., static light scattering,[1,2,7,9,10,34] refractometry,[13,16,18,19,25] and viscometry,[14-20,22-26,29-32,41-43] that deal with the overall dimensions of the macromolecular chains.

Gel permeation chromatography has been established as a very useful technique for studying macromolecules. One of the principal aims of the GPC method is to de-

0024-9297/87/2220-0658$01.50/0