Intermolecular Correlation in Light Scattering from Dilute Solutions of Block Copolymers[1]

Takeshi Tanaka,[2] Tadao Kotaka* and Hiroshi Inagaki

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan.
Received December 18, 1973

ABSTRACT: The effects of intermolecular correlation on scattered light intensities from block copolymer solutions were examined from the point of view of the distribution function theory developed by Zimm, Albrecht, and Flory and Bueche for homopolymer solutions. The theory predicts distorted Zimm plots for block copolymer solutions with solvents having nearly zero refractive index increment for one of the parent homopolymers. A larger distortion is expected, if the unmasked portion is much smaller relative to the overall dimension of a whole molecule, and if the deviation of the center of mass of the unmasked portion from the molecular center of mass is larger. Thus an AB-diblock copolymer would give a larger distortion, while a BAB-triblock copolymer a smaller distortion, if compared under the same conditions. Series of block copolymers of polystyrene and poly(methyl methacrylate) were prepared anionically. The results were found to be in agreement with the predictions of the theory. An anomalous concentration dependence of scattered light intensities found in this study is also reported.

The concentration and angular dependences of the intensity of light scattered from a dilute solution of macromolecules may be described in a form

$$Kc/I(\theta,c) = 1/MP(\theta) + 2A_2Q'(\theta)c + \ldots \quad (1)$$

where $I(\theta,c)$ is the Rayleigh ratio representing experimentally measurable intensity of excess scattering at angle θ from the solution of solute concentration c (in g/ml), K is the light-scattering constant, M is the molecular weight, and A_2 is the second virial coefficient. The functions $P(\theta)$ and $Q'(\theta)$ represent, respectively, the effects of intra- and intermolecular interferences.[3-5] When experimental data for homopolymer solutions are analyzed following the now well-known method of Zimm,[3] we usually obtain a neat grid of almost parallel curves with respect to both c and θ dependences. More precisely, the slope of $Kc/I(\theta,c)$ against c decreases slightly with increasing θ, if A_2 is positive.[3,6] This implies that $Q'(\theta)$ is very close to unity and a slightly decreasing function of θ. Theoretical interpretations on the effect of the intermolecular interferences have been made by Albrecht,[4] Flory and Bueche,[5] and Yamakawa,[7] leading to the results in agreement with experiments.

However, peculiarly distorted Zimm plots have been reported recently by Prud'homme and Bywater[8] for polyisoprene-polystyrene diblock copolymers in benzene and chlorobenzene, and also by Utiyama *et al.*[9] for a polystyrene-poly(methyl methacrylate) in benzene and toluene. According to their results, $Kc/I(\theta,c)$ *vs.* $\sin^2(\theta/2)$ observed at finite concentrations is no longer linear increasing function but shows upward concavity in the region of low angles. It is noteworthy that the systems are those involving a diblock copolymer and a solvent which has a very small refractive index increment for one of the two constituent homopolymers, *i.e.*, one of the blocks is nearly invisible. They have explained this phenomenon in terms of the intermolecular interferences due to large (apparent) excluded volumes between the more easily visible or unmasked blocks resulted from the less easily visible or masked blocks within the block copolymer molecules.[8,9]

We have been carrying out similar studies on block copolymers of polystyrene (A) and poly(methyl methacrylate) (B) of AB-diblock and BAB-triblock types in several solvents including toluene and *p*-xylene[10-12] which have nearly zero refractive index increments for poly(methyl methacrylate). We have found that the AB-diblock copolymers show essentially the same behavior in toluene with those reported earlier,[8,9] while the BAB-triblock copolymers show somewhat different results. In this article we deal with the problem of the intermolecular correlations in light scattering from dilute solutions of block copolymers by applying the homopolymer theories developed by Zimm,[3] Albrecht,[4] Flory and Bueche,[5] and Yamakawa,[7] introducing as few artificial assumptions as possible. We examine the behavior of the theoretical $Q'(\theta)$ function and compare it with some experimental data, particularly in a hope to elucidate the nature of abnormally distorted Zimm plots, and to determine what information is obtainable from them.

Theoretical Section

General Formulation. Consider a solution of volume V containing n identical copolymer molecules each consisting of $N = N_A + N_B$ properly defined scattering segments of type A and B, respectively. The intensity of excess scattering per unit volume of the solution may be given as

$$I(\theta,c) = \kappa V^{-1}\sum_{i,j} g_i g_j \int F(\mathbf{r}_{ij}) \exp(\mathbf{s}'\mathbf{r}_{ij})\mathrm{d}\mathbf{r}_{ij} \quad (2)$$

where κ is a constant; the function $F(\mathbf{r}_{ij})$ denotes the probability density of $\mathbf{r}_{ij}$ which is the vector separation of scattering segments i and j; the symbol $\mathbf{s}'$ is written for $2\pi i\mathbf{s}/\lambda$, where the vector $\mathbf{s}$ ($|\mathbf{s}| = 2\sin(\theta/2)$) is the difference between two unit vectors in the directions of the incident and scattered lights; $i = (-1)^{1/2}$, λ is the wavelength of light in the medium. The summation in eq 2 is carried out over all $(nN)^2$ pairs of the segments; the segment i may be either one of type A or B, and accordingly the scattering factor g_i is proportional to either $\nu_A m_A$ or $\nu_B m_B$, depending on whether the segment i is of type A or B. Here ν_K and m_K are the refractive index increment and the molar weight of segment K (K = A or B), respectively.

The probability density $F(\mathbf{r}_{ij})\mathrm{d}\mathbf{r}_{ij}$ may be properly written in terms of the McMillan-Mayer distribution functions.[13] Following Zimm,[3] the terms in eq 2 may be regrouped to give the intramolecular interference function $P(\theta,c)$ and the intermolecular interference function $Q(\theta,c)$.[7] These functions and also the second virial coefficient $A_2(c)$ are all considered to be concentration dependent through implicitly assumed c dependence of the distribution functions. However, since the intermolecular correlation has negligible effect on the intramolecular distribution function, we may neglect these concentration dependences. Then we can cast eq 2 into the conventional form

$$Kc/I(\theta,c) = [MP(\theta)]^{-1}\{1 + 2A_2M[Q(\theta)/P(\theta)]c + 0(c^2)\} \quad (3)$$

with $P(\theta) = P(\theta,0)$, $Q(\theta) = Q(\theta,0)$ and $A_2 = A_2(0)$. Here $K = \kappa N_0\nu^2$, N_0 is the Avogadro number, ν is the refractive index increment of the copolymer, and $M = N_A m_A + N_B m_B$ is the molecular weight. Obviously eq 3 is identical with eq 1 by writing $Q'(\theta) = Q(\theta)/[P(\theta)]^2$. For a block copolymer, the factor g_i in eq 2 cannot be absorbed into the constant K. We have to regroup the terms in the double summation into three types. The first two are those in which both i and j segments are either type A or B, and the third are different types. Then we may write

$$P(\theta) = y^2P_A(\theta) + (1 - y)^2P_B(\theta) + 2y(1 - y)P_{AB}(\theta) \quad (4)$$

$$Q(\theta) = y^2Q_A(\theta) + (1 - y)^2Q_B(\theta) + 2y(1 - y)Q_{AB}(\theta) \quad (5)$$

$$y = x\nu_A/\nu$$

and

$$(1 - y) = (1 - x)\nu_B/\nu \quad (6a,b)$$

$$\nu = x\nu_A + (1 - x)\nu_B \quad (7)$$

where x is the weight fraction of A component in the block copolymer, and a linear dependence on composition x has been assumed for the refractive index increment ν.[14,15] For simplicity we have written $P_K(\theta)$ for $P_{KK}(\theta)$, etc. The functions $P_A(\theta)$, $Q_A(\theta)$, etc., are defined, respectively, as

$$P_{KJ}(\theta) = (N_K N_J)^{-1}\sum_i^{N_K}\sum_j^{N_J} V^{-1}\int F_1(1)\exp(\mathbf{s}'\mathbf{r}_{ij})\,\mathrm{d}(1) \quad (8)$$

$$Q_{KJ}(\theta) = \frac{\sum_i^{N_K}\sum_j^{N_J'}\int[F_2(1,2) - F_1(1)F_1(2)]\exp(\mathbf{s}'\mathbf{r}_{ij})\,\mathrm{d}(1,2)}{N_K N_J\int[F_2(1,2) - F_1(1)F_1(2)]\,\mathrm{d}(1,2)} \times$$

$$(\mathrm{K,J} = \mathrm{A\ or\ B}) \quad (9)$$

For the intramolecular $P(\theta)$ function, we have from eq 4 and 8

$$P(\theta) = 1 - \langle s^2\rangle_{\mathrm{app}}w^2/3 + 0(w^4) \quad (10)$$

$$w = 4\pi\sin(\theta/2)/\lambda \quad (11)$$

$$\langle s^2\rangle_{\mathrm{app}} = y^2\langle s^2\rangle_A + (1 - y)^2\langle s^2\rangle_B + 2y(1 - y)\langle s^2\rangle_{AB} \quad (12a)$$

where $\langle s^2\rangle_{\mathrm{app}}$ is the light-scattering apparent radius of gyration of a monodisperse copolymer[15,16] as directly determined by the method of Zimm.[3] For the corresponding true radius of gyration $\langle s^2\rangle$, one has to replace y by the weight fraction x of the copolymer. The quantities $\langle s^2\rangle_A$ and $\langle s^2\rangle_B$ are the mean-square radii of the A and B segments around their centers of mass G_A and G_B, respectively. The quantity $\langle s^2\rangle_{AB}$ may be written by the relation

$$\langle s^2\rangle_{AB} = (1/2)(\langle s^2\rangle_A + \langle s^2\rangle_B + \langle l^2\rangle) \quad (12b)$$

with $\langle l^2\rangle$ being the mean-square distance between G_A and G_B within the copolymer molecule.

Evaluation of the $Q(\theta)$ Function. For evaluating the $Q(\theta)$ function, we introduce the following assumptions: (1) the K segments are spherically symmetrically distributed around their center of mass G_K; (2) the potential of the average force $U(\mathbf{R}_{12})$ acting between two molecules is a function only of the vector separation $\mathbf{R}_{12}$ of the centers of mass of the two molecules and is independent of their mutual orientation; and finally (3) the perturbation of the internal coordinates of a molecule due to the neighboring molecule in the bimolecular cluster is uniform for all the segments.

Applying the superposition principle as suggested by Zimm[17] and Albrecht,[4] we may write the function $F_2(1,2)$ in terms of $U(\mathbf{R}_{12})$ as

$$F_2(1,2) = F_1(1)F_1(2)\exp[-U(\mathbf{R}_{12})/kT] \quad (13)$$

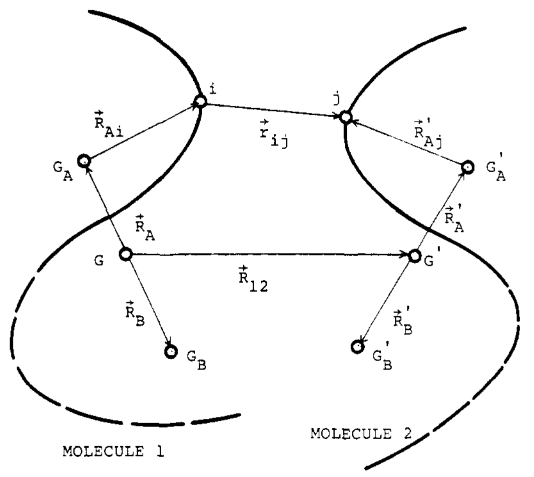

Figure 1. Schematic representation of the model (see text); G, G_A, and G_B represent the positions of the centers of mass of whole copolymer chain, A part, and B part of molecule 1, respectively; and the single prime superscript refers to molecule 2.

Introducing eq 13 into eq 9 we can derive $Q_{KJ}(\theta)$. Below we will show the derivation of $Q_A(\theta)$ as an example. Let $\mathbf{R}_A$ be the vector separation between G and G_A within molecule 1, and $\mathbf{r}_{Ai}$ be a vector to the ith A segment from G_A, while $\mathbf{R}_A'$ and $\mathbf{r}_{Aj}'$ are those of molecule 2 in the bimolecular cluster (see Figure 1). Writing $\mathrm{d}(1,2) = \mathrm{d}V\mathrm{d}\mathbf{R}_{12}\mathrm{d}(1)_I\mathrm{d}(2)_I$, where $(1)_I$ refers to the internal coordinates only, and setting $\mathbf{r}_{ij} = \mathbf{R}_{12} - \mathbf{R}_A + \mathbf{R}_A' - \mathbf{r}_{Ai} + \mathbf{r}_{Aj}'$, we obtain from eq 9 and 13 the following expression after integrating over volume

$$Q_A(\theta) = \frac{\int[1 - \exp\{-U(\mathbf{R}_{12})/kT\}]\exp(\mathbf{s}'\mathbf{R}_{12})\,\mathrm{d}\mathbf{R}_{12}}{\int[1 - \exp\{-U(\mathbf{R}_{12})/kT\}]\,\mathrm{d}\mathbf{R}_{12}} \times \frac{\sum_i^{N_A}\sum_j^{N_A'}\int F_1(1)_I F_1(2)_I\exp[\mathbf{s}'(\mathbf{R}_{A'} - \mathbf{R}_A + \mathbf{r}_{Aj}' - \mathbf{r}_{Ai})]\mathrm{d}(1)_I\mathrm{d}(2)_I}{N_A^2\int F_1(1)_I F_1(2)_I\mathrm{d}(1)_I\mathrm{d}(2)_I} \quad (14)$$

Further writing

$$F_1(1)_I\mathrm{d}(1)_I = \prod_{K=A}^{B} F(\mathbf{R}_K)\mathrm{d}\mathbf{R}_K\prod_{i=1}^{N_K}F(\mathbf{r}_{Ki})\mathrm{d}\mathbf{r}_{Ki}$$

where $F(\mathbf{v})$'s denote the probability density of the vector $\mathbf{v}$ specified in the argument, and integrating over all coordinates except those of $\mathbf{R}_A$, $\mathbf{R}_A'$, $\mathbf{r}_{Ai}$ and $\mathbf{r}_{Aj}'$, we can write $Q_A(\theta)$ as the product of three functions

$$Q_A(\theta) = \Phi(\theta)S_A(\theta)G_A(\theta) \quad (15)$$

$$\Phi(\theta) = \frac{\int[1 - \exp\{-U(\mathbf{R}_{12})/kT\}]\exp(\mathbf{s}'\mathbf{R}_{12})\,\mathrm{d}\mathbf{R}_{12}}{\int[1 - \exp\{-U(\mathbf{R}_{12})/kT\}]\,\mathrm{d}\mathbf{R}_{12}} \quad (16)$$

$$[S_A(\theta)]^{1/2} = N_A^{-1}\sum_i^{N_A}\int F(\mathbf{r}_{Ai})\exp(\mathbf{s}'\mathbf{r}_{Ai})\mathrm{d}\mathbf{r}_{Ai}/\int F(\mathbf{r}_{Ai})\mathrm{d}\mathbf{r}_{Ai} \quad (17)$$

$$[G_A(\theta)]^{1/2} = \int F(\mathbf{R}_A)\exp(\mathbf{s}'\mathbf{R}_A)\mathrm{d}\mathbf{R}_A/\int F(\mathbf{R}_A)\mathrm{d}\mathbf{R}_A \quad (18)$$

Other functions $Q_B(\theta)$ and $Q_{AB}(\theta)$ may be calculated similarly. Putting all these results together, we find

$$Q(\theta) = \Phi(\theta)S(\theta)G(\theta) = \Phi(\theta)[y^2S_A(\theta)G_A(\theta) + (1 - y)^2S_B(\theta)G_B(\theta) + 2y(1 - y)S_{AB}(\theta)G_{AB}(\theta)] \quad (19)$$

Obviously $G(\theta)$ is related to the uneven distribution of A and B segments, or in other words, to the deviation of the optical center from the molecular center of mass within a

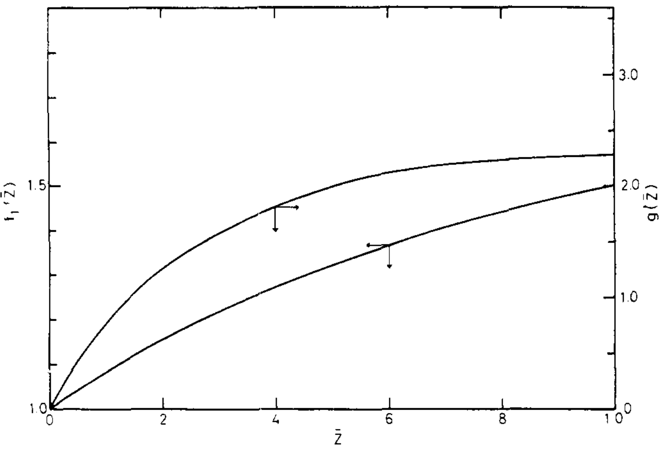

Figure 2. Plots of functions $f_1(\bar{Z})$ and $g(\bar{Z})$ against $\bar{Z}$. See eq 24 and 34.

molecule. The function $G(\theta)$ may be calculated for several simple models.[12]

On the other hand, $S(\theta)$ is related to the distribution of each type of segments around its center of mass. For the model employed here, this may be identified with $P(\theta)$, as far as the variation of the internal coordinates of the first molecule due to the second one has been neglected. However, we will distinguish them for the time being by attaching *, just to find out how much of difference could be resulted from them. Then the $S(\theta)$ and $G(\theta)$ functions may be expanded in w^2 to give

$$S_K(\theta)G_K(\theta) = 1 - (\langle s^2\rangle_K^* + r_K^2)w^2/3 + 0(w^4) \quad (20a)$$

$$S_{AB}(\theta)G_{AB}(\theta) = 1 - (\langle s^2\rangle_{AB}^* - r_A r_B)w^2/3 + 0(w^4) \quad (20b)$$

For eq 20b, we used eq 12b and $\langle l^2\rangle = \langle(\mathbf{R}_A + \mathbf{R}_B)^2\rangle$.

Finally the $\Phi(\theta)$ function is to be evaluated. Apparently the function reflects the excluded volume interactions of all the intermolecular segment contacts, regardless of the segments being visible or invisible. Since we have already assumed a simple smoothed density model, it would be adequate to employ the Flory–Krigbaum potential[18,19] for $U(\mathbf{R}_{12})$

$$U(\mathbf{R}_{12})/kT = N^2\langle X\rangle(3/4\pi\langle s^2\rangle^*)^{3/2} \exp[-3\mathbf{R}_{12}^2/4\langle s^2\rangle^*] \quad (21)$$

Here $\langle s^2\rangle^*$ is the mean-square radius of gyration of a molecule in a bimolecular cluster. For a homopolymer, the parameter $\langle X\rangle$ is the binary cluster integral between the segment pair. However for a copolymer this is a complicated function of the interactions involving both homo- and heterocontacts. Therefore as the first-order approximation, we replace $\langle X\rangle$ by the average over the single contact terms

$$N^2\langle X\rangle = N_A^2X_{AA} + N_B^2X_{BB} + 2N_AN_BX_{AB} \quad (22)$$

where X_{JK} is the binary cluster integral for a J–K contact. Substitution of eq 21 into eq 16 leads to an expression similar to that obtained by Flory and Bueche[5] for a homopolymer solution

$$\Phi(\theta) = 1 + \sum_{q=1}^{\infty}(-\langle s^2\rangle^* w^2/3)^q f_q(\bar{Z})/q! \quad (23)$$

$$f_q(\bar{Z}) = \left[\sum_{p=1}^{\infty}(-\bar{Z})^p/p!p^{3/2+q}\right] \Big/ \left[\sum_{p=1}^{\infty}(-\bar{Z})^p/p!p^{3/2}\right] \quad (24)$$

$$\bar{Z} = N^2\langle X\rangle(3/4\pi\langle s^2\rangle^*)^{3/2} \quad (25)$$

The first function $f_1(\bar{Z})$ in the series was calculated numerically for $\bar{Z} \leq 10$. The results are plotted in Figure 2, which was found to be approximated by

$$f_1(\bar{Z}) \fallingdotseq (1 + 0.272\bar{Z})^{0.325} \quad (26)$$

with the numerical constants chosen so as to give the correct initial slope at $\bar{Z} = 0$. The error involved exceeds in no case 0.3% for $\bar{Z} \leq 5$ and 2% for $5 \leq \bar{Z} \leq 10$. The calculation of $f_1(\bar{Z})$ has been done by various authors upto the double contact term for a few statistical models such as a random-flight model,[4,7] a uniform density sphere model,[4] and a Gaussian density body model.[5]

Application to Experiments. Here we introduce an experimentally measurable function $\psi(\theta)$ as

$$[I(\theta,0)/I(\theta,c) - 1]/2A_2Mc = \psi(\theta) + 0(c) = [P(\theta)]^{-1}Q(\theta) + 0(c) \quad (27)$$

Substituting eq 10, 20, and 23 into eq 27, we have

$$\psi(\theta) = 1 - \bar{r}^2w^2/3 + 0(w^4) \quad (28)$$

$$\bar{r}^2 = \langle s^2\rangle^*[f_1(\bar{Z}) - \delta_{app}(\bar{Z})] + \Delta_{app} \quad (29)$$

$$\delta_{app}(\bar{Z}) = (\langle s^2\rangle_{app} - \langle s^2\rangle_{app}^*)/\langle s^2\rangle^* \quad (30)$$

$$\Delta_{app} = [yr_A - (1 - y)r_B]^2 = [x(1 - x)(\nu_A - \nu_B)/\nu]^2\langle l^2\rangle \quad (31)$$

Equations 28–31 show that plots of ln $[(I(\theta,0)/I(\theta,c) - 1)/c]$ *vs.* $\sin^2(\theta/2)$ known as the Guinier plot[20-22] allow one to determine A_2 and $\bar{r}^2$ from their intercept and initial slope, respectively, after extrapolating to zero concentration. The quantity $\bar{r}^2$ apparently consists of three contributions. (1) The first one reflects the intermolecular excluded volumes, *i.e.*, the dimension of the whole molecule; (2) the second one represents an usually trivial difference between the apparent radii of gyration of an isolated molecule and a molecule in a bimolecular cluster, and the correction from the c-dependent term of $P(\theta,c)$ should be of the same order of magnitude; and (3) the third one represents (optical) average of uneven distribution of the A and B segments around the molecular center of mass.

To explore the use of eq 28–31, let us first consider a homopolymer solution in which A = B so that $\nu_A = \nu_B$, $\langle s^2\rangle_{app} = \langle s^2\rangle$, etc. Then we have

$$\bar{r}^2 = \langle s^2\rangle^*[f_1(\bar{Z}) - \delta(\bar{Z})] \quad (32a)$$

$$\delta(\bar{Z}) = \langle s^2\rangle/\langle s^2\rangle^* - 1 \quad (32b)$$

For estimating $\delta(\bar{Z})$, Kurata's equation[23] for the expansion factor of a molecule in a bimolecular cluster and corresponding Fixman's equation[24] for an isolated molecule may be combined to give

$$\delta(\bar{Z}) = (1 + 0.026\bar{Z})^{2/3} - 1 \quad (33)$$

Combining an adequate expression of A_2 with eq 32 to eliminate $\langle s^2\rangle^*$, we have

$$(2A_2M^2/N_0)(3/4\pi\bar{r}^2)^{3/2} = g(\bar{Z}) = \bar{Z}h_0(\bar{Z})/[f_1(\bar{Z}) - \delta(\bar{Z})]^{3/2} \quad (34)$$

$$\bar{Z}h_0(\bar{Z}) = \sum_{p=1}^{\infty}(-\bar{Z})^p/p!p^{3/2} \quad (35)$$

where the $\bar{Z}h_0(\bar{Z})$ function is the one known as the Flory–Krigbaum–Orofino function of A_2 derived by Orofino and Flory.[19,25] Figure 2 shows numerical results of the $g(\bar{Z})$ function calculated from eq 24 and 32–35. Thus from measurable quantities A_2, M, and $\bar{r}^2$, we can estimate $\bar{Z}$ by eq 34, then $\langle s^2\rangle^*$ by eq 26, 32 and 33, and finally $\langle s^2\rangle$ from eq 33. The last quantity must coincide with the directly determined value from the $P(\theta)$ function.

Now we turn our attention to more interesting case of copolymer solutions with a solvent having zero refractive index increment for one of the parent homopolymers, say B, so that the B segments do not scatter light. Setting $\nu_B = 0$, we can rewrite eq 29 as

$$\bar{r}^2 = \langle s^2\rangle^*[f_1(\bar{Z}) - \delta_A(\bar{Z})] + (1-x)^2\langle l^2\rangle^* \qquad (36a)$$

$$\delta_A(\bar{Z}) = (\langle s^2\rangle_A - \langle s^2\rangle_A{}^*)/\langle s^2\rangle^* \qquad (36b)$$

Note that $(1-x)^2\langle l^2\rangle^* = r_A{}^2$. In eq 36, we have all three contributions to $\bar{r}^2$ so that $\bar{Z}$ cannot be determined from A_2 and $\bar{r}^2$ data alone. Apparently the correction terms are dependent not only on the gross feature of the copolymer chain, *i.e.*, M and x, but also on the detailed sequence-length distribution. For a crude estimation of these terms, we employ a random-flight model with simple architecture. Then for block copolymers of $(AB)_k$-type, we have

$$\langle l^2\rangle_A = 2\langle s^2\rangle/k^2 \qquad (37a)$$

$$\langle s^2\rangle_A = [1 - (N_B/Nk^2)]\langle s^2\rangle \qquad (37b)$$

$$\langle s^2\rangle_B = [1 - (N_A/Nk^2)]\langle s^2\rangle \qquad (37c)$$

For those of $B(AB)_k$-type, we have

$$\langle l^2\rangle = \langle s^2\rangle/k(k+1) \qquad (37d)$$

$$\langle s^2\rangle_A = [1 - (N_B/Nk)]\langle s^2\rangle \qquad (37e)$$

$$\langle s^2\rangle_B = [1 + N_A/N(k+1)]\langle s^2\rangle \qquad (37f)$$

For those of $(AB)_k$ A-type, exchange A and B in eq 37d, e, and f. Strictly speaking $\langle s^2\rangle$ in eq 37 must be (mean-square end-to-end distance/6). However the difference between these two quantities is trivial, unless the mean-square lengths per unit mass of the parent homopolymers differ greatly. Thus the last term in eq 36a may be readily estimated. For $\delta_A(\bar{Z})$, we have

$$\delta_A(\bar{Z}) = (\langle s^2\rangle_A{}^*/\langle s^2\rangle^*)\delta(\bar{Z}) \qquad (38)$$

Presumably eq 38 is generally valid, regardless of the models employed. These contributions may be combined with $f_1(\bar{Z})$ to evaluate a new $g(\bar{Z})$ function. Then the same procedure as described for homopolymers applies for estimating $\langle s^2\rangle^*$ and $\langle s^2\rangle$.

For more general cases in which B segments are also visible ($\nu_A \neq \nu_b \neq 0$), we have to return to the original eq 29. For $\langle l^2\rangle$ we may use eq 37 to correct the effect of nonzero ν_B. For $\delta_{app}(\bar{Z})$, we have

$$\delta_{app}(\bar{Z}) = (\langle s^2\rangle_{app}{}^*/\langle s^2\rangle^*)\delta(\bar{Z}) \qquad (39)$$

However the estimation of eq 39 poses a problem in some cases because of the following reasons. For block copolymers for which $\langle l^2\rangle$ is generally not zero, $\langle s^2\rangle_{app}$ becomes an infinitely large negative value as ν approaches to zero.[15] Therefore the ratio$\langle s^2\rangle_{app}{}^*/\langle s^2\rangle^*$ also assumes an infinitely large negative value, and Δ_{app} assumes an infinitely large positive value. Consequently in such a case the optical artifact would become overwhelmingly large, and the analysis of this kind itself would become meaningless. On the other hand, if ν is large, $\langle s^2\rangle_{app}{}^*$ approaches to $\langle s^2\rangle^*$, and Δ_{app} also becomes small. Then we can apply the procedure similar to that described above to estimate $\langle s^2\rangle$ of block copolymers.

Here we should like to comment on the low-angle anomaly of Zimm plots such as reported by Prud'homme and Bywater[8] and Utiyama *et al.*[9] The $Q'(\theta)$ function in eq 1 can be expanded in powers of w^2 as

$$Q'(\theta) = [P(\theta)]^{-1}\psi(\theta) = 1 - (\bar{r}^2 - \langle s^2\rangle_{app})w^2/3 + 0(w^4) \qquad (40)$$

According to the behavior of $\bar{r}^2$ discussed so far, the quantity $(\bar{r}^2 - \langle s^2\rangle_{app})$ would be influenced by three molecular factors: (1) one is the type of the copolymer chain or the sequence-length distribution; (2) the second is the refractive index of the solvent involved; and (3) the third is the thermodynamic properties of the copolymer solution.

For a homopolymer solution, simply $\bar{r}^2 \simeq \langle s^2\rangle^*$ and $\langle s^2\rangle_{app} = \langle s^2\rangle$, leading to $Q'(\theta) \simeq 1$. More specifically, eq 26, 32, and 33 lead to

$$Q'(\theta) = 1 - 0.0538\bar{Z}(\langle s^2\rangle w^2/3) + 0(\bar{Z}^2 w^4) \qquad (41)$$

which is in agreement with the result of a Gaussian-density body model of Flory and Bueche,[4,5] if $\delta(\bar{Z})$ in eq 29 is neglected.

For a block copolymer solution, especially as AB-diblock copolymer in a solvent having $\nu_B = 0$, $(\bar{r}^2 - \langle s^2\rangle_{app}) = \bar{r}^2 - \langle s^2\rangle_A$ which is far from zero, if x is not large. Therefore $Q'(\theta)$ decreases much more rapidly than in the case of homopolymers, resulting in the low-angle anomaly in the Zimm plots.[8,9] On the other hand, if the solvent quality is increased especially toward the B blocks, $\bar{r}^2$ becomes larger, while $\langle s^2\rangle_A$ becomes larger but less rapidly or even remains virtually unchanged. Then the low-angle anomaly becomes more significant. As to the effect of solvent refractive index, we may say that the anomaly would become negligible, as ν^2 is increased by a proper choice of solvents (*cf.* eq 30 and 31 with eq 37). This is in agreement with experiments.[8,12] On the other hand, when ν^2 becomes smaller, the anomaly should be more and more pronounced.[8,9] Finally in the limit of vanishing ν^2, the optical artifacts become predominant, as discussed above. All these effects would result in large negative slopes of Zimm plots at $w^2 = 0$ even at infinite dilution, thus yielding negative apparent mean-square radii of gyration for block copolymers.[15,16]

For block copolymers having large number of blocks, *i.e.*, large k in eq 37, and random copolymers as a limiting case of large k, we may say that Δ_{app} becomes zero and $\langle s^2\rangle_{app}$ approaches to $\langle s^2\rangle$. The low-angle anomaly should disappear for such copolymers, unless ν^2 is extremely small. It is interesting to note that even for a BAB triblock copolymer the contribution of Δ_{app} is only one fourth of that of an AB-diblock copolymer, when compared at a common level of M and x. Hence the anomaly should be less significant even in a solvent having $\nu_B = 0$. This would explain why we failed to notice the low-angle anomaly in our earlier work on polystyrene and poly(methyl methacrylate) block copolymers of BAB type in toluene.[10] At this point it is of interest to comment on our earlier work on solutions of polystyrene (A) and poly(methyl methacrylate) (B) diblock copolymer in *p*-xylene, which has $\nu_A = 0.114$ and $\nu_B = 0.007$ at 30° and is a Θ solvent for poly(methyl methacrylate) ($\Theta \simeq 40°$). In this system, again we failed to observe the low-angle anomaly of the type being discussed here. But rather we noticed a different type of anomaly. It has been successfully ascribed to formation of intermolecular aggregates in which invisible B blocks form the core and visible A blocks surrounding the core solubilize the micelle.[11] In terms of the present theory we may say that for such a model $\Delta_{app} \simeq r_A{}^2$ should be small and $\langle s^2\rangle_{app} \simeq \langle s^2\rangle_A$ should be close to $\langle s^2\rangle$. Then the low-angle anomaly should be insignificant.

Experimental Section

Materials and Methods. Block copolymer samples of polystyrene (PST) and poly(methyl methacrylate) (PMMA) of AB-diblock type were prepared by an anionic polymerization technique.[26] The preparation was carried out at −78° in tetrahydrofuran (H_4furan) with cumyl potassium-H_4furan solution[27] as the initiator. The detail was described elsewhere.[10,28] Here we only mention the following two points. In each preparation 1,1-diphenylethylene was used as an intermediate to suppress grafting of living PST to MMA units,[29] and an aliquot of the living PST (*i.e.*, the precursor PST) was recovered for the convenience of later analysis.

Each crude sample was subjected to extraction with boiling cyclohexane to remove free PST, then to freeze-drying, and finally

Table I
Characteristics of Polymer Samples

Precursor PST			Block Copolymers						
			ST-content				$10^{-4}\ M_{app}$[b]		
Code	$10^{-4}\ M_w$	M_w/M_n[a]	Code	x	$10^{-4}\ M_w$	M_w/M_n[a]	MEK	$C_2H_4Cl_2$	Toluene
53H	19.8	1.10	53B	0.51	44.0	1.23	43.5	44.2	47.6
54H	39.5	1.09	54B	0.42	93.0	1.08	85.0	89.6	94.0
63H	39.6	1.20*	63B30	0.24	150 ± 10		149		157
			63B50	0.49	76.4	1.13	68.7	76.5	83.3
			63B70	0.69	64.0		54.1		63.5
61H	159		61B	0.60	230 ± 10		235		238
27H	67.1	1.22	27B[c]	0.41	147.4	1.19	145		141

[a] Values of M_n by osmometry in toluene at 30.0° except one (*) by gpc. [b] For M_{app} values of ν at 30.0° for 436 nm light employed were for PST 0.232 (MEK), 0.168 ($C_2H_4Cl_2$), and 0.113 (toluene); and for PMMA 0.113 (MEK), 0.050 ($C_2H_4Cl_2$), and 0.004 (toluene). For block copolymers, values of ν were in good agreement with those calculated by eq. 7. [c] A BAB-triblock copolymer (see ref 10).

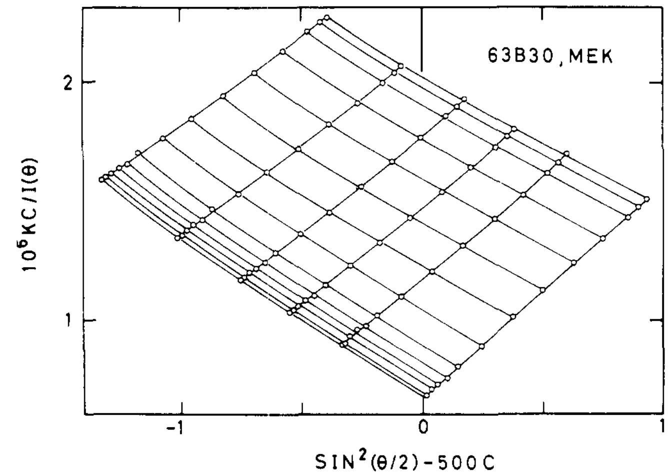

Figure 3. Zimm plot for the PST-PMMA diblock copolymer 63B30 in butanone.

to extraction with boiling acetonitrile to remove free PMMA. To detect contaminating homopolymers in the block copolymer samples, thin-layer chromatographic analysis[30,31] was applied. The presence of free PST was detected with chloroform as a developer, by which PST was eluted upto the solvent front, while block copolymers remained at the origin. For detecting free PMMA, a mixture of benzene and butanone (MEK) was used as a developer, by which block copolymers were eluted half way toward the solvent front, while PMMA remained at the origin. The procedures were repeated until the presence of any homopolymers became undetectable. Some samples were also subjected to density gradient centrifugation in 1,2-dibromo-1,1-difluoroethane and benzene mixture.[32] By these methods the presence of as low as 1% homopolymers was detectable.

Characterization of the polymer samples was carried out according to our laboratory routine which was described elsewhere in greater detail.[10] Comonomer composition was determined by combustion analysis. Osmotic pressure measurements were made on a Knauer electric membrane osmometer with a variable temperature controller. Determination of intrinsic viscosity $[\eta]$ was made on Ubbelohde dilution viscometers. Refractive index increment was measured with 436-nm wavelength light using a Shimadzu (Debye-type) differential refractometer with a thermostatically controlled cell. The refractive index increments of the copolymer samples were found to be well approximated by eq 7.

Light-scattering measurements were made on a Fica light-scattering photometer Model 50. A newly devised cylindrical cell with a ground cap was used. The constant of the apparatus was evaluated with pure benzene as a reference liquid, by taking $R(90°) = 46.4 \times 10^{-6}$ for the Rayleigh ratio and $\rho_u = 0.42$ for the corresponding depolarization at 25°.[33] Scattered light intensities were measured at 13 different angles ranging from 15 to 150° with vertically polarized light of 436-nm wavelength. The ratio $I(\theta)/I(90°)$ observed for benzene was found to be 1.000 ± 0.007 at each angle, and no correction was necessary for the imperfectness of the cells. Neither reflection correction was made, since the refractive index of vat liquid, *p*-xylene, was very close to that of the cells and the solvents employed. Corrections for the effect of the optical anisotropy were made by measuring at 90° with horizontally polarized light.[34] They were usually negligibly small. For some samples measurements were made in three solvents, butanone (MEK), 1,2-dichloroethane, and toluene all at 30.0 ± 0.1° and some others only in MEK and toluene. Solutions and solvents were cleared either by filtration through an ultracellafilter membrane (with the pore size $\phi = 0.3\ \mu$) or by centrifugation at a rotor speed between 15,000 and 25,000 rpm for 150 min at a room temperature. Molecular weights were determined by the conventional method of Zimm.[3]

Results

Characterization. According to Stockmayer *et al.*[14] and Benoit *et al.*[15,16,35] the molecular weight of a copolymer determined by the method of Zimm is an apparent value given by

$$M_{app} = M_w + 2P[(\nu_A - \nu_B)/\nu] + Q[(\nu_A - \nu_B)/\nu]^2 \quad (42)$$

where M_w is the true molecular weight, and P and Q are parameters representing the heterogeneity of the copolymer sample. For block copolymers these quantities can be conveniently related with the hetrogeneities of the precursor homopolymers, the average composition and the number-average molecular weight M_n of the copolymers.[10,29] The values of M_w were determined by using these relations.[10]

All the characterization data of the polymer samples used in this study are summarized in Table I. The block copolymers are coded as series B and their precursor PST as series H. Each pair is given the same code number. These results show that the samples are moderately homogeneous in both molecular weight and composition, and they contain negligible amount (<1%) of free homopolymers, if any present.

Angular Dependence of Scattered Light Intensities. Figures 3 and 4 show typical Zimm plots for sample 63B30 in MEK and in toluene, respectively. In the abscissa we employed $\sin^2(\theta/2)$ minus constant × c instead of the conventional $\sin^2(\theta/2)$ plus constant × c for the sake of easy recognition. Both solvents are good solvents for both PST and PMMA. The solvent MEK has reasonably large values of ν for both polymers, while toluene has a nearly zero value of ν for PMMA. The Zimm plot in MEK is completely normal (Figure 3), as anticipated from the theory discussed above. The correction terms in $Q'(\theta)$ are estimated by eq 37 as $\Delta_{app} = 0.047\langle s^2\rangle$ and $\langle s^2\rangle_{app} = 0.961\langle s^2\rangle$, predicting a trivial deviation from a homopolymer behavior. On the other hand, a peculiar distortion of the Zimm plot is observed in toluene data (Figure 4). We see that the angular dependence is almost linear at $c = 0$. However it shows an upward curvature at low angles, which becomes more significant with increasing concen-

Table II
Light-Scattering and Intrinsic Viscosity Data for Some Block Copolymer Solutions

Code	ST Content x	$y = x\nu_A/\nu$	$10^{-4} M_{app}$	$10^{-2} A_2 M_{app}$	$\langle s^2\rangle_{app}^{1/2}$ (Å)	$(\bar{r}^2)^{1/2}$ (Å)	$[\eta]$ (dl/g)
		PST–PMMA Diblock Copolymers in Toluene at 30.0°					
63B30	0.24	0.898	157	1.4	292	543	2.23
63B50	0.49	0.965	83.3	2.1	270	436	1.58
63B70	0.69	0.984	63.5	1.3	253	258	1.34
PST-63H	1.00	1.00	39.6	1.4	249	247	1.12
54B	0.42	0.953	94.0	1.8	274	453	1.65
PST-54H	1.00	1.00	39.5	1.4	255	250	
61B	0.60	0.977	238	4.3	620	784	3.83
PST-61H	1.00	1.00	159	4.3	628	671	
		Polystyrene–Polyisoprene Diblock Copolymers in Chlorobenzene at 35°[a]					
SI-a-6	0.48	1.054	104	3.8	279	714	
SI-a-7	0.50	1.051	17.0	1.2		247	
SI-b-7	0.76	1.014	55.3	3.1	257	389	

[a] Data reported by Prud'homme and Bywater.[8]

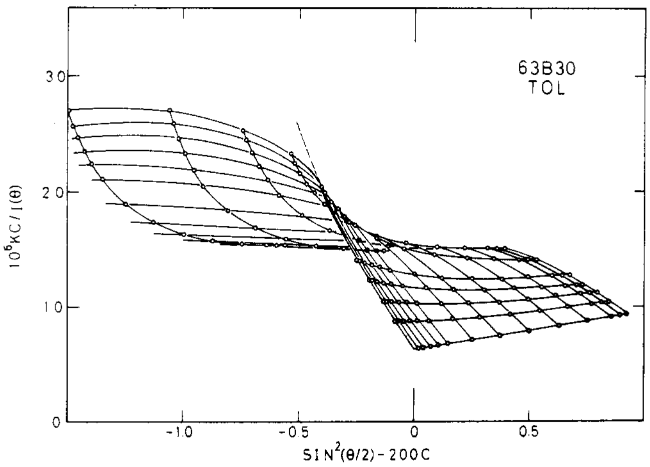

Figure 4. Zimm plot for the PST–PMMA diblock copolymer 63B30 in toluene.

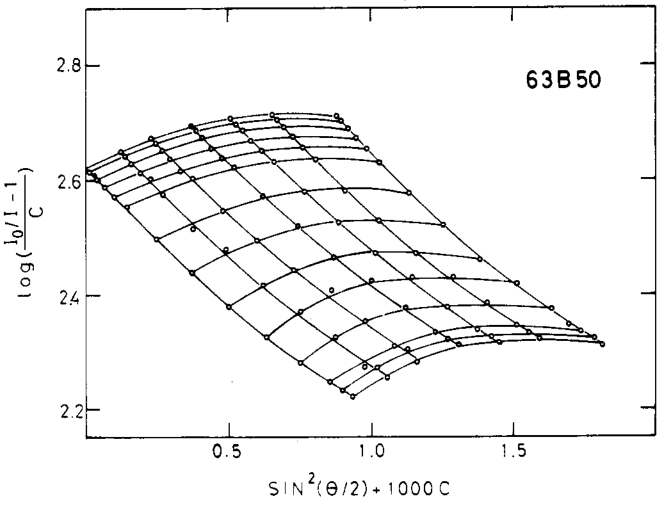

Figure 5. Guinier plot, ln $[(I(\theta,0)/I(\theta,c) - 1)/c]$ *vs.* $\sin^2(\theta/2) + 1000c$, for the PST–PMMA diblock copolymer 63B50 in toluene.

tration. Also we notice that the $Kc/I(0,c)$ *vs.* c curve becomes significantly downward concave in high concentration region ($c > 0.007$), which seems to be outside of the region the present theory being applicable. A closer examination of this anomaly will be given later. Qualitatively similar behavior were observed for every diblock sample–toluene system examined. When samples having the same composition are examined, the anomaly becomes more significant with increasing M_w. On the other hand, when a series of samples having an identical PST block but PMMA block of varying M are examined, the anomaly becomes more significant with composition x, *i.e.*, with increasing M of PMMA block. The anomaly in the θ dependence especially observed in low concentration region is in qualitative agreement with the theory: The correction terms in eq 37 for 63B30–toluene solution are $\Delta_{app} = 0.869\langle s^2\rangle$ and $\langle s^2\rangle_{app} = 0.476\langle s^2\rangle$, predicting negative initial slope in $Kc/I(\theta,c)$ *vs.* $\sin^2(\theta/2)$.

All the data were treated by the procedure described above to estimate values of A_2 and $\bar{r}^2$ from the Guinier plot.[20-22] A typical example is shown in Figure 5 for 63B50–toluene solution. We notice that the initial slope of the curve extrapolated to $\theta = 0$ is proportional to the third virial coefficient A_3, which is found to be positive for all the solutions examined here. Values of A_2 and $\bar{r}^2$, together with M_{app} and $\langle s^2\rangle_{app}$ determined from $P(\theta)$ data, are summarized in Table II. The table also lists the data reported by Prud'homme and Bywater[8] for polystyrene–polyisoprene (ST–IP) diblock copolymers in chlorobenzene for the sake of comparison.

The physical meaning of the quantity $\bar{r}^2$ is clear according to the discussion given in the Theoretical Section. However, this quantity, if looked at from a different angle, may be expressed as

$$2\bar{r}^2 = R_{EX}'^2 = \frac{\int \mathbf{R}_{12}'^2\{1 - \exp[-U'(\mathbf{R}_{12}')/kT]\}d\mathbf{R}_{12}'}{\int\{1 - \exp[-U'(\mathbf{R}_{12}')/kT]\}d\mathbf{R}_{12}'} \quad (43)$$

where $U'(\mathbf{R}_{12}')$ is the potential of average force operating between two molecules when their optical centers (if $\nu_B = 0$, the centers of mass G_A of visible A blocks) are separated by the distance $\mathbf{R}_{12}'$. In case of homopolymers, the optical center and the center of mass coincide so that $U'(\mathbf{R}_{12}') = U(\mathbf{R}_{12})$ and $2\bar{r}^2 = R_{EX}^2$, where R_{EX}^2 is the so-called mean-square radius of excluded volume defined by[22]

$$R_{EX}^2 = \frac{\int \mathbf{R}_{12}^2\{1 - \exp[-U(\mathbf{R}_{12})/kT]\}d\mathbf{R}_{12}}{\int\{1 - \exp[-U(\mathbf{R}_{12})/kT]\}d\mathbf{R}_{12}} \quad (44)$$

Apparently for a block copolymer the two quantities, R_{EX}^2 and $R_{EX}'^2$ ($= 2\bar{r}^2$) do not coincide, because the two centers usually do not coincide. Prud'homme and Bywater[8] have reported values of R_{EX}^2 obtained for ST–IP diblock copolymers in chlorobenzene. However the values reported by them (designated as $\bar{r}^2$ in Table III of their article[8]) should be $R_{EX}'^2$ defined by eq 43 in a more exact sence. According to the present theory these two quantities are related by

$$R_{EX}^2 = R_{EX}'^2 - 2\Delta_{app} = 2\langle s^2\rangle^*[f_1(\bar{Z}) - \delta_{app}(\bar{Z})] \quad (45)$$

Table III

Values of Excluded Volume V_{EX}, Excluded Volume Parameter $\bar{Z}$, Root-Mean-Square Radius of Excluded Volume $(R_{EX}^2/2)^{1/2}$, and Root-Mean-Square Radius of Gyration $\langle s^2\rangle^{1/2}$ Calculated from Light Scattering $Q(\theta)$ Function and Intrinsic Viscosity Data for Some Block Copolymers

Code	10^{-8} V_{EX} (Å³)	$\bar{Z}$	$(R_{EX}^2)^{1/2}$ (Å)	$\langle s^2\rangle^{1/2}$ (Å)	
				From $Q(\theta)$	From $[\eta]$
PST–PMMA Diblock Copolymers in Toluene at 30.0°					
63B30	7.8	1.4	458	440	477
63B50	5.8	2.0	384	362	344
63B70	2.7	(10)			298
PST-63H (54H)	1.8	2.2	231	236	239
54B	6.4	2.2	390	367	381
61B	34	1.5	721	690	656
61H	23	1.2	671	653	628[a]
PST–Polyisoprene Diblock Copolymers in Chlorobenzene at 35°[b]					
SI-a-6	13	1.4	544	522	
SI-a-7	0.7	1.9	192	183	
SI-b-6	5.6	2.4	372	345	

[a] Calculated from light scattering $P(\theta)$ function. [b] Calculated from the data of Prud'homme and Bywater.[8]

(Note that $\Delta_{app} = r_A^2$, if $\nu_B = 0$.) Calculated values of $\bar{Z}$, $R_{EX}^2/2$, and $\langle s^2\rangle$ (from $\psi(\theta)$) are summarized in Table III.

Concentration Dependence of Scattered Light Intensities. Next we turn our attention to the concentration dependence of scattered light intensities. Here we examine the variation of scattered light intensities for a series of samples, each having an identical PST block (its molecular weight $M_A = 4.0 \times 10^5$) but a PMMA block of different molecular weight M_B. The ratios M_B/M_A of the samples are roughly 3.0 for 63B30, 1.4 for 54B, 1.0 for 63B50, 0.5 for 63B70, and 0 for PST-54H and -63H. Figure 6 shows the results in the form $K_Ac_A/I(0,c_A)$ *vs.* c_A, where $c_A = xc$ is the concentration of PST part, and the constant $K_A = K(\nu_A/\nu)^2$ refers to the PST part. The intercept of these plots at $c_A = 0$ gives the molecular weight of the PST part, M_A (with small corrections due to the PMMA blocks), and the initial slope is $2A_2(\nu_A/\nu)^2$. The slope in turn is proportional to the intermolecular excluded volume V_{EX}[25] by the relation

$$(2M^2/N_0)A_2 = V_{EX} = \int \{1 - \exp[-U(\mathbf{R}_{12})/kT]\}d\mathbf{R}_{12} \quad (46)$$

(Note that if $\nu_B = 0$, the slope is N_0V_{EX}/M_A^2.) Figure 6 shows that V_{EX} becomes larger with increasing M_B. Values of V_{EX} for the present systems are listed also in Table III.

As pointed out in the preceding section, the curves for the block copolymers become downward concave in the region of higher concentrations, although almost linear at lower concentrations. While those for PST-54H and -63H are linear in all the concentration region examined here. Such an anomaly is more significant for the sample 63B30 having large PMMA block attached. The inflection of each curve appears to be taking place in the region of total concentration $c = 0.006 \sim 0.008$.

Discussion

Analysis of the $\psi(\theta)$ Function. As demonstrated above, toluene solutions of PST–PMMA diblock copolymers resulted in distorted Zimm plots. In the Theoretcial Section, we have shown that at least in low angle and concentration the anomaly can be explained by applying normal light-scattering laws without introducing artificial parameters which are difficult to relate to molecular parameters. In this sense we may say that distorted Zimm plots are simply a result of normal behavior of the $\psi(\theta)$ function of block copolymer solutions.[8] We have further shown how the anomaly or rather the $\psi(\theta)$ function depends on molecular structure, solvent properties, etc., and suggested its use for estimating $\langle s^2\rangle$ of a block copolymer, which is often difficult to be determined unambiguously. Values of $\langle s^2\rangle$ thus estimated from $\psi(\theta)$ are listed in Table III.

For a test of the method, the values of $\langle s^2\rangle$ should be compared with those determined by some other methods. This can be easily done with homopolymers, for which $\langle s^2\rangle$ can be determined from the $P(\theta)$ function. However, such a test on homopolymers is rather meaningless, since both experimentally[3,6] and theoretically[4,5,7] the $Q'(\theta)$ function has been known to be nearly unity in the range of θ and c of practical interest. The coincidence of the two sets of $\langle s^2\rangle$ values is self-evident for homopolymers (*cf.* the data for PST-61H and -63H in Table III). The test should be made on block copolymers, for which $\psi(\theta)$ plays a more important role. However, unfortunately we have at present no other plausible methods of determining $\langle s^2\rangle$ of a block copolymer especially in solvents having $\nu_B \simeq 0$. Therefore we estimated $\langle s^2\rangle$ from $[\eta]$ data, using the Flory–Fox viscosity equation[36,19]

$$[\eta] = 6^{3/2}\Phi\langle s^2\rangle^{3/2}/M_w \quad (47)$$

with $10^{-21}\Phi = 2.2$,[19,25,36,37] which seems valid in certain cases for block copolymer solutions.[10] Values of $\langle s^2\rangle$ estimated from $[\eta]$ data are also listed in Table III. We find that the coincidence between the two sets of $\langle s^2\rangle$ values is fairly good.

Admittedly our treatment may be too crude in several respects. The model employed including the Flory–Krigbaum potential is perhaps an oversimplification. First of all, the nonisotropic and uneven distribution of unlike segments in a block copolymer molecule has to be taken into account so that the potential $U(R_{12})$ becomes a function not only of the distance but also of the mutual orientation of the two molecules involved. However, as we have seen in eq 29, the major contribution to $\bar{r}^2$ comes from the first term $\langle s^2\rangle^* f_1(\bar{Z})$, if ν^2 is not too small. For the Flory–Krigbaum potential, the value of $\bar{Z}$ is usually less than 3, and hence $1 \leq f_1(\bar{Z}) \leq 1.2$ in the range of $\bar{Z}$ of practical interests. Then presumably the particular choice of the model would not too seriously affect the value of $f(\bar{Z})$, unless we deal with a case in which unlike segments are extremely incompatible.

Secondly the estimation of $\langle l^2\rangle$ in eq 29 using eq 37 for a random-flight model would be more problematic. Here we get involved in the controversial problem of the conformation of block copolymers in dilute solution.[38-45] So far two possibilities have been suggested. One is a segregated conformation, in which unlike segment separation or intrachain phase separation occurs, giving few heterocontacts;

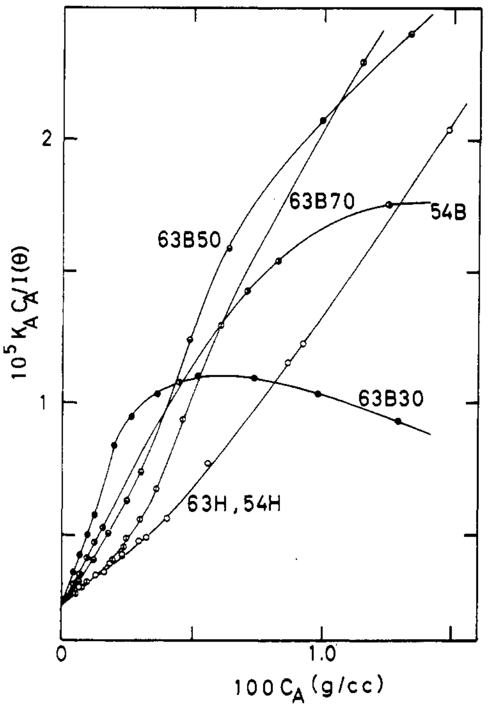

Figure 6. Plots of $K_A c_A/I(0,c)$ *vs.* c_A for some PST-PMMA diblock copolymers and their precursor homo-PST in toluene. Note that all the PST blocks have an identical molecular weight.

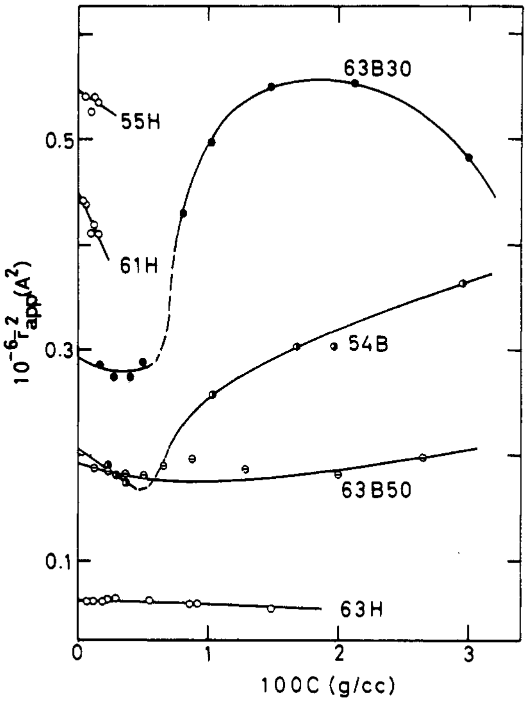

Figure 7. Plots of $\bar{r}_{app}^2$ *vs.* c for some PST-PMMA diblock copolymers and homo-PST's in toluene.

and the other is a random-coil conformation in which unlike segments are interpenetrating, giving a large number of heterocontacts. One would expect a larger value of $\langle l^2 \rangle$ for the former rather than the latter. If we assume a segregated conformation for an AB-diblock copolymer in which the A and B blocks are completely separated in space by a hypothetical plane passing through the A-B junction point, we have the ratio $\langle l^2 \rangle / \langle s^2 \rangle$ larger by a factor of 1.265 than the corresponding value of a random coil model.[12] If we employ this model to calculate $\langle s^2 \rangle$ by eq 29, we should find that the values should be only a few per cent smaller than those listed in Table III. Apparently these two models would represent two opposite extremes. Then we may say that the present analysis would give reasonably accurate values of $\langle s^2 \rangle$, which are insensitive to the choice of a particular model. In other words, this implies that we are unable to distinguish a segregated conformation and a random-flight conformation from the $\psi(\theta)$ analysis.

In connection of the problem of the block copolymer conformation, we should like to add one more comment here, although our main objective of this article is not to discuss this problem. One often argues that measurements of $\langle s^2 \rangle_{app}$ which is equal to $\langle s^2 \rangle_A$ in a solvent having $\nu_B = 0$ should yield information concerning the conformation of a block copolymer in dilute solution.[8,9] Namely for a segregated conformation, one would anticipate that $\langle s^2 \rangle_A$ would be similar in value to that of the precursor homopolymer A in the same solvent. However these expectations appear to be too optimistic. First of all, the segregated conformation such as assumed above is hardly realizable in a common solvent such as toluene for PST-PMMA block copolymers, because of the highly unfavorable entropic effect of such conformation. Secondly the effects of repulsive interactions between unlike segments might not be so simple as one would intuitively anticipate. As shown by eq 37, already some separation occurs even in a random-flight conformation, *i.e.*, $\langle l^2 \rangle = 2\langle s^2 \rangle$. The incompatible interaction due to the heterocontacts would make $\langle l^2 \rangle$ larger, and at the same time, this would tend to suppress the expansion of the individual blocks, *i.e.*, to make $\langle s^2 \rangle_A$ smaller. This situation is somewhat similar to a mixture of two homopolymers in a common solvent, in which addition of one polymer can bring the other polymer to the Θ state.[46] The actual conformation must be somewhere between these two extreme models. The present data listed in Table II show that in most cases values of $\langle s^2 \rangle_A$ are larger than those of the precursor polystyrenes except for one sample 61B. Incidentally this sample has the largest molecular weight among those examined here. The implication of these results will be discussed elsewhere in greater detail.[12]

Scattering at Higher Concentrations. We have seen that the scattered-light intensities from toluene solutions of the PST-PMMA diblock copolymers increase anomalously in higher concentration region ($c > 0.005 \sim 0.007$, *cf.* Figure 6). Similar behavior were observed also in PMMA-PST-PMMA triblock copolymer solutions.[12] Possible explanations for such an anomaly may be as follows. At high concentrations, ordering of the copolymer molecules might be induced presumably by the incompatible interactions between the PST and PMMA blocks. Also the environment around the visible PST blocks becomes unfavorable toward them, because the PMMA blocks would act as if a nonsolvent were added to the system. This is similar to the situation in a homopolymer mixture.[46]

The anomaly in the c dependence may be looked at from a somewhat different angle by plotting a new quantity $\bar{r}_{app}^2$ *vs.* c relation, where $\bar{r}_{app}^2$ is a value of $\bar{r}^2$ defined at a finite concentration. Figure 7 shows the results. For PST samples, $\bar{r}_{app}^2$ appears to be decreasing with increasing concentration, presumably reflecting that the chain dimensions become smaller as predicted by some previous theories.[47,16,7b] On the other hand, for sample 63B30, $\bar{r}_{app}^2$ is first nearly a constant and shows a sudden increase by a factor of roughly 2 at about $c \simeq 0.007$. Sample 54B also shows a similar behavior, while other samples 63B50 and 63B70, which have shorter PMMA blocks, behave in much the same way as the homopolymers. The behavior of samples 63B30 and 54B may be an indication that some kind of intermolecular ordering is underway even in a concentration region as low as 0.01. The anomaly of course cannot be observed in solvents such as butanone having relatively large values of ν for both PST and PMMA. Interestingly a viscometric study covering this concentration region show no anomaly in the viscosity–concentration relationship.[48] This implies that the ordering, if ever, in the dilute solution does not correspond to the formation of somewhat rigid two-phase structure which would give rise to an anomaly in the rheological properties.[48,49] The toluene solution of sample 63B30, which exhibited the most pronounced anomaly, becomes blue at about $c \simeq 0.10$ and turns iridescent at about $c \simeq 0.15$. This clearly indicates the formation of ordered structure, which might be similar to the two-phase structure found in the bulk state.[50] Such colored solutions, often called polymeric liquid crystals, have been reported in several articles.[51-53] However, at present, the relation between the two-phase structure found in concentrated solutions and in bulk and the ordering in dilute solution which are believed to have been found here is still not clear.

References and Notes

(1) This work was supported by a grant from the Ministry of Education (No. B 8732), 1971–1972.

(2) On leave from Kyoto University to Department of Chemistry, University of Manchester, Manchester M13, 9PL, England.

(3) B. H. Zimm, *J. Chem. Phys.*, **16**, 1093, 1099 (1948).

(4) A. C. Albrecht, *J. Chem. Phys.*, **27**, 1002, 1014 (1957).

(5) P. J. Flory and A. M. Bueche, *J. Polym. Sci.*, **27**, 219 (1958).

(6) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **18**, 1211 (1950).

(7) (a) H. Yamakawa, *J. Chem. Phys.*, **34**, 1360 (1961); (b) "Modern Theory of Polymer Solutions," Harper & Row, New York, N. Y., 1971.

(8) J. Prud'homme and S. Bywater, *Macromolecules*, **4**, 543 (1971).

(9) (a) H. Utiyama, M. Fukuda, M. Mizumori, Y. Tsunashima, and M. Kurata, Abstracts, 20th Polymer Symposium of the Society of Polymer Science, Japan, held at Tokyo, October 1971. (b) H. Utiyama, T. Takenaka, M. Mizumori and M. Fukuda, *Rep. Progr. Polym. Phys. Jap.*, **15**, 79 (1972).

(10) H. Ohnuma, T. Kotaka, and H. Inagaki, *Polymer*, **10**, 501 (1969).

(11) T. Tanaka, T. Kotaka, and H. Inagaki, *Polym. J.*, **3**, 338 (1972).

(12) T. Tanaka, Ph.D. Dissertation, Kyoto University, 1973.

(13) W. G. McMillan and J. E. Mayer, *J. Chem. Phys.*, **13**, 276 (1945).

(14) W. H. Stockmayer, L. D. Moore, Jr., M. Fixman, and B. N. Epstein, *J. Polym. Sci.*, **16**, 517 (1955).

(15) H. Benoit and C. Wippler, *J. Chim. Phys.*, **57**, 524 (1960).

(16) H. Benoit and D. Froelich in "Application of Light Scattering to Copolymers," M. B. Huglin, Ed., Academic Press, New York, N. Y., 1972.

(17) B. H. Zimm, *J. Chem. Phys.*, **14**, 164 (1946).

(18) P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

(19) P. J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, N. Y., 1953.

(20) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **20**, 85 (1952).

(21) A. Guinier and G. Fournet, Small-Angle Scattering of X-Rays, John Wiley, New York, N. Y., 1955.

(22) W. Burchard, *Polymer*, **10**, 29 (1969).

(23) M. Kurata, M. Fukatsu, H. Sotobayashi, and H. Yamakawa, *J. Chem. Phys.*, **41**, 139 (1964).

(24) M. Fixman, *J. Chem. Phys.*, **23**, 1656 (1955); *ibid.*, **36**, 3123 (1962).

(25) T. A. Orofino and P. J. Flory, *J. Chem. Phys.*, **26**, 1067 (1957).

(26) (a) M. Szwarc, *Nature (London)*, **178**, 1168 (1956); *Fortschr. Hochpolym. Forsch.*, **2**, 275 (1960); (b) M. Morton, R. Milkovich, E. B. McIntyre, and L. J. Bradley, *J. Polym. Sci., Part A*, **1**, 443 (1963).

(27) A Gift from Dr. T. Fujimoto and Professor M. Nagasawa of Nagoya Univ.

(28) T. Kotaka, T. Tanaka, and H. Inagaki, *Polym. J.*, **3**, 327 (1972).

(29) D. Freyss, P. Rempp, and H. Benoit, *J. Polym. Sci., Part B*, **2**, 217 (1964).

(30) H. Inagaki, H. Matsuda, and F. Kamiyama, *Macromolecules*, **1**, 520 (1968).

(31) (a) F. Kamiyama, H. Inagaki, and T. Kotaka, *Polym. J.*, **3**, 470 (1972); (b) T. Tanaka, T. Uda, and T. Kotaka, unpublished experiments.

(32) A. Nakazawa and J. J. Hermans, *J. Polym. Sci., Part A2*, **9**, 1871 (1971); A. Nakazawa, T. Tanaka, and T. Kotaka, unpublished experiments.

(33) G. Dezelic, *J. Chem. Phys.*, **45**, 185 (1966).

(34) H. Utiyama and M. Kurata, *Bull. Inst. Chem. Res., Kyoto Univ.*, **42**, 128 (1964).

(35) W. Bushuk and H. Benoit, *Can. J. Chem.*, **36**, 1616 (1958).

(36) P. J. Flory and T. G Fox, *J. Amer. Chem. Soc.*, **22**, 1904 (1951).

(37) W. R. Krigbaum, *J. Amer. Chem. Soc.*, **36**, 3758 (1954).

(38) I. M. Burnett, P. Meares, and C. Patton, *Trans. Faraday Soc.*, **58**, 737 (1962).

(39) S. Krause, *J. Phys. Chem.*, **68**, 1948 (1964).

(40) H. Inagaki, *Macromol. Chem.*, **86**, 289 (1965).

(41) D. Froelich and H. Benoit, *Macromol. Chem.*, **92**, 224 (1966).

(42) (a) A. Dondos, D. Froelich, P. Rempp, and H. Benoit, *Makromol. Chem.*, **92**, 224 (1965); (b) A. Dondos, *ibid.*, **147**, 123 (1971); (c) A. Dondos, P. Rempp, and H. Benoit, *Polymer*, **13**, 97 (1972).

(43) (a) L. A. Utracki, R. Simha, and L. J. Fetters, *J. Polym. Sci., Part A2*, **6**, 2051 (1968); (b) L. A. Utracki and R. Simha, *Macromolecules*, **1**, 505 (1968).

(44) D. N. Cramond and J. R. Urwin, *Eur. Polym. J.*, **5**, 35 (1969).

(45) (a) T. Kotaka, H. Ohnuma, and H. Inagaki, *Polymer*, **10**, 517 (1969); (b) H. Ohnuma, T. Kotaka, and H. Inagaki, *Polym. J.*, **1**, 716 (1970).

(46) R. Kuhn, H.-J, Cantow, and W. Burchard, *Angew. Makromol. Chem.*, **2**, 146 (1968).

(47) W. R. Krigbaum with T. Kawai and K. Saito, *J. Polym. Sci.*, **26**, 213 (1957).

(48) T. Tanaka and T. Kotaka, unpublished experiments.

(49) T. Kotaka and J. L. White, *Trans. Soc. Rheol.*, **17**, 587 (1973).

(50) See, for example, G. E. Molau, Ed., Colloidal and Morphological Behavior of Block and Graft Copolymers, Plenum Press, New York, N. Y., 1971.

(51) (a) A. Skoulios, G. Finaz, and J. Parrod, *C. R. Acad. Sci., Ser. C*, **251**, 739 (1960); (b) A. Skoulios, G. Tsouladze, and E. Franta, *J. Polym. Sci., Part C*, **4**, 507 (1963).

(52) B. Gallot, R. Mayer, and C. Sadron, *C. R. Acad. Sci., Ser. C*, **263**, 42 (1966).

(53) E. Vanzo, *J. Polym. Sci., Part A1*, **4**, 1727 (1966).