Light-Scattering Studies of a Polystyrene–Poly(methyl methacrylate) Two-Block Copolymer in Dilute Solutions

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ABSTRACT: Light-scattering measurements were made on a two-block copolymer of polystyrene and poly(methyl methacrylate) using benzene and toluene as the solvent that is isorefractive to poly(methyl methacrylate). The molecular weight of the sample was 1.53×10^6 and its styrene content by weight was 0.38. Both the benzene and toluene solutions exhibited an anomalous angular dependence of the reciprocal scattering function at finite solute concentrations. A reasonable explanation to the anomaly is given in which a long-range spherically symmetric potential is used for interaction between polystyrene subchains. The mean-square distance between the centers of mass of two polystyrene subchains decreases with increase in polymer concentration, which causes the solutions to exhibit negative third virial coefficients. The mean-square radius in toluene of the polystyrene in the two-block copolymer was significantly larger than that of the homopolystyrene of equal molecular weight indicating the effect of the repulsive interaction between dissimilar segments.

The study of the molecular conformations and interactions of block copolymers consisting of incompatible polymer pairs has been the subject of extensive investigation,[1-17] but a unified conclusion does not seem to have been obtained yet. This is apparently because of the lack of success in achieving the unambiguous characterization of size and interaction of the individual block within the molecule by the usual experimental methods which include osmotic pressure, intrinsic viscosity, and conventional light scattering.[18,19] The two conformations often discussed as plausible are: (1) unlike segments rarely contact and the molecular size is close to a certain average of the dimensions of the corresponding homopolymers of equal molecular weight; (2) the domains of dissimilar segments overlap to a great extent leading to the molecular expansion due to the heterocontact repulsion. The former is frequently referred to as the "segregated structure."

One can circumvent the difficulty by performing the direct measurement of the size of only one type of block by means of light scattering which makes use of such a solvent as isorefractive to the other type of block, and by comparing the size with that of the homopolymer of equal molecular weight. This approach has been known for some time,[20,21] but no extensive investigation was performed until the recent work of Prud'homme and Bywater on polystyrene–polyisoprene two-block copolymers.[22]

In this present article we describe experimental results obtained by adopting such an approach on a two-block copolymer of polystyrene and poly(methyl methacrylate). The mean square radius of the polystyrene in the block copolymer could be measured with reasonable precision by choosing benzene and toluene as the two isorefractive solvents to the poly(methyl methacrylate) subchain. An unusual uprising of the reciprocal scattering function in the range of small scattering angles was observed at finite solute concentrations as a salient feature of the light-scattering results.[23] This anomaly has been demonstrated as a consequence of the long-range nature of interaction between the polystyrene subchains, which is provided by the masked poly(methyl methacrylate) subchain. This view agrees with that described by Prud'homme and Bywater.[22] The mean-square distance between two polystyrene subchains has been found to decrease with polymer concentration, however, in contrast to the results of these authors. The mean-square radii of the polystyrene in the block copolymer and the homopolystyrene of equal molecular weight were compared and discussed in terms of the overlapping of dissimilar segments in the block copolymer molecule.

Experimental Section

Samples of the two-block copolymer of styrene and methyl methacrylate and the homopolystyrene of the same molecular weight as the polystyrene in the block copolymer were prepared by the anionic polymerization in a high-vacuum apparatus described in detail previously.[24] The reaction was carried out at −78° under 10^{-6} mm by using *sec*-butyllithium as the initiator and tetrahydrofuran as solvent. In the polymerization of styrene monomer, which was carried out first, the seeding process was employed according to the procedure of Morton *et al.*[25] After the completion of styrene polymerization part of the reaction mixture was separated and terminated under vacuum with *n*-butyl alcohol. The homopolystyrene thus prepared should have the molecular weight identical with that of the polystyrene in the block copolymer. It was repeatedly precipitated from a benzene solution into methanol and finally freeze-dried from a benzene solution. It was designated as RS-13. The rest of the reaction mixture was used as a precursor for the further reaction with methyl methacrylate monomer. According to the procedure of Freyss *et al.*,[26] 1,1-diphenylethylene was added first to convert styryl carbanions

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Table I
Refractometric Constants Used for the Calculation of Numerical Results of Light-Scattering Measurements

			$d\tilde{n}/dc$ (ml/g)		
Solvent	Temp (°C)	$\tilde{n}_0$	Polystyrene	Poly(methyl methacrylate)	BMM-313
		λ_0 = 4358 Å			
Benzene	30	1.5164	0.1122[a]	−0.0025	0.0402
Toluene	30	1.5121	0.1134[b]	0.0011	0.0451
	69	1.4900			
		λ_0 = 5461 Å			
Benzene	30	1.4987	0.1078[a]	0.0000	0.0405
Toluene	30	1.4950	0.1096[b]	0.0031	0.0443

[a] D. McIntyre, A. Wims, L. C. Williams, and L. Mandelkern, *J. Phys. Chem.*, **66,** 1932 (1962). Correction for the temperature difference is applied to the original data for 40°. [b] J. H. O'Mara and D. McIntyre, *J. Phys. Chem.*, **63,** 1435 (1959).

Table II
Light-Scattering Results for the Homopolystyrene RS-13 and the Two-Block Copolymer BMM-313 of Styrene and Methyl Methacrylate

Solvent	Temp (°C)	λ_0 (Å)	$M \times 10^{-6}$	$A_2 \times 10^4$	$A_2^* \times 10^4$	$\langle S^2\rangle^{1/2}$ (Å)
		RS-13 (m = 1.00)				
Benzene	30	4358	0.589	3.56		362
		5461	0.589	3.30		358
Toluene	30	4358	0.586	3.05		349
		BMM-313 (m = 0.386)				
Benzene	30	4358	(1.53)	1.48	9.93	375
		5461	(1.53)	1.25	8.39	371
Toluene	30	4358	1.53	1.65	11.1	394
	69	4358	(1.53)	4.92	33.0	475

into diphenylmethyl carbanions. Methyl methacrylate was subsequently added and the reaction was continued for 12 hr at −78° under continuous stirring. The reaction was terminated under vacuum with n-butyl alcohol. The block copolymer was subjected to the boiling point extraction with cyclohexane to remove homopolystyrene if it were present. In addition, the block copolymer was subjected to the preferential precipitation from a tetrahydrofuran solution of 3% polymer concentration by the addition of cyclohexane to a final composition of 3:7 (v/v) tetrahydrofuran-cyclohexane. Only homopolystyrene is soluble in the mixture. To remove homopolymer of methyl methacrylate the block copolymer was subjected to the extraction with acetoanilide. It was finally freeze-dried from a benzene solution and designated as BMM-313.

The styrene content by weight m of the block copolymer determined by the elementary analysis was 0.38. The molecular weights of BMM-313 and RS-13 were determined by means of light scattering as 1.53×10^6 and 0.589×10^6, respectively. The styrene content 0.385 calculated from the molecular weights so obtained agrees well with the result of elementary analysis. Both the samples yielded satisfactorily sharp schlieren patterns of boundary sedimentation indicating the narrow distribution in the molecular weight.

The light-scattering instrument used and the procedure employed in the present study were described in detail elsewhere.[27,28] The high precision and sensitivity of the instrument were found extremely useful in measurements using isorefractive solvents to poly(methyl methacrylate), not only because the scattered light intensity was unavoidably reduced due to the small specific refractive index increment of the polymer solution but because the curved concentration dependence of the reciprocal scattering function, which is shown later, necessitated the measurements to very low polymer concentration for the precise extrapolation to zero concentration. The capability of the instrument of measuring the scattered light intensity at angles as low as 9° was also found valuable as described subsequently. The vertically polarized incident lights of wavelengths of 4358 and 5461 Å were used for the measurement. Measurements with the horizontally polarized incident light at a right angle were also made. The optical anisotropy was found negligibly small. The test solutions were made dust free by centrifugation for 2 hr at $4 \times 10^4 g$, and the absence of dust was checked on each test solution by viewing through a telescope at a small angle to the incident beam. Square-root plots were used to represent the data for the reasons described in a previous paper.[28] The mean-square radius could be determined correct to ±5%.

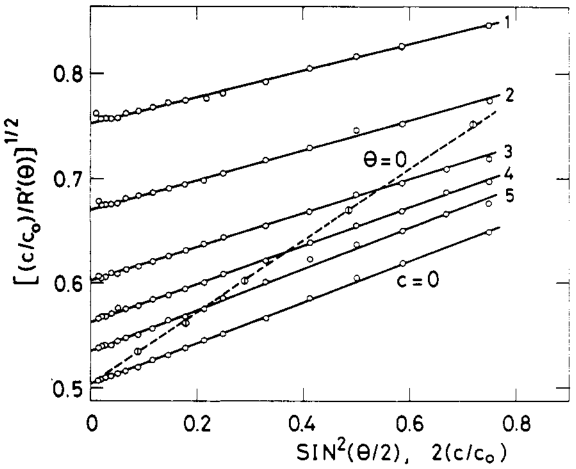

Figure 1. Light-scattering results on the homopolystyrene sample RS-13 at 30° with the incident light of 4358 Å. Toluene was used as solvent. The apparent reduced scattered intensity R' is converted into the real value by multiplying by the apparatus constant $\phi = 6.08 \times 10^{-4}$. The relative concentrations (c/c_0) are 0.359 (1), 0.244 (2), 0.145 (3), 0.0898 (4), 0.0445 (5), and c_0 is 0.704×10^{-2} g/ml. Circles with a vertical line within them represent values extrapolated at zero scattering angle, and are plotted *vs.* $2(c/c_0)$.

Refractometric constants used in the present study are summarized in Table I. The specific refractive index increment for BMM-313 was too small to be measured with sufficient accuracy. Therefore, for the internal consistency of the measurements in various solvents with the blue and green incident lights it may be reasonable, rather than to use the data of the direct measurement, to use the values calculated from the Gladstone-Dale equation

$$d\tilde{n}/dc = R_2 - (\tilde{n}_0 - 1)/\rho_2$$

using two constant values for the parameter R_2 and the polymer density ρ_2, where $\tilde{n}$ is the refractive index of solvent. The numerical values listed in Table I are calculated unless otherwise indicated by taking the polymer densities of polystyrene and poly(methyl methacrylate) as 1.05 and 1.20, respectively,[29] and R_2 as 0.6026 (4358 Å) and 0.5810 (5461 Å) for polystyrene and as 0.4278 (4358 Å) and 0.4156 (5461 Å) for poly(methyl methacrylate). These values of R_2 are chosen so as to best fit the published experimental results of specific refractive index increment.[30,31]

Experimental Results

Figure 1 shows the light-scattering results as a square-root plot on the homopolystyrene RS-13. The measurements were made at 30° with the incident light of 4358 Å using toluene as solvent. Since the mean-square radius is small, square roots of the reciprocal scattering function are seen to increase linearly with $\sin^2(\theta/2)$ at any polymer concentration investigated. The points for values obtained by the extrapolation to zero scattering angle also follow a straight line when plotted *vs.* polymer concentra-

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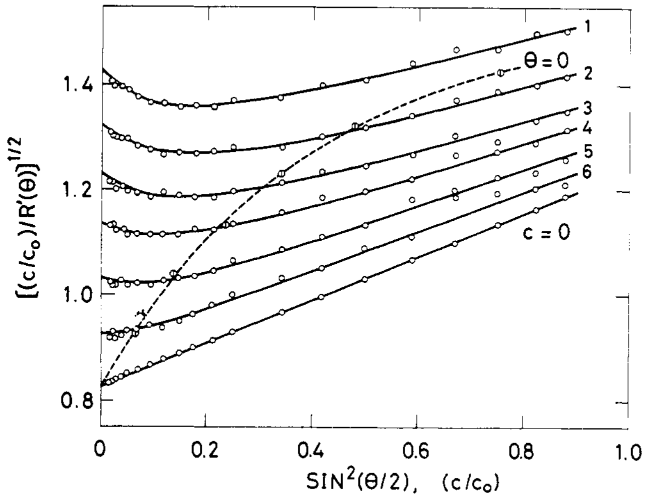

Figure 2. Light-scattering results on the two-block copolymer BMM-313 in toluene at 30° with the incident light of 4358 Å. Symbols used are similar as in Figure 1. The relative concentrations are 0.754 (1), 0.480 (2), 0.337 (3), 0.234 (4), 0.145 (5), 0.0700 (6), and c_0 is 0.691×10^{-2} g/ml.

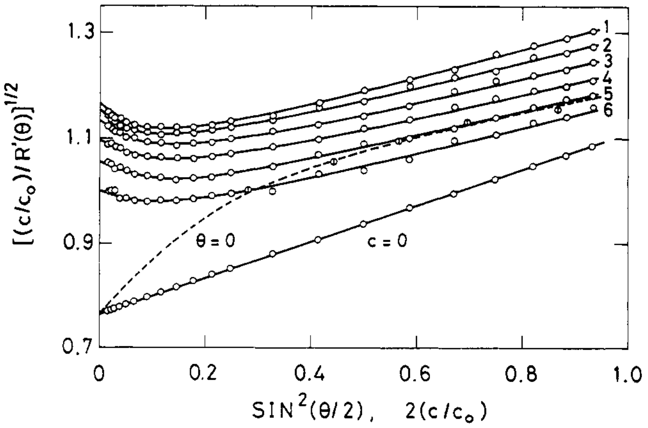

Figure 3. Light-scattering results on the two-block copolymer BMM-313 in benzene at 30° with the incident light of 4358 Å. Symbols used are similar as in Figure 1. The apparatus constant ϕ is 6.13×10^{-4}. The relative concentrations (c/c_0) are 0.528 (1), 0.433 (2), 0.348 (3), 0.283 (4), 0.211 (5), 0.141 (6), and c_0 is 1.02×10^{-2} g/ml.

tion. These results indicate that the measurement of the scattered light intensity could be performed with sufficient precision to angles as low as 9°. The measurements were also made using benzene as solvent. The light-scattering data obtained therefrom are summarized in Table II.

In contrast, the results on the two-block copolymer BMM-313 are quite anomalous as shown in Figure 2 and 3 where toluene and benzene are the solvents used, respectively. In the range of small scattering angles the plotted points are seen to increase with decrease in the scattering angle. The upsweep becomes less pronounced, however, with decrease in polymer concentration. It is also noted as anomalous that the points for zero scattering angle show a downward curvature when plotted *vs.* polymer concentration.

Let us examine the two results more in detail. For toluene solutions both the extrapolations of the experimental data to zero scattering angle and to zero polymer concentration could be made unambiguously. The extrapolations might have been difficult, however, without the capability of the instrument of accurately measuring the intensity of light scattered at small scattering angles and at low light levels as mentioned previously. The molecular weight obtained stands in satisfactory agreement with that calculated from the molecular weight of RS-13 and the weight fraction of styrene of BMM-313 determined by the elementary analysis. This result is consistent with having used the calculated value of $d\tilde{n}/dc$ for BMM-313 as an algebraic sum of those for polystyrene and poly(methyl methacrylate) assuming the same value of styrene content for the block copolymer.

For benzene solutions the downward curvature exhibited by points plotted *vs.* polymer concentration seems still pronounced at the lowest concentration investigated (0.1428×10^{-2} g/ml). The curvature becomes less at large scattering angles, though. The upsweep in the small angular range does not appear at a glance to increase with concentration as in Figure 2, but no essential difference exists between the two light-scattering results, the fact being simply that the concentration range investigated was narrower. Because the unambiguous extrapolation to zero solute concentration was difficult, we determined the ordinate intercept of the double extrapolation to zero scattering angle and zero polymer concentration so as to obtain the molecular weight of 1.53×10^6. The second virial coefficient was estimated, though approximately, from the limiting tangent of the extrapolation. For small scattering angles the extrapolations of the experimental data to zero polymer concentration were performed by reference to the extrapolation of points for zero scattering angle. The mean-square radii thus estimated are summarized in Table II.

The light-scattering measurements were also made at an elevated temperature of 69° using toluene as solvent. The anomaly in the result became less distinct than that observed at 30°. Since the apparatus constant at the temperature was unknown, we estimated A_2 by assuming the molecular weight as 1.53×10^6.

It is seen from Table II that the mean-square radius of the polystyrene in the two-block copolymer is significantly larger in toluene at 30° than that of the homopolymer RS-13 of equal molecular weight. This result apparently indicates the expansion of the polystyrene subchain through the repulsive interaction with chain elements of the poly(methyl methacrylate) subchain. When benzene is used as solvent, the similar data for the two polymers do not seem to differ beyond the experimental error. But we cannot conclude this without reservation, because some uncertainty may be involved in the procedure of the nonlinear extrapolation to zero polymer concentration. It may be pointed out that the mean square radius of the polystyrene in the block copolymer could be further underestimated unless experimental data for sufficiently small solute concentrations are available.

Discussion

We first discuss the upsweep of the reciprocal scattering function observed at finite solute concentrations in the range of small scattering angles. This type of anomaly was first reported by Doty *et al.* on charged polyelectrolytes[32,33] and synthetic polyampholyte,[34] and more recently by Burchard on poly(vinyl carbanilates)[35] and by Prud'homme and Bywater on polystyrene–polyisoprene two-block copolymers.[22] Doty and his coworkers explained the anomalous phenomenon as due to the loss by interference of light scattered from different molecules when the intermolecular potential became unusually long range. They

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discussed the potential by adopting the general equation derived by Zernicke and Prins[36] and Fournet[37]

$$R(\theta)/KcM \equiv P^*(\theta, c) = P(\theta)\{1 + (N_A c/M)\int_0^\infty [1 - e^{-U(r)/kT}] \times 4\pi r^2 (\sin hr/hr) \mathrm{d}r\}^{-1} \quad (1)$$

In this equation, $R(\theta)$ is the reduced scattered intensity, c the solute concentration in grams per milliliter, M the molecular weight of the solute, $P(\theta)$ the particle scattering factor, N_A Avogadro's number, r the distance between the centers of two molecules, $U(r)$ a spherically symmetric potential, k the Boltzmann constant, T the absolute temperature, and K and h are given by

$$K = 4\pi^2 \tilde{n}_0^2 (\mathrm{d}\tilde{n}/\mathrm{d}c)^2 / \lambda_0^4 N_A$$

$$h = 4\tilde{n}_0/\lambda_0 \sin(\theta/2)$$

where $\mathrm{d}\tilde{n}/\mathrm{d}c$ is the specific refractive index increment of the solution, λ_0 the wavelength of the incident light in vacuum, and θ is the scattering angle. In eq 1 the radial distribution function was approximated by the first term, *e.g.*, $\exp[-U(r)/kT]$, of its series expansion in powers of the solute concentration. Therefore, eq 1 should be regarded as valid only at sufficiently low concentrations.

The unavailability of the explicit form of the intermolecular potential does not allow the direct comparison of experimental results with eq 1 over the whole range of the scattering angle. However, the analysis of low-angle data yields a quantitative measure of the range of interaction[35,38] By expanding ($\sin hr/hr$) in h and retaining terms up to h^2, eq 1 is rewritten as

$$P^*(\theta,c) = P(\theta)[1 + (BN_A/M)\langle r^2\rangle^{3/2} c(1 - h^2\langle r^2\rangle/6)]^{-1} \quad (2)$$

where

$$\langle r^2\rangle = \frac{\int_0^\infty [1 - \exp(-U(r)/kT)] 4\pi r^4 \mathrm{d}r}{\int_0^\infty [1 - \exp(-U(r)/kT)] 4\pi r^2 \mathrm{d}r} \quad (3)$$

$$B = \langle r^2\rangle^{-3/2} \int_0^\infty [1 - \exp(-U(r)/kT)] 4\pi r^2 \mathrm{d}r \quad (4)$$

Using the approximation

$$\langle \sin hr/hr\rangle = \exp(-h^2\langle r^2\rangle/6) \quad (5)$$

eq 2 is replaced by

$$P^*(\theta,c) = P(\theta)[1 + (BN_A/M)\langle r^2\rangle^{3/2} c \exp(-h^2\langle r^2\rangle/6)]^{-1} \quad (6)$$

This equation indicates that the ordinate intercept and the initial slope in the plot of log $[(P(\theta)/P^*(\theta)) - 1]$ *vs.* $\sin^2(\theta/2)$ yield B and $\langle r^2\rangle$, respectively. The latter quantity represents the mean-square distance between the centers of gravity of polystyrene in the two-block copolymer and the former is a constant characteristic of the type of the radial distribution function. Figure 4 and 5 illustrate such plots of the experimental data for toluene and benzene solutions, respectively. It is noted in the both figures that the initial negative slope increases with the macromolecular concentration. Consistently with this result the value of $B\langle r^2\rangle^{3/2}c$ estimated from the ordinate intercept increases less rapidly than the first power of concentration as already revealed by the downward curvature in the plot of the zero-angle value of the reciprocal scattering function *vs.* concentration (*e.g.*, Figure 2 and 3). Under the assumption that the approximation of the radial distribution function by $\exp[-U(r)/kT]$ is valid and the particle scattering factor remains unchanged in the concentration range covered by the present investigation, we are led to conclude that $\langle r^2\rangle$ decreases with concentration as shown in Figure 6. The adoption of these concentration dependences of $\langle r^2\rangle$ in eq 6 yields both the intercept and the limiting slope which quantitatively agree with the experimental results as shown by the broken lines in Figure 4 and 5. It should be understood in addition from eq 6 that the concentration dependence of $[P^*(\theta,c)]^{-1}$ becomes less curved at higher scattering angles due to the factor of $\exp(-h^2\langle r^2\rangle/6)$, a behavior that the present experimental results also reveal.

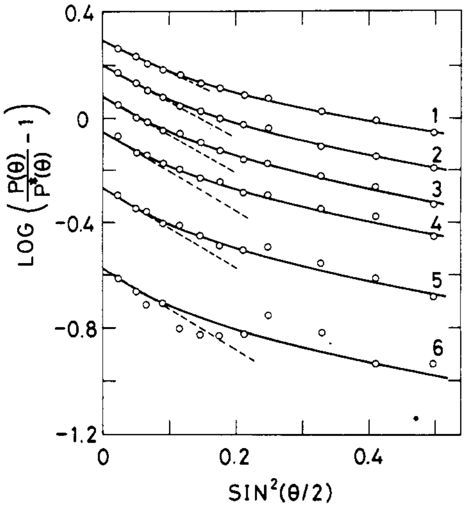

Figure 4. Plots of log $\{[P(\theta)/P^*(\theta)] - 1\}$ *vs.* $\sin^2(\theta/2)$ for toluene solutions of the two-block copolymer BMM-313 at various polymer concentrations (see the legend to Figure 2).

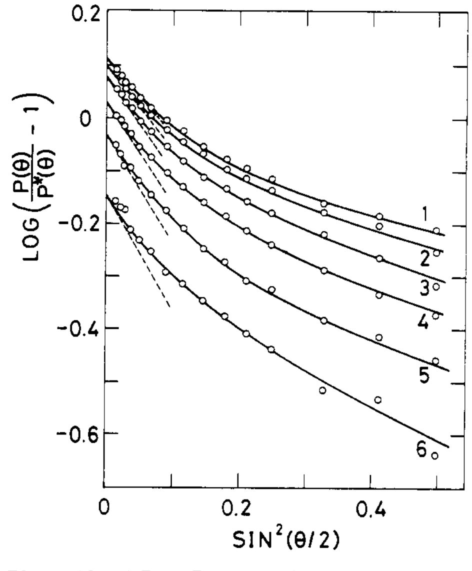

Figure 5. Plots of log $\{[P(\theta)/P^*(\theta)] - 1\}$ *vs.* $\sin^2(\theta/2)$ for benzene solutions of the two-block copolymer BMM-313 at various polymer concentrations (see the legend to Figure 3).

The decrease of $\langle r^2\rangle$ with concentration which causes the solution to exhibit the negative third virial coefficient seems to be a behavior characteristic of the system with a long-range intermolecular potential. Doty and Steiner[32]

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(36) F. Zernicke and J. A. Prins, *Z. Phys.*, 41, 184 (1927).

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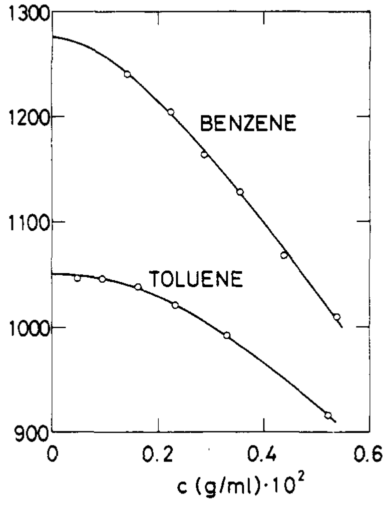

Figure 6. Mean-square distances of interaction as function of the concentration.

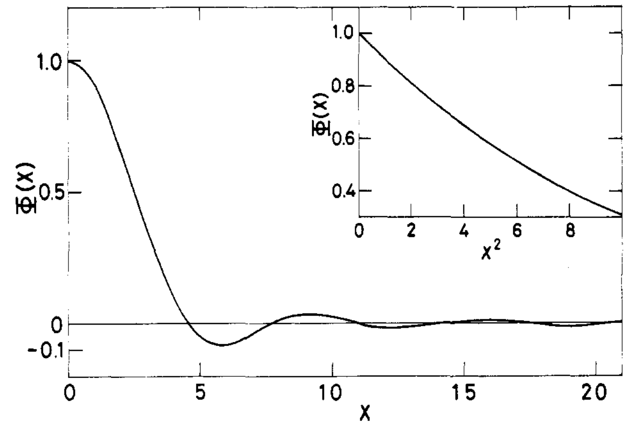

Figure 7. Dependence of the function $\Phi(X)$ of eq 9 on X with the inset showing its dependence on X^2.

obtained the similar results on bovine serum albumin solutions at pH 3.2 in an unbuffered aqueous solution, and tried to fit their experimental results to eq 1 with a hard-sphere potential under the assumption that $\langle r^2\rangle$ decays as $c^{-2/3}$. Burchard and Cowie[38] have recently reanalyzed the dissymmetry data of Doty and Steiner and showed that $\langle r^2\rangle$ decreases with concentration in all the three types of potential investigated in the original paper. The results reported by Prud'homme and Bywater[22] on polystyrene–polyisoprene two-block copolymers are at variance with these in that $\langle r^2\rangle$ is constant independent of polymer concentration. The reason for the descrepancy is now unknown. In this connection, one word is necessary about the second virial coefficient as defined by $A_2 = (N_A/2M^2)B\langle r^2\rangle^{3/2}$. Although the molecular weight of the whole copolymer enters in M in this equation, the interaction potential $U(r)$ should be considered as operating between the centers of the two unmasked chains. Therefore, if we regard the masked chain as providing in effect the interaction potential between two unmasked chains, the second virial coefficient for the polystyrene subchain is given by $A_2^* = A_2 m^{-2}$. The numerical results are summarized in Table III. We note that $\langle r^2\rangle$ is larger in benzene than in toluene, presumably due to the fact that poly(methyl methacrylate) is more expanded in the former solvent.[29]

Table III
Numerical Results for Potential Parameters Estimated from the Light-Scattering Data According to the Procedure Described in the Text

Solvent	Temp (°C)	$\lim_{c\to 0}\langle r^2\rangle^{1/2}$ (Å)	B	a (Å)	b (Å)	ϵ/kT
Benzene	30	1280	0.60	510	1460	0.062
Toluene	30	1050	1.23	496	1340	0.046

It may be pointed out in this connection that the solvent systems of stronger heterocontact repulsive interaction would yield larger values of $\langle r^2\rangle$. The molecular weight of poly(methyl methacrylate) relative to that of polystyrene should also affect the magnitude of $\langle r^2\rangle$. The importance of each of these factors cannot be evaluated as long as the analysis is restricted to the low-angle data. No attempt is possible, however, to treat quantitatively the angular dependence over the whole range of the scattering angle, because the rigorous form of $U(r)$ is unavailable as previously mentioned. But there are sufficient reasons to believe that an attempt to analyze the angular dependence with a hypothetical potential should be of some value to gain insight into each of the above effects.

We put forward a potential

$$U(r) = \begin{Bmatrix} \infty & (0 \le r \le a) \\ \epsilon & (a < r \le b) \\ 0 & (b < r) \end{Bmatrix} \tag{7}$$

on the basis of the following reasoning. We approximate the interaction of homopolystyrene molecules by a hard-sphere potential of diameter a and consider its modification when poly(methyl methacrylate) is linked to one end. Since the centers of gravity of two subchains in the two-block copolymer are in average separated at a distance, the poly(methyl methacrylate) subchain provides a long-range potential for the interaction of polystyrene subchains, which is assumed to extend as far as b. It does not mean, however, that the direct contact of polystyrene subchain is always prohibited by the presence of the poly(methyl methacrylate) subchain. It is indeed allowed depending upon the configuration and orientation of the copolymer molecule. The contact probability may increase or the potential may decrease with distance between a and b, but we approximate it by a constant ϵ. The sizes in solution of the polystyrene and poly(methyl methacrylate) subchains may affect the magnitudes of the parameters, a and b, respectively and the heterocontact repulsion the ϵ value.

Using this potential in eq 1 and carrying out the integration, one obtains

$$\frac{Kc}{R(\theta)} = \frac{1}{MP(\theta)}\left\{1 + \frac{4\pi N_A c}{M}\left[(1 - A)\frac{a^3}{3}\Phi(X_a) + A\frac{b^3}{3}\Phi(X_b)\right]\right\} \tag{8}$$

where $A = 1 - \exp(-\epsilon/kT)$, and Φ is given by

$$\Phi(X) = 3(\sin X - X\cos X)/X^3 \tag{9}$$

with

$$\begin{aligned} X_a &= ha \\ X_b &= hb \end{aligned} \tag{10}$$

The function $\Phi(X)$ is unity when $X = 0$ and tends to zero for large X as shown in Figure 7. Equation 8 reduces to the scattering of rigid spheres with diameter a and b when the energy $\epsilon = 0$ and $\epsilon = \infty$, respectively.

Let us examine eq 8 if it exhibits the anomaly as obtained in the experiment and see the effects of the magnitudes of the potential energy ϵ and the distance b. For the sake of convenience, eq 8 is rewritten in a square-root

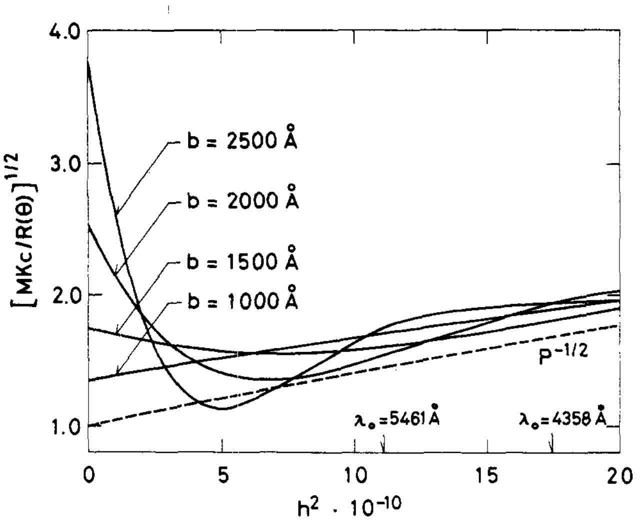

Figure 8. Plots of $[KcM/R(\theta)]^{1/2}$ *vs.* h^2 (eq 8) for various b values as indicated in the figure, with $M = 1.53 \times 10^6$, $c = 2.0 \times 10^{-3}$ g/ml, $\tilde{n}_0 = 1.5$, and $a = 500$ Å. The particle scattering factor for a Gaussian chain with $\langle S^2\rangle^{1/2} = 500$ Å is used for $P(\theta)$. The arrows to the abscissa indicate the largest limit accessible to experiments ($\theta = 150°$) for the incident lights of 4358 and 5461 Å.

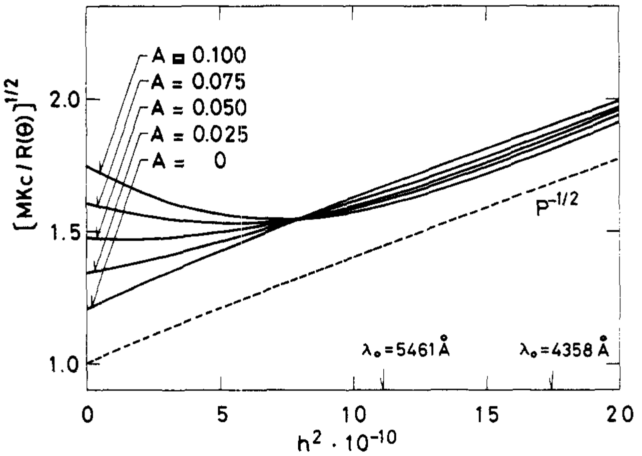

Figure 9. Plots of $[KcM/R(\theta)]^{1/2}$ *vs.* h^2 (eq 8) for various A values as indicated in the figure. The values used for other parameters are the same as in Figure 7 except b is fixed as 1500 Å.

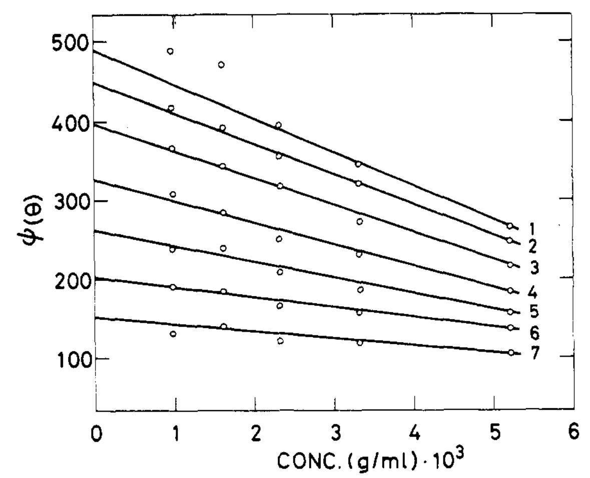

Figure 10. Extrapolations of $\psi(\theta)$ (eq 11) for the selected angles at zero solute concentration. The values were calculated from the experimental data of Figure 2. The scattering angles for the plotted points are, from top to bottom, 14.5, 26, 40, 60, 80, 100, and 140.

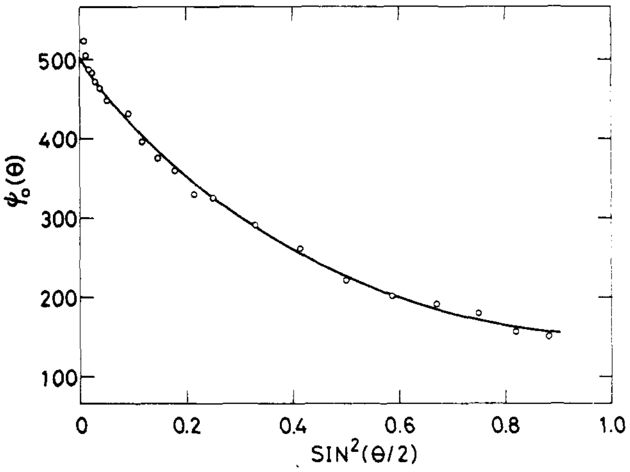

Figure 11. Estimate of ψ_0 (eq 12) at zero-scattering angle from the plot of ψ_0 *vs.* $\sin^2(\theta/2)$. The values were calculated from the data of Figure 2.

form and plotted in Figure 8 for various values of b where we put $M = 1.53 \times 10^6$, $c = 2.0 \times 10^{-3}$ g/ml, $\tilde{n}_0 = 1.5$, $A = 0.1$, $a = 500$ Å, and for $P(\theta)$ is used the particle scattering factor for a Gaussian chain of $\langle S^2\rangle^{1/2} = 500$ Å. The largest limit of the abscissa accessible to the experiment ($\theta = 150°$) is indicated by the arrow for the incident lights of the two wavelengths. Significant anomaly is not seen when the b value remains as small as 1000 Å, nearly a straight line being obtained with a slope somewhat smaller than that for $P^{-1/2}$. However, the limiting slope for b = 1500 Å becomes negative and a minimum appears at about $h^2 = 7.5 \times 10^{10}$. The initial decrease with h^2 becomes steeper with increase of b from 1500 to 2500 Å and another local maximum begins to appear explicitly. The curves tend to $P^{-1/2}$ at large abscissa values. Figure 9 shows the effect of the magnitude of the energy ϵ. The parameter values used are the same as in Figure 8 except the b value is fixed as 1500 Å. The scattering from the rigid sphere of diameter a is shown by the dotted curve indicated as $A = 0$. With increase in the energy the similar anomaly as seen in Figure 8 becomes evident. Since the range of h^2 accessible to the experiment is wider for incident lights of shorter wavelengths, the anomaly may look more pronounced when the incident lights of longer wavelengths are used.

Apparently the aberrant light-scattering behavior is essentially described by the function $\Phi(X)$. When the b value is as small as 500 Å, for example, the value of X_b attainable in the angular range of observation is also very small and $\Phi(X)$ remains virtually constant, unity. On the contrary, for the b value of 2500 Å, X_b attains as large as 10 and $\Phi(X_b)$ decreases from unity to essentially zero as the scattering angle is varied from zero to 60°. One obtains as a result the sudden decrease of the reciprocal scattering function. This behavior is biased by the factor of Ab^3 in eq 8.

Since eq 8 seems to reproduce the aberrant light-scattering behavior quite satisfactorily, we are tempted to proceed to the comparison of the experimental results with eq 8. In order to make the comparison at infinite dilution, we introduce the following quantities

$$\psi(\theta) = \left\{\frac{[Kc/R(\theta)]}{\lim\limits_{c\to 0}[Kc/R(\theta)]} - 1\right\}\frac{1}{c} \qquad (11)$$

$$\psi_0(\theta) = \lim_{c\to 0}\psi(\theta) \qquad (12)$$

$$\Psi(\theta) = \psi_0(\theta)/\lim_{\theta\to 0}\psi_0(\theta) \qquad (13)$$

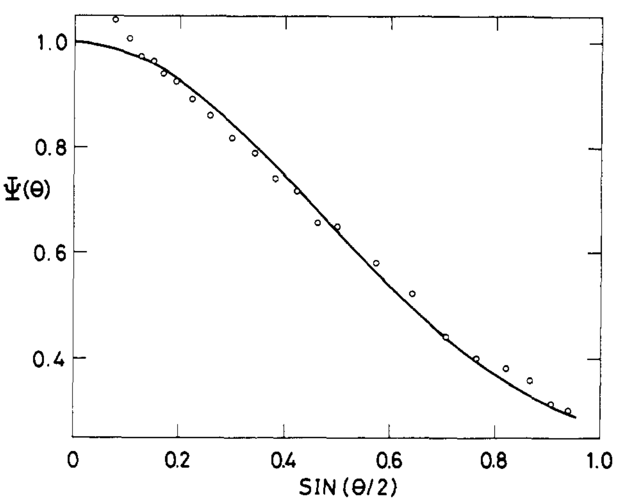

Figure 12. Comparison of theory (eq 13, full curve) and experimental results (open circles) of BMM-313 in toluene at 30° with the incident light of 4358 Å. The parameter values used in the calculation are taken from Table III.

The function $\Psi(\theta)$ is theoretically given by eq 8 as $(1 - \alpha)\Phi(X_a) + \alpha\Phi(X_b)$ with $\alpha = Ab^3/[(1 - A)a^3 + Ab^3]$. The extrapolation of $\psi(\theta)$ to infinite dilution is shown in Figure 10 for some selected angles on the experimental data shown in Figure 2. The plotted points fall on a straight line at each scattering angle, its slope being proportional to the apparent third virial coefficient. The values of $\psi_0(\theta)$ so obtained are plotted in Figure 11 *vs.* $\sin^2(\theta/2)$ to estimate the value extrapolated at $\theta = 0$. This plot permits the more linear extrapolation than that *vs.* $\sin(\theta/2)$ as verified theoretically by the inset in Figure 7. Although $\Psi(\theta)$ contains three adjustable parameters, *e.g.*, a, b, and A, it can be shown that the parameter values can be estimated without introducing serious arbitrariness, and the results obtained are summarized in Table III. The theoretical values of $\Psi(\theta)$ calculated by using these values stand in satisfactory agreement with experimental data as shown in Figure 12 for toluene solutions as an illustration.

Comparison of the parameter values so obtained for toluene and benzene solutions is certainly instructive in view of the fact that for poly(methyl methacrylate) benzene is better solvent than toluene, while the two solvents are similar for polystyrene in the goodness as solvent. The a value is almost the same for the two solvents, but both b and ϵ/kT are significantly larger in benzene than in toluene in agreement with our expectation. If, on the contrary, b and ϵ/kT values are smaller under the circumstances that either the molecular weight of the poly(methyl methacrylate) subchain is small or the solvent is poor for it the anomaly may look less distinct. The former perhaps explains why this type of aberrant light-scattering behavior has long been left unfound.

Thus, we have given a reasonable explanation to the aberrant light-scattering results, *e.g.*, the upsweep of the reciprocal scattering function at small scattering angles at finite solute concentrations and the negative third virial coefficient, obtained on the two-block copolymer when the isorefractive solvents were used. We have also shown that the radius of gyration of the unmasked subchain can be precisely determined provided that the measurements be made to sufficiently low concentrations. The gyration radius of the polystyrene subchain could not be determined with precision when benzene was used as solvent, because the requirement was not fulfilled. However, the measurements were carried out with success by using toluene as solvent, and the gyration radius obtained is significantly larger than that of homopolystyrene RS-13 of equal molecular weight, indicating the effect of the heterocontact repulsion. Therefore, the present investigation supports the model that the domains of dissimilar segments overlap to a great extent in the two-block copolymer. It is indeed difficult to assume the presence of such a strong force as to induce segments to take the "segregated structure." The magnitude of the binary cluster integral of the heterocontact interaction relative to that of the homocontact one could be estimated on the basis of the random-coil statistics, which will be described in a separate report.

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Determination of Intramolecular Motion in a Random-Coil Polymer by Means of Quasielastic Light Scattering

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ABSTRACT: Quasielastic light-scattering measurements have been made which determine both the translational diffusion coefficient D and the longest internal relaxation time τ_1 for a polystyrene having weight-average molecular weight 27.3×10^6 in dilute solutions in cyclohexane at 35.4° and in 2-butanone at 25.0°. Solute concentrations ranged from 0.04×10^{-3} to 0.16×10^{-3} g-cm^{-3} in cyclohexane and from 0.07×10^{-3} to 0.37×10^{-3} g-cm^{-3} in 2-butanone. The values of τ_1 obtained are in essential agreement with values calculated from normal-coordinate theories. A discussion is given of corrections required when the self-beating spectrometer signal is processed by an analog-to-digital converter and an autocorrelator.

Since the appearance of methods for accurately determining the breadth and shape of the Rayleigh line in the spectrum of scattered light, there has been considerable interest in applying these methods to the determination of intramolecular motion in macromolecules having internal degrees of freedom. One system in which internal motion is of particular interest is the random-coil molecule in dilute solution. The theoretical basis for interpreting quasielastic scattering in this system was given by Pecora,[1-5] who showed that the spectrum of the Rayleigh line should consist of a Lorentzian component due to the

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