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Light Scattering from Ternary Solutions. 1. Dilute Solutions of Polystyrene and Poly(methyl methacrylate)

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ABSTRACT: The Flory–Huggins interaction parameter χ_{12} between unlike polymers in dilute ternary solutions of polystyrene, poly(methyl methacrylate), and bromobenzene was evaluated by light scattering conducted under the special condition that we call an "optical Θ state". In this state, the scattering components relevant to the polymer–solvent interactions exactly cancel each other, and this permits observation of the heteropolymer interaction only. Measurements were made for several blends of the polymers, covering a wide range of molecular weight. In all the cases examined, the concentration envelope of the Zimm plot was represented by a straight line extending to a remarkably high concentration. It was thus possible to evaluate χ_{12} with high precision, despite its small magnitude (typically, of the order of 10^{-3}). It was established that χ_{12} decreases with an increase in molecular weight. The observed trend of χ_{12} was shown to be nearly quantitatively consistent with dilute solution theories. It seems that χ_{12} becomes concentration dependent above a certain, relatively high concentration and that this characteristic concentration is molecular weight dependent.

Introduction

Quantitative discussion of the polymer–polymer interaction in a ternary solution of two polymers 1 and 2 and a solvent has usually involved determining the phase diagram to calculate the Flory–Huggins interaction parameter χ_{12} between the two polymers.[1-3] The phase diagram approach, however, is tedious and may not always provide accurate results.[3] Moreover, it is basically incapable of providing information off the loci of the binodals. As is well-known, the Flory–Huggins solvent–polymer interaction parameter χ_{0i}, where the subscript 0 denotes the solvent and i the polymer, depends on both the molecular weight and concentration of the polymer.[4-6] The few previous studies on ternary solutions imply that χ_{12} also depends on either or both of them.[2,3] In order to establish these dependencies and comprehensively understand the behavior of a ternary solution, it is necessary to evaluate χ_{12} as a function of molecular weight and of concentration continuously from the dilute limit up to the region of phase separation.

The light scattering method in principle meets this requirement. There have been several interesting light scattering studies. Notably, Scholte[5,6] has accurately determined χ_{0i} of binary solutions by this method. He also studied the spinodal of polystyrene (PS)–cyclohexane systems, showing the advantage of this method.[6] The spinodal approach was later used by van den Esker and Vrij[3] to investigate PS–polyisobutylene (PIB)–toluene ternary solutions. They chose toluene as solvent because PIB scatters little light in it, and this offered a certain advantage in their later analysis.[7] This technique of optically masking one of the polymer components has been commonly employed to study ternary solutions[8-10] as well as block copolymer solutions.[11-15]

A dilute ternary solution study by light scattering originates from the work of Stockmayer and Stanley,[16] who investigated mixtures of PS and poly(methyl methacrylate) (PMMA) in a solvent giving large refractive index increments (of the same sign) to the polymers. More systematic work along this line has been reported by Kratochvil et al.,[17,18] who evaluated the second virial coefficient between unlike polymers. As opposed to one's intuitive expectation, this parameter was found to decrease as the value of χ_{12}, calculated according to Krause's procedure,[19] increases, an unexplained result.

Generally, it is difficult to precisely determine χ_{12}, especially in dilute solution. The effects of polymer–solvent interactions are usually so large that they are likely to mask the relatively small contribution from a polymer–polymer interaction. The report of Hyde and Tanner[8] on the PS–PIB–cyclohexane system clearly indicates the difficulty of this kind. According to concentrated solution studies,[1,3] χ_{12} of this system is expected to be positive, possibly of the order of 10^{-2}. However, the dilute solution work could show only that it is zero with estimated error limits from 10^{-2} to as large as 10^{-1}.

In a previous note,[20] we have proposed a light scattering method that may overcome the difficulty and simplify experiments. It is based on the use of a solvent in which the refractive index increments of the two polymers are opposite in sign so that the scattering components relevant to polymer–solvent interactions cancel each other. It should be possible in this way to observe the polymer–polymer interaction selectively.

In this work, we apply this technique to dilute ternary solutions of PS and PMMA. To our knowledge,[16,21] this

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polymer pair is characterized by a relatively weak interaction between them, and hence the system appears to be suitable for testing the validity of the method. If it works satisfactorily for this system, it should be even more promising for those systems characterized by a stronger polymer–polymer interaction.

Method

We combine the theory of light scattering from multicomponent solutions[22-24] with the Flory–Huggins expression[25] for the free energy of mixing two monodisperse polymers 1 and 2 with a solvent to obtain the following formula, which is valid for low polymer concentrations:[16]

$$R_0/(K^*V_0\phi) = A + B\phi + \mathcal{O}(\phi^2) \tag{1}$$

$$A = \psi_1^2 m_1 x_1 + \psi_2^2 m_2 x_2 \tag{2}$$

$$B = -(\psi_1 m_1 x_1 + \psi_2 m_2 x_2)[\psi_1 m_1 x_1(1 - 2\chi_{01}) + \psi_2 m_2 x_2(1 - 2\chi_{02})] - 2\psi_1\psi_2 m_1 m_2 x_1 x_2 \chi_{12} \tag{3}$$

with

$$K^* = (4\pi^2 n^2)/(N_A \lambda_0^4) \tag{4}$$

$$\phi = \phi_1 + \phi_2 \tag{5}$$

$$x_1 = 1 - x_2 = \phi_1/\phi \tag{6}$$

$$\psi_i = \partial n/\partial \phi_i, \qquad i = 1 \text{ or } 2 \tag{7}$$

In the above equations, R_0 is the forward scattering intensity excess over that of the solvent, n is the refractive index of the solution, N_A is the Avogadro number, λ_0 is the wavelength in vacuum, V_0 is the solvent molar volume, and m_i is the degree of chain length, i.e., the ratio of the molar volume of polymer i to V_0; the concentration ϕ_i is defined as a volume fraction *before mixing*, i.e.

$$\phi_i = w_i v_i / (\sum_i w_i v_i) \tag{8}$$

where w_i is the weight fraction of component i having a specific volume v_i in the pure state (i = 0, 1, or 2). When the polymers are polydisperse, the degrees of chain length may be regarded as weight-average values.[26] This approximation is valid only when the distribution is not too broad, since the interaction parameters are generally molecular weight dependent.

Equations 1–3 indicate that if χ_{01} and χ_{02} are determined by independent experiments, χ_{12} can be evaluated by studying a ternary solution. However, one cannot except a high precision in this way, since the first term in eq 3 is usually very large as compared with the second term. We thus propose carrying out measurements under the condition

$$\psi_1 m_1 x_1 + \psi_2 m_2 x_2 = 0 \tag{9}$$

which transforms eq 1–3 to

$$K^*V_0\phi/R_0 = A' + B'\phi + \mathcal{O}(\phi^2) \tag{10}$$

$$A' = (\psi_1^2 m_1 x_1 + \psi_2^2 m_2 x_2)^{-1} \tag{11}$$

$$B' = 2\psi_1\psi_2 m_1 m_2 x_1 x_2 A'^2 \chi_{12} \tag{12}$$

Clearly, then, the initial slope of the ϕ/R_0 vs. ϕ plot is directly proportional to χ_{12} *regardless of the thermodynamic properties of the solvent.*

A similar situation may occur in a common Θ solvent in which both χ_{01} and χ_{02} are equal to $^1/_2$, and thus the coefficient in eq 3 is again proportional to χ_{12}. In practice, such a solvent will hardly ever be found. In contrast, the condition in eq 9, which we shall call an *optical Θ condition*, may be relatively easily met: one has only to find a common solvent whose refractive index is between those of the polymers so that ψ_1 and ψ_2 are opposite in sign. With such a solvent, one can adjust either molecular weights or blending ratio x_i so as to satisfy eq 9. Since $\psi_1\psi_2$ is negative in such a solvent, the coefficient B' in eq 12 is negative, if χ_{12} is positive. In other words, the scattering intensity increases more rapidly than does ϕ, which makes determination of R_0 easier than in a conventional (i.e., $\psi_1\psi_2 > 0$) solvent.

Another advantage of using an optical Θ solvent becomes evident when one deals with a symmetrical system, a system in which $\chi_{01} = \chi_{02}$, $m_1 = m_2$, and $x_1 = x_2$ (but $\psi_1 = -\psi_2$). Examining the light scattering equation combined with the Flory–Huggins formula in nonexpanded form (see, e.g., ref 3 and 24), we see that all the terms that are equal to or higher than the second power of ϕ simultaneously vanish in a symmetrical system. Provided that χ_{12} is independent of ϕ, the ϕ/R_0 vs. ϕ plot is thus linear up to the spinodal, at which R_0 becomes "infinitely" large. For this reason, we may expect to determine χ_{12} with high precision, even when it is small. In addition, it can be easily shown that errors associated with incomplete satisfaction of eq 9 becomes minimal when $\chi_{01} = \chi_{02}$ (cf. eq 3).

Figure 1 shows plots of ϕ/R_0 vs. ϕ computed for several different optical conditions. It was assumed that $x_1 = x_2 = {}^1/_2$, $m_1 = m_2 = 2 \times 10^4$, $\chi_{01} = \chi_{02} = 0.47$, and $\chi_{12} = 0.003$. These parameter values crudely approximate those of one of the PS–PMMA–bromobenzene systems to be studied below. The solid curves are for $\chi_{12} = 0.003$, and the broken curves are for $\chi_{12} = 0$. When $\psi_1\psi_2 > 0$ (curves 1 and 1′ in plots a and b of Figure 1), the scattering curves exhibit large curvature, and their initial slopes are large. When $\psi_1 = -\psi_2$ (curves 3 and 3′), they have no curvature, and the slopes are proportional to χ_{12}, as already stated. When either ψ_1 or ψ_2 is zero (curves 2 and 2′), the initial slopes of the solid and broken curves are identical. In other words, a *dilute* solution study under this condition provides no information on χ_{12}. When polymer concentration is low, the differences between the solid and broken curves are rather trivial for this particular system with a small value of χ_{12} (see Figure 1b). This indicates the aforementioned difficulty with dilute solution studies. The case with $\psi_1 = 2\psi_2$ (curves 1 and 1′ in Figure 1b) should be particularly noted: indeed the initial slope of the solid curve is slightly larger than that of the broken curve, but the latter becomes equal to the former at a concentration as low as about 0.1% and then exceeds it. Obviously, when χ_{12} is larger the scattering curve becomes more convex, and the concentration at which the two curves intersect becomes smaller. Qualitatively erroneous conclusions may result from experiments carried out under such a (conventional) optical condition, unless measurements are made at unusually low concentrations. We suscept that conflicting results reported in the literature may be at least partly due to this cause.

Experimental Section

Polymer Samples and Characterization. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) samples were anionically prepared in tetrahydrofuran at −78°C with *n*- or *sec*-butyllithium initiator.[13,27] Two PS samples, coded PC200 and F80, were purchased from Pressure Chemicals Co. Ltd. and Toyo Soda Co. Ltd., Japan, respectively. The weight-average molecular weight M_w of each sample was determined by light scattering in 2-butanone and/or bromobenzene, and the weight- to number-average molecular weight ratio M_w/M_n was estimated by gel permeation chromatography after being corrected for axial dispersion.[27] The sample characteristics are listed in Table I. The table shows that all the samples have reasonably narrow distribution.

Table I
Molecular Characteristics of Polymer Samples[a]

sample		$10^{-4}M_w$[b,c]	$10^{-4}M_w$	M_w/M_n[c]	10^4A_2	χ_{0i}	$\langle S^2\rangle_z^{1/2}$, Å	α_w^2
PS	PC200		242	1.30	2.05	0.4743	770	2.37
	F80	77.5[b]	80.6	1.01	2.71	0.4661	370	2.09
	49H	28.3[c]		1.10		(0.455)		(1.75)
	57H	32.2[c]	32.4	1.02	3.45	0.4568	218	1.71
	39H	2.45[c]		1.27		(0.412)		(1.29)
PMMA	75M	214[b]	219	1.35	1.57	0.4752	660	2.53
	78M	62.7[b]	62.5	1.45	2.33	0.4633	334	2.20
	31M	21.1[b]	20.2	1.27	2.89	0.4544		(1.83)
	91M	2.45[c]		1.04		(0.414)		(1.35)

[a] Bromobenzene, 30 °C unless otherwise indicated; values in parentheses were estimated. [b] 2-Butanone, 30 °C. [c] GPC value.

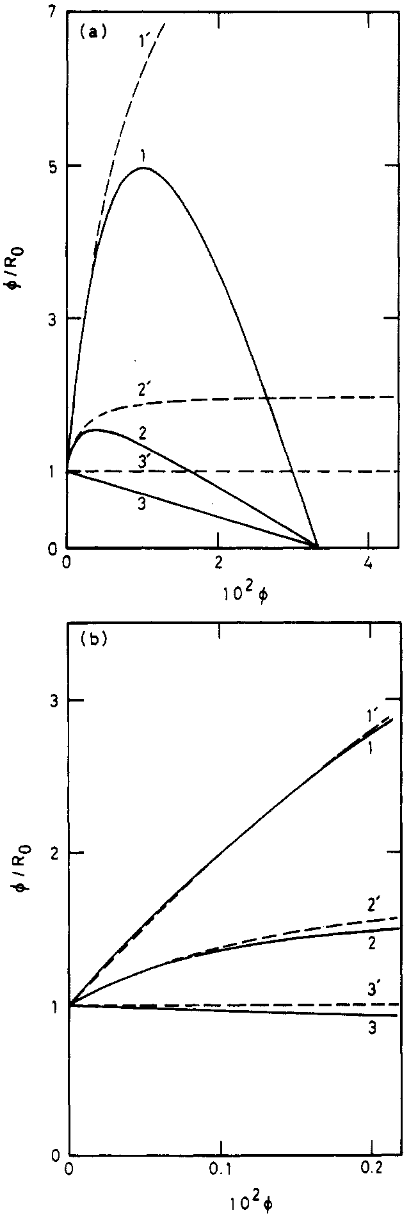

Figure 1. Plots of ϕ/R_0 vs. ϕ for a ternary solution with $m_1 = m_2 = 2 \times 10^4$, $x_1 = x_2 = {}^1/_2$, $\chi_{01} = \chi_{02} = 0.47$, and $\chi_{12} = 0.003$ (solid curves) or $\chi_{12} = 0$ (broken curves). Optical conditions are $\psi_1 = 2\psi_2$ (curves 1 and 1'), $\psi_1\psi_2 = 0$ (curves 2 and 2'), and $\psi_1 = -\psi_2$ (curves 3 and 3'). The ordinate scale is normalized to unity at $\phi = 0$. Part b represents details of (a) near $\phi = 0$.

Refractive Index Increments. The weight fraction based refractive index increments $\partial n/\partial w$ of PS and PMMA in bromobenzene at 30 °C were determined on a Union Giken differential refractometer Model RM102, Japan. As the specific volumes of PS and PMA, we take values of $v_{PS} = 0.935$ and $v_{PMMA} = 0.825$ at 30 °C, which were obtained by extrapolating the liquid polymer data of Richardson and Savill[28] for PS and of Wittmann and Kovacs[29] for PMMA. This gives values of $\psi = \partial n/\partial\phi$: $\psi_{PS} = 0.0518$ and $\psi_{PMMA} = -0.0607$.

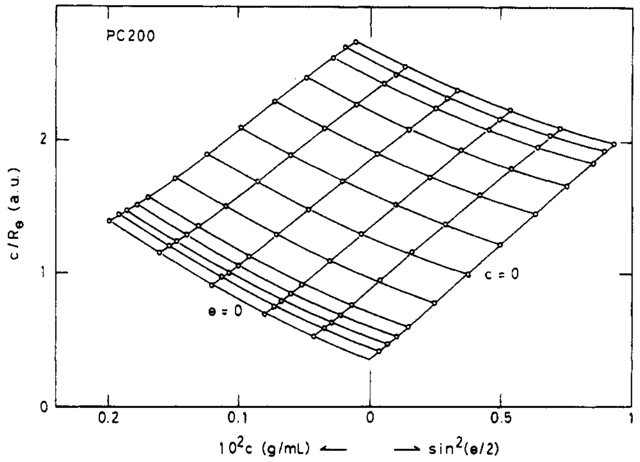

Figure 2. Zimm plot for PS (PC200)-bromobenzene binary solution at 30 °C: R_θ is the scattering intensity (in arbitrary units) at scattering angle θ.

Light Scattering. Measurements were made in bromobenzene at 30 °C on a Fica light scattering photometer Model 50, France. Scattered light intensities were measured in most cases at 12 different angles from 22.5° to 150° with vertically polarized light of 436-nm wavelength. Details have been described elsewhere.[13]

The solvent and solutions were clarified by filtration through two ultracellafilter membranes with a pore size of 0.2 or 0.45 μm. To obtain a dust-free solution of relatively high concentration, a filtered dilute solution placed in a light scattering cell was brought to the desired concentration by evaporating the solvent in a vacuum oven at ambient temperature.

Light scattering measurements were made on four combinations of the samples, each consisting of a PS and a PMMA of similar molecular weight, blended in such a ratio as to meet the condition in eq 9. For the purpose of later discussion, measurements were also made on several polymer-solvent binary solutions, even though these were unnecessary to evaluate χ_{12} itself, as already described.

Results and Discussion

Typical light scattering results obtained for PS- and PMMA-bromobenzene binary solutions are presented in Figures 2 and 3. The molecular weight of each polymer determined in bromobenzene agreed well with that determined in 2-butanone or estimated by GPC (see Table I). The second virial coefficient A_2 evaluated from the conventional Zimm plot, i.e., K^*c/R_0 vs. c plot with c in g/mL, is related to the Flory-Huggins χ_{0i} parameter through

$$A_2 = (v_i^2/V_0)(1/2 - \chi_{0i}) \qquad (13)$$

Table I includes values of χ_{0i} as well as α_w^2, the weight-

Table II
Light Scattering Results for PS-PMMA-Bromobenzene Ternary Solutions at 30 °C

blend						χ_{12}^{0} [d]	
PS	PMMA	ξ_{PS} [a]	$1/A'$ [b]	$\langle S^2\rangle_{app}^{1/2}$, [c] Å	χ_{12}	FKOm-Fm	KY-YT
PC200	75M	0.455	58.3 (60.1)	720 (713)	0.0026	0.020	0.024
F80	78M	0.427	17.6 (18.1)	345 (350)	0.0030	0.018	0.022
49H	31M	0.407	6.20 (6.33)		0.0040	0.018	0.021
39H	91M	0.479	0.62 (0.64)		0.0117	0.031	0.031

[a] Weight fraction of PS. [b] $A' = (K^*V_0\phi/R_0)_{\phi=0}$; values in parentheses were calculated. [c] Apparent radius of gyration; values in parentheses were calculated. [d] FKOm: Flory-Krigbaum-Orofino modified equation; Fm: Flory modified equation; KY: Kurata-Yamakawa equation; YT: Yamakawa-Tanaka equation.

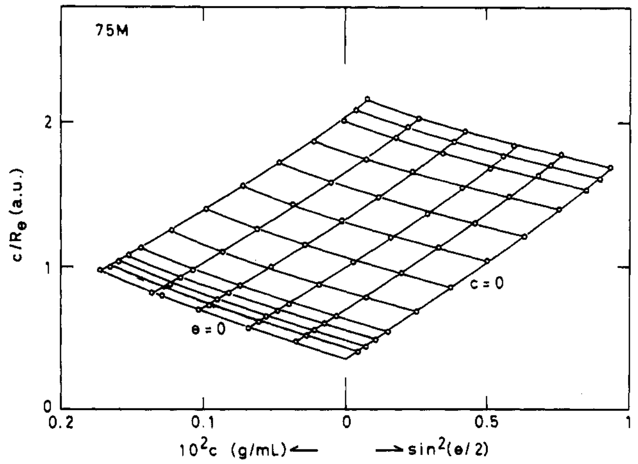

Figure 3. Zimm plot for PMMA (75M)-bromobenzene binary solution at 30 °C: see the caption for Figure 2.

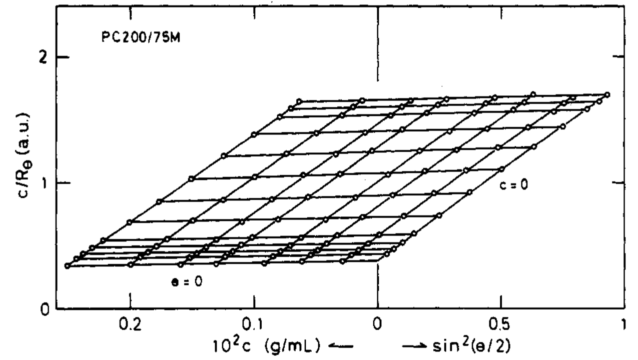

Figure 4. Zimm plot for PS (PC200)-PMMA (75M)-bromobenzene ternary solution at 30 °C: see the caption for Figure 2.

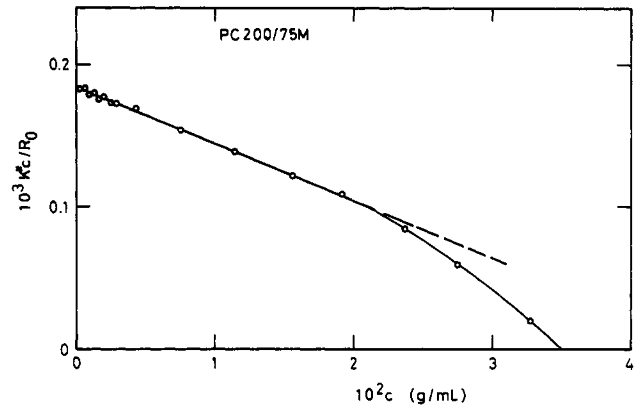

Figure 5. Plot of K^*c/R_0 vs. c for PS (PC200)-PMMA (75M)-bromobenzene ternary solution at 30 °C.

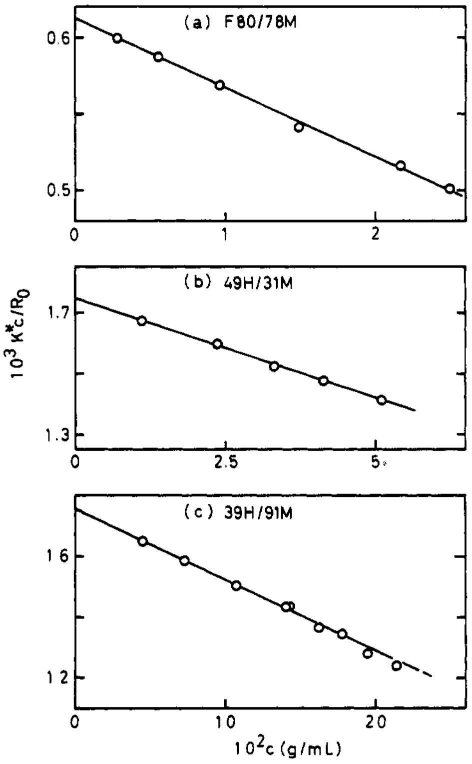

Figure 6. Plots of K^*c/R_0 vs. c for PS-PMMA-bromobenzene ternary solutions at 30 °C.

average square expansion factor, calculated from the observed z-average square radius $\langle S^2\rangle_z$ by assuming the Schulz-Zimm function for the molecular weight distribution and the following values of unperturbed radius:[30]

$$\begin{aligned} \langle S^2\rangle_{w,0}^{1/2} &= 0.294 M_w^{1/2}\ \text{Å} \qquad \text{(PS)} \\ &= 0.253 M_w^{1/2}\ \text{Å} \qquad \text{(PMMA)} \end{aligned}$$

These data indicate that bromobenzene is a good solvent with nearly equal solubility toward PS and PMMA. Our systems are thus regarded as nearly symmetrical.

Figure 4 shows the Zimm plot obtained for dilute solutions of the blend of the PS and PMMA samples presented in Figures 2 and 3. The ordinate intercept of the zero-θ (or zero-c) curve and the apparent radius of gyration obtained from the zero-c curve agreed within experimental error with calculated values A' and $\langle S^2\rangle_{app}$, respectively, where A' is given by eq 11 and $\langle S^2\rangle_{app}$ by[31]

$$\langle S^2\rangle_{app} = A'(\psi_1{}^2 m_1 x_1 \langle S^2\rangle_{z,1} + \psi_2{}^2 m_2 x_2 \langle S^2\rangle_{z,2})$$

This was the case with all the blend systems examined (see Table II). The concentration envelopes, i.e., the zero-θ curves, of the binary systems have fairly large slopes (Figures 2 and 3), whereas that of the ternary system has a very small, *negative* slope. Thus, it is immediately clear that the system is characterized by a small, *positive* χ_{12}. However, its absolute value may be too small to precisely evaluate from these low-concentration data.

In Figure 5, the concentration envelope of the same system is extended to a higher concentration range. As predicted, the curve is linear up to a considerably high concentration. Similar results for other blends are presented in Figure 6. In the system composed of the lowest molecular weight samples, linearity seems to hold up to a concentration as high as 0.2 g/mL (Figure 6c). It is unlikely that the curves have a different slope at very low concentrations, where measurements were not made (cf. Figure 5). We thus evaluated χ_{12} from the slopes of the linear portions of the curves. The results are listed in Table II.

Table II reveals that χ_{12} is molecular weight dependent: the larger the molecular weights are, the smaller χ_{12} is. To our knowledge, this is the first observation of the molecular weight dependency of χ_{12} in dilute solution.

This trend of χ_{12} is similar to that of the second virial coefficient A_2 in a binary solution, which generally decreases with an increase in molecular weight. According to the dilute solution theory, the second virial coefficient between polymer molecules of the same type is given in the form[32]

$$A_2 = 4\pi^{3/2}N_AM^{-2}\alpha^3\langle S^2\rangle_0^{3/2}\Psi(\bar{Z}) \qquad (14)$$

where Ψ is the interpenetration factor, which is a function only of $\bar{Z}$, i.e., the excluded volume parameter Z divided by the cubic expansion factor

$$\bar{Z} = Z/\alpha^3 \qquad (15)$$

We now consider a ternary solution that is symmetrical with respect to the two polymers and assume that an excess interaction χ_{12}^0 is operative between unlike polymer segments. Since polymer conformation and hence α are little perturbed by an intermolecular interaction, the parameter $\bar{Z}$ between unlike polymers is larger by an amount proportional to χ_{12}^0 than that between like polymers. Since, furthermore, $(\partial A_2/\partial\bar{Z})_\alpha$ is proportional to $\mathrm{d}\Psi/\mathrm{d}\bar{Z}$ (see eq 14), an observed (apparent) value of χ_{12} must be related to the "true" value, i.e., χ_{12}^0, by

$$\chi_{12} = (\mathrm{d}\Psi/\mathrm{d}\bar{Z})\chi_{12}^0 \qquad (16)$$

where χ_{12}^0 has been assumed to be small. The function $\mathrm{d}\Psi/\mathrm{d}\bar{Z}$ converges to unity for small $\bar{Z}$ and decreases with an increase in $\bar{Z}$, and hence in molecular weight.[32] Thus eq 16 explains the behavior of our (nearly symmetrical) systems.

It may be interesting to discuss this matter somewhat quantitatively. Several theoretical expressions are available with regard to Ψ and α: the modified Flory–Krigbaum–Orofino equation[33] for Ψ and the modified Flory equation[33] for α are given by

$$\Psi = \ln(1 + 5.73\bar{Z})/5.73 \qquad (17)$$

$$\alpha^5 - \alpha^3 = 1.276Z \qquad (18)$$

On the basis of the values of α of the two polymers given in Table II, we calculate $\bar{Z}_{\mathrm{PS}}$ and $\bar{Z}_{\mathrm{PMMA}}$ according to eq 18 and 15. Since $\bar{Z}_{\mathrm{PS}}$ and $\bar{Z}_{\mathrm{PMMA}}$ are close to each other in our systems, the value of $\bar{Z}$ to be inserted in eq 16 and 17 may be approximately given by (see note 34)

$$\bar{Z} = (\bar{Z}_{\mathrm{PS}}\bar{Z}_{\mathrm{PMMA}})^{1/2} \qquad (19)$$

Values of χ_{12}^0 estimated in this way are listed in Table II. A similar estimation was made based on the combination of the Kurata–Yamakawa theory[36] on Ψ and the Yamakawa–Tanaka theory[37] on α to obtain the results given in the same table. Even though absolute values of χ_{12}^0 are somewhat different for the use of different theories, they no longer seem dependent on molecular weight.

Hence we conclude that (i) the trend of χ_{12} herein observed is a real phenomenon originating from an excluded volume effect, and (ii) the present light scattering method allows determination of χ_{12} with fair precision: (iii) the value of χ_{12}^0 between PS and PMMA is likely to be 0.025 ± 0.005. Discussion on this estimate will be given elsewhere.[38]

Some comments are due with regard to the behavior of χ_{12} at higher concentrations. Figure 5 shows that linearity in the c/R_0 vs. c curve breaks at a concentration of about 0.02 g/mL, beyond which R_0 increases more rapidly with increasing concentration, approaching the spinodal defined as the intercept with the horizontal axis. If we estimate the value of χ_{12} at the spinodal[3] by tentatively assuming that all χ's are independent of concentration, we have $\chi_{12}^{\mathrm{sp}} = 0.0034$ (the estimated value of χ_{12} is insensitive to absolute values of χ_{01} and χ_{02}, insofar as symmetry of the system is preserved). This value is significantly larger than the dilute limit value of 0.0026 (Table II), and this suggests that χ_{12} is dependent also on concentration. It is likely that χ_{12} is nearly constant in the range where the concentration envelope is linear, and it becomes concentration dependent beyond a certain concentration. This characteristic concentration appears to be dependent on molecular weight (cf. Figures 5 and 6). Quantitative discussion on this matter will be given in a separate paper.[39]

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Combined Integrated and Dynamic Light Scattering by Poly(γ-benzyl glutamate) in a Helicogenic Solvent[†]

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ABSTRACT: Simultaneous static and dynamic light scattering measurements were performed on poly(γ-benzyl glutamate) (PBG) in dimethylformamide (DMF) over a wide molecular weight range ($37\,000 \leq M_w \leq 560\,000$). The measurements independently demonstrate that the pitch of the helix formed by PBG in DMF is h = 1.5 Å, which coincides with the value found by Pauling and Corey for the α-helical structure in the solid state. The helix in solution cannot be described by a rigid rod but rather by a wormlike chain with considerable flexibility. By accounting in particular for the polydispersity of the samples the Kuhn statistical segment length was determined to be $\lambda^{-1} = 1400 \pm 100$ Å, which is smaller than reported in the literature. Theoretical calculations of the radius of gyration and of the hydrodynamic radius reveal that the neglect of polydispersity effects leads to an overestimate of the chain stiffness.

Introduction

Some time ago, Doty, Blout, and co-workers[1-4] found that under certain conditions, e.g., with slight variation of temperature or solvent composition, some polypeptides undergo a remarkably sharp transition from flexible or coiled structures to more or less rigid helices. Among these, PBG is one of the most thoroughly investigated polymers, and numerous publications deal with the cooperative phenomena of the helix–coil transition.[5-12] Others are concerned with the structure and the chain stiffness of the helix in solution.[13-23] The helix parameters have been explored for the solid state by means of X-ray diffraction[24,25] and still serve as helpful guides also for the helical structure in solution. However, it is still unclear whether the helical structure of PBG in solution is identical with the solid-state helix.

In solution long helical chains cannot be expected to show the behavior of completely rigid rods, but the helix will undergo bending motions which eventually will lead to a coiled structure in the limit of very large molecules. Commonly the chain stiffness is characterized by either the Kuhn preferential statistical length λ^{-1} or the Kratky–Porod persistence length a. In the Kuhn model[26] the segments of length λ^{-1} are considered as rigid rods linked together by flexible joints, whereas Kratky and Porod[27] considered a "limiting continuous chain",[28] which nowadays is commonly called the "wormlike" chain model. Kratky and Porod showed that in the limit of very long chains i.e., many Kuhn segments per chain, the Kuhn length is just twice the persistence length $\lambda^{-1} = 2a$. The persistence length is defined by the condition that the average scalar product of the two tangent vectors $\vec{b}_j$ and $\vec{b}_{j+n}$ at the chain positions j and $j + n$ has decayed to $1/e$, i.e., $\langle(\vec{b}_j\vec{b}_{j+n})\rangle = 1/e$, which corresponds to an average angle between the two ends of a persistence unit of $\vartheta = 68.4°$.

The purpose of the present paper is to demonstrate that a highly accurate determination of the persistence length is obtained if the measurements of static (or frequency integrated) (ILS) and of dynamic (or quasi-elastic) (QLS) light scattering are performed simultaneously.

Static light scattering has been frequently applied to study the rigidity of polymers in solution. Based on the Kratky–Porod wormlike chain model, the radius of gyration[29,30] and the particle scattering factor[31-33] were calculated for monodisperse and polydisperse systems. Unfortunately, uncertainties in the mass per unit length, M_L, and mostly unknown polydispersities of the samples made the interpretation of the static light scattering data somewhat ambiguous.

Theoretical investigations of flexible polymers suggested[34] that a combination of static and dynamic light scattering should allow a precise and extensive characterization of polymers in solution. The first simultaneously measured ILS and QLS results[35] confirmed these expectations, and it appeared natural to apply this combination of light scattering techniques also to stiff polymers. The main advantage of recording ILS and QLS simultaneously is the fact that the *same* set of photons is averaged (ILS) and correlated (QLS). Thus, the ILS and QLS data originate from the same source of scatterers.

Until recently,[36,37] there has been no adequate theoretical treatment of the influence of chain stiffness on QLS.

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