Conformation of Block Copolymers in Dilute Solution. Monte Carlo Calculations and Light-Scattering Studies on Diblock Copolymer Systems

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Received January 26, 1976

ABSTRACT: Conformational properties of AB-diblock copolymers in dilute solution were examined by two different methods. One is computer simulation on a self-avoiding type lattice-walk model. The other is light-scattering measurements made with solvents having zero refractive index increments for one of the two blocks, say B. Existing light-scattering data of this kind as well as ours were analyzed taking the small visibility of the B block into account. Both methods led to a common conclusion that the mean-square radii of gyration of the individual blocks are almost the same as those of the homopolymers equivalent to the respective blocks, in any case. On the other hand, the computer simulation indicated that the mean-square distance between the centers of mass of the two blocks increases noticeably with increasing A–B repulsive interactions, making the conformation of the overall chain as well as those of the individual blocks more asymmetrical. It was indicated that such an effect of the heterocontact interactions would be less significant as the individual blocks become more expanded due to the excluded volume effects within the respective blocks (i.e., with the solvent quality becoming better toward the parent homopolymers). A possible range over which this center-to-center distance may vary was suggested.

A clear concept of the conformation of individual block copolymer chains is essential in describing the solution and morphological behavior. Up to now two typical conformations have been proposed as plausible models to describe block copolymer conformation in dilute solution:[1,2] One is the "quasi-random coil" conformation in which dissimilar blocks more or less interpenetrate each other, allowing heterocontacts. The other is the "segregated" conformation in which dissimilar blocks occupy distinctly different domains in space. In spite of a number of efforts,[1-10] neither of those has been definitely established, partly because the concept of the "segregated" conformation itself is still ambiguous. Moreover, most of the tests attempted so far appear to have been designed by intuition without really knowing the implication of such models, thereby having led to no definite conclusions.

In this article we examine the conformational properties of AB-diblock copolymers by two different methods. One is a computer simulation by the Monte Carlo method, which has been proved useful to study the excluded volume effect in homopolymers.[11,12] In view of the generally incompatible nature of two different homopolymers in solution as well as in bulk, we employed a simple lattice-walk model of allowing intersections within each block but imposing nonintersecting repulsive interactions between dissimilar blocks. Through examination of this model we have attempted to elucidate the conformational properties of a block copolymer chain under the influence of such interactions. In the second method, we examine the theoretical basis of interpreting light-scattering data from block-copolymer solutions. Particularly, we analyze light-scattering data obtained in so-called isorefractive solvents, i.e., those having nearly zero refractive index increments for one of the two blocks, say the B block. Obviously such measurements allow us to estimate the dimension of the "visible" A block, from which one would expect to deduce a more definite information on the chain conformation.[6-10,3f] However, one should be careful in the data analysis, since the measurements are usually made with solvents in which the B block is still slightly visible. Even a small visibility can make an unexpectedly large contribution.[3f-5] We have devised a method of estimating this contribution quantitatively, and analyzed existing light-scattering data with this method including our data obtained in isorefractive solvents. As a result, we have obtained a simple picture of the chain conformation of diblock copolymers. The results will be reported herein.

Monte Carlo Calculations

Model and Method. A precise description of the conformation of an AB-diblock copolymer could be given, for example, by specifying the distributions of the A and B segments around the molecular center of mass. However, most practical purposes will be achieved if one knows certain dimensional parameters such as the average dimensions of the individual blocks and the distance between the centers of mass of the two blocks. In general the mean-square radius $\langle S^2\rangle$ and the mean-square end-to-end distance $\langle R^2\rangle$ of the overall chain are respectively given by

$$\langle S^2\rangle = x\langle S^2\rangle_{\mathrm{A}} + y\langle S^2\rangle_{\mathrm{B}} + xy\langle G^2\rangle \tag{1a}$$

$$\langle R^2\rangle = \langle R^2\rangle_{\mathrm{A}} + \langle R^2\rangle_{\mathrm{B}} - 2\langle R_{\mathrm{A}}R_{\mathrm{B}}\cos(R_{\mathrm{A}}{}^{\wedge}R_{\mathrm{B}})\rangle \tag{1b}$$

where $x = 1 - y$ is the weight fraction of the A block; $\langle S^2\rangle_{\mathrm{K}}$ and $\langle R^2\rangle_{\mathrm{K}}$ are the dimensions of the K block (K = A or B); $\langle G^2\rangle$ is the mean-square distance between the centers of mass of the A and B blocks; and $(R_{\mathrm{A}}{}^{\wedge}R_{\mathrm{B}})$ is the angle between the A and B end-to-end vectors. We define the expansion factors α^2, $\alpha_K{}^2$, $\alpha_G{}^2$, $\alpha_R{}^2$, and $\alpha_{RK}{}^2$ as follows:

$$\alpha^2 = \langle S^2\rangle/\langle S^2\rangle_0 \tag{2a}$$

$$\alpha_{\mathrm{K}}{}^2 = \langle S^2\rangle_{\mathrm{K}}/\langle S^2\rangle_{\mathrm{K},0} \qquad \mathrm{K} = \mathrm{A\ or\ B} \tag{2b}$$

$$\alpha_G{}^2 = \langle G^2\rangle/\langle G^2\rangle_0 \tag{2c}$$

$$\alpha_R{}^2 = \langle R^2\rangle/\langle R^2\rangle_0 \tag{2d}$$

$$\alpha_{R\mathrm{K}}{}^2 = \langle R^2\rangle_{\mathrm{K}}/\langle R^2\rangle_{\mathrm{K},0} \qquad \mathrm{K} = \mathrm{A\ or\ B} \tag{2e}$$

The subscript 0 denotes the unperturbed state where the excluded volume effects between all the A–A, B–B, and A–B segments vanish simultaneously. Our first purpose here is to evaluate the above α's for a hypothetical chain where the excluded volume effects exist only between the A–B segments.

To this end we consider walks on a three-dimensional (6 choice) cubic lattice. In view of the nature of our problem this particular choice of the lattice should not affect the final conclusions. First, a random walk (in which the self-intersections are allowed) of $N_{\mathrm{A}} - 1$ steps of the A segments is generated. Another random walk of N_{B} steps of the B segments originates from the end point of the A-type walk. If the B-type walk intersects with the first A-type walk, both are discarded. If there are no intersections, the coordinates of each

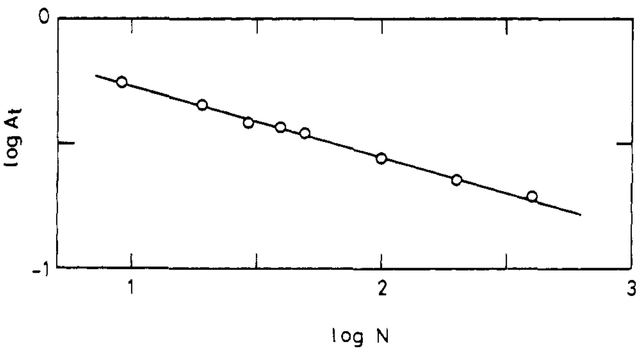

Figure 1. Plots of chain attrition At vs. number of steps N for symmetrical diblock copolymer chains on a cubic lattice.

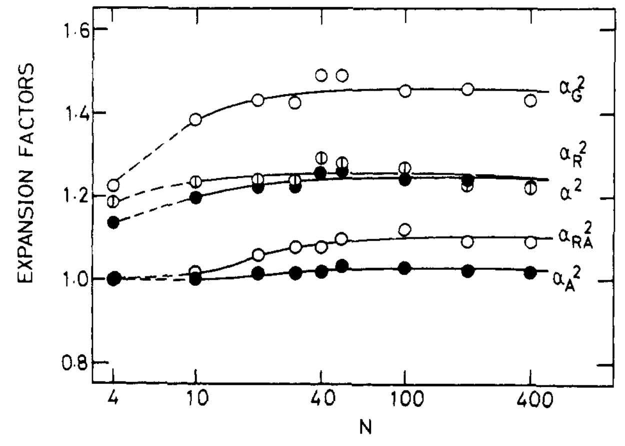

Figure 2. Plots of expansion factors α vs. number of steps N for symmetrical diblock copolymer chains on a cubic lattice with interaction parameter $\xi_{AB} = 0$.

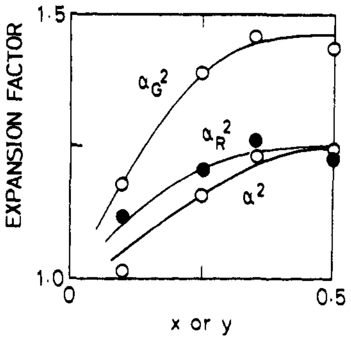

Figure 3. Dependence of expansion factors α on composition x for diblock copolymer chains on a cubic lattice with interaction parameter $\xi_{AB} = 0$ and the number of steps $N = 200$.

step are stored as a successful trial. Thus a sample of a chain corresponding to an AB-diblock copolymer is generated with N_A A segments and N_B B segments of identical lengths, and in which only A–B interactions exist. To reduce the computation time, the chain enrichment technique of Wall and Erpenbeck[12a] was applied for longer chains ($N = N_A + N_B \geq 50$). After a certain number of the successful samples (which ranged from 2000 to 700) had been generated, the quantities defined by eq 1 and 2 were calculated. The lengths of the chains N ranged from 10 to 400 segments.

In order to examine the variation of the α's with the magnitude of the A–B interactions, we introduced an interaction parameter ξ_{AB} for an A and a B segment being in contact, i.e., occupying the lattice sites immediately adjacent to each other. If the ith successful trial has η_i pairs of such heterocontacts, we multiply the quantities in question by the weight factor $e^{-\eta_i\xi_{AB}}$. Then, for example, $\langle S^2\rangle_A$ was calculated from[11]

$$\langle S^2\rangle_A = \sum_i S_{A,i}{}^2\, e^{-\eta_i\xi_{AB}} \Big/ \sum_i e^{-\eta_i\xi_{AB}} \tag{3}$$

where the summation extends over all the samples which, of course, have no A–B intersections. The computation was made with a Facom 230-48 digital computer (Fujitsu Ltd., Tokyo, Japan) of our Institute.

Results and Discussion

For homopolymers with large N, the chain attrition At(N) can be expressed by[11,12]

$$\mathrm{At}(N) = e^{-\lambda N} \tag{4}$$

where λ is the so-called attrition constant dependent upon the type of lattice employed. Figure 1 shows the attrition for our block copolymer model with $x = N_A/N = \frac{1}{2}$. For this 10 to 400 range of N it is expressed by

$$\mathrm{At}(N) = N^{-0.28} \tag{5}$$

That is, the attrition for our model is very small. As opposed to the homopolymer case, ln At is not proportional to N but only to ln N.[12b] This is predictable from eq 3: The attrition for homopolymers of length $N = N_A + N_B$ may be split into three terms,

$$\mathrm{At}(N) = \mathrm{At}(N_A)\mathrm{At}(N_B)\mathrm{At}(N_A, N_B) \tag{6}$$

where At(N_A) and At(N_B) are the attrition for the independent chains of length N_A and N_B, respectively, and At(N_A, N_B) expresses the contribution from tying them together. From eq 4 and 6, we have At(N_A, N_B) ~ 1. Namely, ln At(N_A, N_B) is not proportional to N. This implies that the self-avoiding-type segment interactions take place mostly among segments located nearby along the chain rather than among remote ones. (It sounds somewhat unreasonable to refer to such interactions as *long-range* interactions.) For an AB-diblock copolymer chain which has only one A–B junction along the chain, the probability of interactions between dissimilar blocks should be much smaller than those within the same blocks. Therefore we expect that the excluded volume effects arising from the heterocontacts (which we are going to examine) would have only minor effects on the chain conformation. This point will be verified in the following.

First we consider the case where $\xi_{AB} = 0$. Figure 2 shows the variation of α's with N. The composition is fixed at $x = \frac{1}{2}$, i.e., $N_A = N_B = N/2$. It is seen that, as N increases, all the α's corverge to certain finite values which are not much larger than unity. Plots of α's against N^{-1} give these asymptotes, i.e.,

$$\langle S^2\rangle = 1.22\langle S^2\rangle_0 \tag{7a}$$

$$\langle S^2\rangle_K = 1.02\langle S^2\rangle_{K,0} \tag{7b}$$

$$\langle G^2\rangle = 1.43\langle G^2\rangle_0 \tag{7c}$$

$$\langle R^2\rangle = 1.22\langle R^2\rangle_0 \tag{7d}$$

$$\langle R^2\rangle_K = 1.09\langle R^2\rangle_{K,0} \tag{7e}$$

with K = A or B. All the above quantities are proportional to N as in the case of the unperturbed chains. The asymptote is the largest for $\langle G^2\rangle$ and the smallest for $\langle S^2\rangle_K$. Above all it should be noted that $\langle S^2\rangle_A$ is almost the same as $\langle S^2\rangle_{A,0}$, while $\langle R^2\rangle_A$ is relatively larger than $\langle R^2\rangle_{A,0}$. This shows that excluded volume effects due to the heterocontacts perturb the chain not only by pushing apart the A and B blocks, but also by tending the segment distribution within each block more asymmetric, still keeping the value of $\langle S^2\rangle_K$ (K = A or B) practically unchanged. These features appear to be essentially

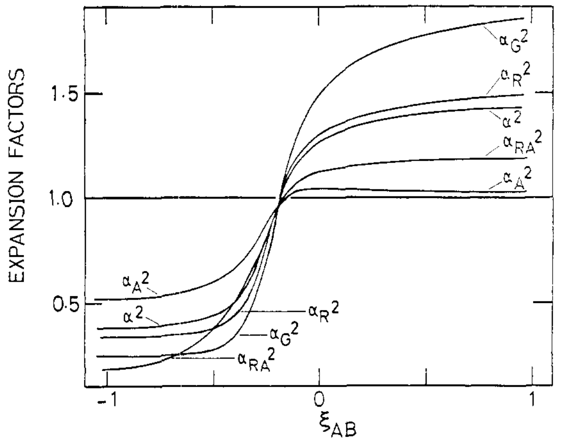

Figure 4. Variation of expansion factors α with interaction parameter ξ_{AB} for a symmetrical diblock copolymer chain on a cubic lattice; number of steps $N = 100$.

the same for nonequimolar ($N_A \neq N_B$) AB-diblock copolymer chains: Calculations made for the nonequimolar cases with a fixed number of steps ($N = 200$) indicate that the $\alpha_K{}^2$ is very close to unity (≤ 1.02) for any composition x. Figure 3 shows the x dependence of the other parameters such as α^2, $\alpha_R{}^2$, and $\alpha_G{}^2$. These values are nearly the same as the values for the equimolar case, unless the chain architecture becomes too asymmetrical, say x or $y < 1/4$.

In this connection, the results of our previous model calculation are of interest.[5] If we assume a "segregated" conformation for an equimolar 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, then we have $\langle S^2\rangle_A = 1.02\langle S^2\rangle_{A,0}$, $\langle R^2\rangle_A = 5/3\langle R^2\rangle_{A,0}$, and $\langle G^2\rangle = 2.19\langle G^2\rangle_0$ from the random-flight statistics.[13a] These values should be compared with those of eq 7. Obviously such a conformation is unrealistic, since the conformational entropy is infinitely small as compared with that of a random flight diblock copolymer chain without the segregating plane.[5] However, the qualitative coincidence of the behavior of this model and of the above lattice-walk model is indeed noteworthy. A real block copolymer chain as well as the present lattice-walk model would lie somewhere between these two extremes, i.e., the random flight model and the hypothetical "segregated" model, as far as the values of $\langle S^2\rangle_A$, $\langle R^2\rangle_A$, and $\langle G^2\rangle$ are concerned. For all these models the value of $\langle S^2\rangle_A$ remains practically constant.

In the next place we examine the variation of α's with the magnitude of the A–B interactions. In Figure 4, the α's are plotted against the interaction parameter ξ_{AB}. As seen in the figure, the $\alpha_A{}^2$ becomes unity at a slightly negative ξ_{AB} value ($\xi_{AB} = \xi_{AB}{}^0 = -0.18$). The other quantities such as the α^2 and $\alpha_G{}^2$ also become unity in the proximity of this point. (Our present data are not sufficient to answer the interesting question of whether all the α's become unity at a single value of ξ_{AB}.) As the ξ_{AB} increases, the α^2, $\alpha_G{}^2$, and so forth increase monotonously, while the $\alpha_A{}^2$ increases in the proximity of $\xi_{AB} = \xi_{AB}{}^0$, but rapidly levels off. It is confirmed again that $\alpha_A{}^2$ never exceeds unity by more than a few percent, irrespective of the magnitude of the A–B (repulsive) interactions. A qualitatively similar result was obtained by Bendler and Šolc based on a somewhat different model.[13b] The slope of the curve at $\xi_{AB} = \xi_{AB}{}^0$ should correspond to the first-order coefficient of the perturbation theory calculated by Froelich and Benoit[14,15] and by us[16] previously if the two models can ever be correlated to each other quantitatively.

So far we have confined ourselves to the special case in which the θ state common to the parent homopolymers was assumed, and only the heterocontact interactions were introduced. To describe the chain conformation more generally, we now introduce new parameters γ, γ_R, and σ defined respectively by

$$\gamma = \langle S^2\rangle_A / \langle S^2\rangle_{H\text{-}A} \tag{8a}$$

$$\gamma_R = \langle R^2\rangle_A / \langle R^2\rangle_{H\text{-}A} \tag{8b}$$

$$\sigma = \langle G^2\rangle / (2\langle S^2\rangle_{H\text{-}A} + 2\langle S^2\rangle_{H\text{-}B}) \tag{8c}$$

where $\langle S^2\rangle_{H\text{-}K}$, for example, is the radius of the K-homopolymer chain which is identical with the K block, both placed in the same environment. First, we consider the hypothetical case in which the A–B interactions are absent and hence the A and B block behave independently. Then, the quantity $\langle G^2\rangle$ may be given by $\langle G^2\rangle = \langle G^2\rangle_A + \langle G^2\rangle_B$, where $\langle G^2\rangle_K$ is the mean-square distance between the center of mass of the K block and the A–B junction point. For vanishing K–K interactions (the unperturbed K chain), $\langle G^2\rangle_K$ is identical with $2\langle S^2\rangle_K$[17] (and hence $\sigma = 1$), but it should be slightly larger than $2\langle S^2\rangle_K$ for the perturbed K chain. The deviation should be similar in magnitude to that between $\langle R^2\rangle$ and $6\langle S^2\rangle$, i.e., just a few percent.[12a] Thus, σ should be very close to unity in this hypothetical state. Obviously, the other parameters γ and γ_R should be identical with unity. On the other hand, in the presence of the A–B repulsive interactions alone, i.e., in the θ state common to the parent homopolymers, we have already found that

$$\gamma = 1.02 \tag{7b'}$$

$$\gamma_R = 1.09 \tag{7e'}$$

$$\sigma = 1.43 \tag{7c'}$$

The parameters γ and γ_R as well are expected to be very close to unity in any case. As the A and B homopolymers become more expanded, the probability of the intersections of the dissimilar blocks should become smaller, and hence the perturbation due to the heterocontacts should become less significant. Then, there is no reason to believe that γ and γ_R should become larger than the values given by eq 7′ in a common good solvent toward the parent homopolymers. By the same reason the value of σ would become smaller than the value given by eq 7c′, coming closer to unity, as the homopolymers become more expanded in the given environment.

This view may be supported by the calculations on homopolymers due to Wall and Erpenbeck.[12a] They have calculated the dimensions of certain specific portions of self-avoiding chains on a tetrahedral lattice. For example, we can calculate from their data the ratio $\langle R_{ij}{}^2\rangle_N / \langle R^2\rangle_{|i-j|}$, where $\langle R_{ij}{}^2\rangle_N$ is the mean-square distance between the ith and the jth segments in the chain of length N, and $\langle R^2\rangle_{|i-j|}$ is the mean-square end-to-end distance of the chain of length $|i-j|$. This ratio for $i = 0$ and $j = N/2$ corresponds to our γ_R for a symmetrical diblock copolymer in the corresponding state (i.e., the identical A–A, B–B, and A–B interactions). The other parameter σ can be estimated similarly if we assume that $\langle R_{ij}{}^2\rangle_N \sim 6\langle S_{ij}{}^2\rangle_N$. Figure 5 shows the plots of γ_R and σ, thus estimated, against N for the homopolymer-equivalent symmetrical-diblock copolymers. Apparently the values of γ_R and σ are independent of N, giving

$$\gamma_R = 1.05 \tag{9a}$$

$$\sigma = 1.16 \tag{9b}$$

As expected, γ_R is closer to unity than the corresponding value of 1.09 given by eq 7e′ and σ is smaller than 1.43 of eq 7c′. Almost the same results are obtained from the data of Alexandrowicz and Accad[12c] (4-choice simple cubic lattice). If we make similar calculations on the mean-square radii, we will have a γ value much closer to unity (≤ 1.02). This must be so,

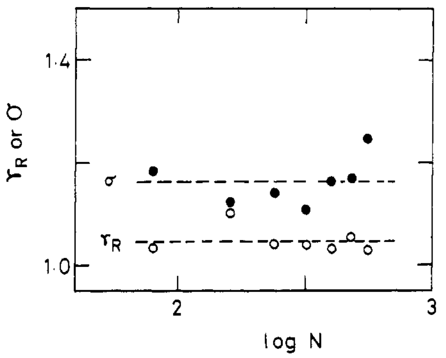

Figure 5. Plots of parameter γ_R and σ vs. number of steps N for homopolymer-equivalent symmetrical diblock copolymer chains on a tetrahedral lattice; calculated from the data of Wall and Erpenbeck[12] (see text).

since the variation of the mean-square radius of each block is less significant than that of the mean-square distance, as suggested before (cf. eq 7). Correspondingly, the true σ value of the homopolymer-equivalent block copolymer should be somewhat larger than 1.16 of eq 9b. It is increased to 1.25 by setting $\gamma = 1.02$.

In conclusion we may remark that $\langle S^2\rangle_A$ (or $\langle S^2\rangle_B$) in a diblock copolymer is almost the same as $\langle S^2\rangle_{H\text{-}A}$ (or $\langle S^2\rangle_{H\text{-}B}$) in any case, while the parameter σ is also close to unity in the absence of the A–B interactions and becomes larger with the increasing magnitude of the A–B interactions. When compared at a common level of heterocontact interactions, the σ becomes smaller as the individual blocks become more expanded in the given environment. For an equimolar chain it is definitely smaller than the value 2.2 of the hypothetical "segregation" model. We may reasonably assume that it varies from unity to some 1.5, as the computer simulation indicates. For a nonequimolar chain, this upper limit should be somewhat smaller.

Analysis of Light-Scattering Data

The light-scattering apparent radius $\langle S^2\rangle_{\mathrm{app}}$ of a block copolymer without chemical heterogeneity is given by[18]

$$\langle S^2\rangle_{\mathrm{app}} = \mu_A\langle S^2\rangle_A + \mu_B\langle S^2\rangle_B + \mu_A\mu_B\langle G^2\rangle \qquad (10)$$

where $\mu_A = 1 - \mu_B = x\nu_A/(x\nu_A + y\nu_B)$ with ν_A and ν_B being the refractive index increments of the A and B homopolymers, respectively. This equation suggests the possibility of determining the chain dimensions by using at least three solvents having different ν values, but in all of which the chain should have exactly the same conformation.[18] This situation is quite unlikely. Another possibility might be to make measurements in a solvent using three different methods such as the light, the x-ray, and the neutron scattering. This does not sound practical either.

Hence, attempts have been made to make light-scattering measurements in a solvent having, say, $\nu_B = 0$. Then, one can obtain $\langle S^2\rangle_A = \langle S^2\rangle_{\mathrm{app}}$ without ambiguity. Through comparison with independently determined value of $\langle S^2\rangle_{H\text{-}A}$, one can know the influence of the heterocontact interactions on the A block due to invisible B block. Earlier Leng and Benoit[6] carried out such measurements on polystyrene (PS) and poly(methyl methacrylate) (PMMA) block copolymers of PMMA–PS–PMMA type, and recently Prud'homme and Bywater[7] on PS–polyisoprene (PI) diblock copolymers, Utiyama et al.[8,9] on a PS–PMMA diblock sample, and also we[3d,f,5,10] did on PS–PMMA and PMMA–PS–PMMA samples, all using solvents in which the PS blocks are predominantly visible. So far as the diblock copolymers are concerned, $\langle S^2\rangle_{\mathrm{app}}$ were often found considerably larger than $\langle S^2\rangle_{H\text{-}PS}$. Utiyama et al. and Prud'homme and Bywater have expressed somewhat different conclusions, based on their respective observations. However, the conclusions drawn from such measurements might be misleading, unless ν_B is exactly zero, or an adequate correction for the not exactly zero ν_B value is made.

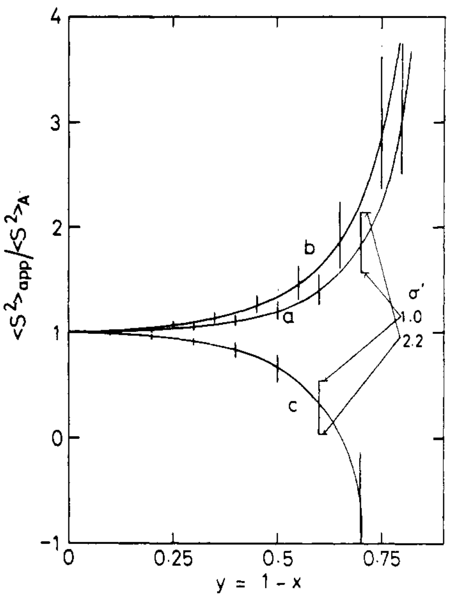

Figure 6. Plots of ratio $\langle S^2\rangle_{\mathrm{app}}/\langle S^2\rangle_A$ vs. B content y $(=1 - x)$ calculated from eq 11 with $\langle S^2\rangle_B/\langle S^2\rangle_A = y/x$; $\nu_B/\nu_A = 0.004/0.113$ (a), 0.007/0.114 (b), and −0.004/0.083 (c): solid curves are for $\sigma' = 1.5$ and the lower and the upper ends of the vertical half-lines correspond respectively to $\sigma' = 1.0$ (random-flight model) and 2.2 (hypothetical "segregation" model) for curves a and b, and to $\sigma' = 2.2$ and 1.0 for curve c (see text).

An approximate estimation of such effects may be made as follows: eq 10 can be rewritten as

$$\langle S^2\rangle_{\mathrm{app}}/\langle S^2\rangle_A = \mu_A(1 + 2\sigma'\mu_B) + \mu_B(1 + 2\sigma'\mu_A)(\langle S^2\rangle_B/\langle S^2\rangle_A) \qquad (11)$$

$$\sigma' = \langle G^2\rangle/(2\langle S^2\rangle_A + 2\langle S^2\rangle_B) \qquad (12)$$

The right-hand side of eq 11 includes two unknowns σ' and $\langle S^2\rangle_B/\langle S^2\rangle_A$, for which adequate approximations are necessary. Approximately the ratio $\langle S^2\rangle_B/\langle S^2\rangle_A$ may be replaced by the ratio $\langle S^2\rangle_{H\text{-}B}/\langle S^2\rangle_{H\text{-}A}$ of the corresponding homopolymers, since the two blocks should perturb each other more or less similarly. Thus, this ratio may be determined from independent measurements. The other parameter σ' cannot be determined independently. Here we tentatively assume that $1 \leq \sigma' \leq 2.2$ to see what results will come out.

The following model calculations will be informative: Here we consider hypothetical solution systems in which both of the blocks are equally expanded, i.e., $\langle S^2\rangle_B/\langle S^2\rangle_A = y/x$, with the σ' value varying from 1.0 (a Gaussian coil model) to as much as 2.2 (a hypothetical "segregation" model). In Figure 6 the values of $\langle S^2\rangle_{\mathrm{app}}/\langle S^2\rangle_A$ for such systems are plotted against the B content y for three different choices of ν_B/ν_A, i.e., 0.004/0.113 (PS–PMMA in the toluene (TOL) case),[10] 0.007/0.114 (PS–PMMA in the TOL/furfuryl alcohol (FAL) = 40/60 by weight case),[9] and −0.004/0.083 (PS–PI in the chlorobenzene (CLB) case).[7] We see a surprisingly large contribution from nearly invisible B blocks, especially when ν_B/ν_A, y, and σ' are large.

Light-Scattering Data and Estimation of $\langle S^2\rangle_A$. Samples of PS–PMMA diblock copolymers examined here and their light-scattering data including the values of $\langle S^2\rangle_{\mathrm{app}}$ and $\langle S^2\rangle_{H\text{-}PS}$ in TOL at 30 °C were reported elsewhere.[10] Here we compiled some additional data obtained for the PS–PMMA diblock sample 54B in TOL with varying temperature from

Table I
Refractive Index Increments ν of Polystyrene, Poly(methyl methacrylate), and Polyisoprene Used in This Work

Solvent	Temp, °C	ν, ml/g PS	ν, ml/g PMMA (PI)
TOL[a]	20	0.109_8	0.001_2
	30	0.113_0	0.004_0
	40	0.116_0	0.006_6
	50	0.118_6	0.008_9
	60	0.121_4	0.011_4
	70	0.124_6	0.014_2
CLB[b]	35	0.083	(−0.004)
TOL/FAL[c]	30		
100/00		0.109_6	0.003_1
80/20		0.111_2	0.004_4
60/40		0.112_8	0.005_8
39/61		0.114_4	0.007_3

[a] In toluene for 4358-Å light; calculated values except for 30 °C (see text). [b] In chlorobenzene for 4358-Å light.[7] [c] In toluene/furfuryl alcohol mixtures (wt ratio) for 5461-Å light; calculated values (see ref 9).

Table II
Characteristics of Polystyrene–Poly(methyl methacrylate) and Polystyrene–Polyisoprene Diblock Copolymer Samples

Code	Type	ST content x	10^{-4} M_w	$10^{-4}M_{PS}$	10^{-4} M_B[f]
53B	PS–PMMA	0.51	44	19.8	21.6
63B30	PS–PMMA	0.24	150	39.6	114
63B50	PS–PMMA	0.49	76.4	39.6	39.0
63B70	PS–PMMA	0.69	64	39.6	19.8
54B	PS–PMMA	0.42	93.0	39.5	53.9
61B	PS–PMMA	0.60	235	159	94
55B	PS–PMMA	0.60	350	217	140
BMM-313[a]	PS–PMMA	0.38	153[c]	58.1[e]	94.9
SI-a-6[b]	PS–PI	0.48	104[d]	49.9[e]	54.1
SI-b-7[b]	PS–PI	0.76	55.3[d]	42.0[e]	13.3

[a] Data reported by Utiyama et al.[8] [b] Data reported by Prud'homme and Bywater.[7] [c] Apparent value obtained in benzene at 30 °C.[8] [d] Apparent value obtained in chlorobenzene at 35 °C.[7] [e] Calculated from $M_{PS} = xM_{app}$. [f] Calculated from $M_B = (1 - x)M_w$ or $(1 - x)M_{app}$; B = PMMA or PI.

21.3 to 69.4 °C. As explained by us[10] before, the measurements in the solvents having $\nu_B \sim 0$ give distorted Zimm plots,[7–10] which make the zero extrapolation from a high concentration region very difficult. Therefore the measurements were carried out in a very low concentration region ($0.05\% < c < 0.3\%$) to obtain reliable values of $\langle S^2\rangle_{app}$. These data together with the independently measured $\langle S^2\rangle_{H\text{-}PS}$ data of the parent PS homopolymers are examined on the basis of eq 11 and 12.

The data reported by other authors[7–9] were examined also in the same light. Below we will briefly describe the methods of analyzing these data. The results will be summarized in Tables I through III.

PS–PMMA in TOL at 30 °C.[10] For our PS–PMMA diblock samples, there are respective precursor PS samples available, which are exactly indentical with the PS blocks. Hence, the values of $\langle S^2\rangle_{H\text{-}PS}$ can be determined without ambiguity. The molecular weight of the PMMA blocks may be approximately given by $M_{PMMA} = yM_w$, since these samples are fairly homogeneous.[10] The values of $\langle S^2\rangle_{H\text{-}PMMA}$ were estimated from the Flory–Fox relation[19a] with[19] $\Phi = 2.2 \times 10^{21}$ and the Mark–Houwink intrinsic viscosity equation: $[\eta] = 7.0 \times 10^{-5}M_w^{0.71}$ (TOL, 30 °C).[20]

The values of ν_{PS} and ν_{PMMA} were 0.113 and 0.004, respectively.[3d] The value of ν_{PMMA} is of vital importance, since the correction in eq 11 is roughly proportional to it. Several literature values at 25 °C for 436-nm light are available. If the temperature difference is taken into account, most of the values are consistent with ours, except a few larger values.

PS–PMMA in TOL at Various Temperatures. Here we require the ν values at respective temperatures. First we estimated the temperature dependence of ν_{PS} by measuring "apparent" molecular weights of a PS sample ($M = 5.6 \times 10^5$) at various temperatures,[21] and adjusting ν_{PS} to give M_w values consistent to that obtained at 30 °C. On the other hand the values of ν_{PMMA} were estimated by using the Gladstone–Dale equation

$$\Delta n_0/\Delta\nu = -\rho \tag{13}$$

where Δn_0 and $\Delta\nu$ are the temperature variation of the solvent refractive index and the ν value, respectively, and ρ is the polymer density (1.05 for PS and 1.19 for PMMA).[25] From the $\Delta\nu_{PS}$ and ρ_{PS} values obtained, we estimated Δn_0 and then $\Delta\nu_{PMMA}$ by eq 13.

The values of $\langle S^2\rangle_{H\text{-}PS}$ and $\langle S^2\rangle_{H\text{-}PMMA}$ were assumed to be independent of temperature. (In fact, they vary slightly with the temperature. Changes of a few percent are expected from $[\eta]$[22] and light-scattering data[21] in the temperature range of 20 to 70 °C. These changes are trivial in view of the other approximations involved.)

PS–PMMA in TOL/FAL Mixed Solvents.[9] Data for a PS–PMMA block copolymer in TOL/FAL mixtures due to Utiyama et al.[9] were analyzed in a similar manner. Here M_{PS} and M_{PMMA} were calculated from $M_{PS} = xM_{app} = M_{app} - M_{PMMA}$, where M_{app} is the apparent molecular weight of the block copolymer measured in benzene at 30 °C[8] ($\nu_{PMMA} \sim 0$), which should be very close to M_{PS}/x. They measured the radii of a PS with the molecular weight very close to M_{PS} given above. These values were used for $\langle S^2\rangle_{H\text{-}PS}$.

The value of $\langle S^2\rangle_{H\text{-}PMMA}$ for a given solvent composition was approximately evaluated as follows. Previously we obtained $[\eta]$ vs. solvent composition with a PMMA ($M_w = 2.0 \times 10^5$) in the same solvents.[4] These data can be used with the Flory–Fox $[\eta]$ equation and the known unperturbed dimension of this polymer[23] ($\langle S^2\rangle_0^{1/2} = 0.22M^{1/2}$ Å) to estimate the excluded volume parameter Z from, for example, the Yamakawa–Tanaka equation:[24]

$$\langle S^2\rangle/\langle S^2\rangle_0 = 0.541 + 0.459(1 + 6.04Z)^{0.46} \tag{14}$$

This equation, in turn, gives $\langle S^2\rangle$ for a given molecular weight, since Z is proportional to $M^{1/2}$. The values of ν_{PS} and ν_{PMMA} were those suggested by the authors.[9]

PS–PI in CLB.[7] Data for PS–PI diblock copolymers in chlorobenzene (CLB) reported by Prud'homme and Bywater[7] were handled as in the previous case. They list a radius value of a PS sample in this solvent.[7] The necessary $\langle S^2\rangle_{H\text{-}PS}$ values were estimated from this value, by making a correction with eq 14 using the known unperturbed dimension of PS.[25] The values of $\langle S^2\rangle_{H\text{-}PI}$ were simply assumed to be equal to $(y/x)\langle S^2\rangle_{H\text{-}PS}$, since no $[\eta]$ data were available.

Correction for the Contribution Due to Slightly Visible Blocks. For the PS–PMMA/TOL system at 30 °C the correction factors for the $\langle S^2\rangle_{app}/\langle S^2\rangle_A$ ratios are relatively small, partly because ν_{PMMA}/ν_{PS} is small (0.035) and partly because the PS and PMMA blocks are similar in dimension in this solvent. On the other hand, the correction factors become surprisingly large for the PS–PMMA:TOL/FAL system. Here the PMMA block becomes more visible as the FAL

Table III
Estimation of Values of $\gamma = \langle S^2\rangle_{PS}/\langle S^2\rangle_{H\text{-}PS}$ for Polystyrene–Poly(methyl methacrylate) and Polystyrene–Polyisoprene Diblock Copolymers in Various Environments

Code	$\langle S^2\rangle_{app}^{1/2}$, Å	$\langle S^2\rangle_{H\text{-}PS}^{1/2,a}$, Å	$\langle S^2\rangle_{H\text{-}B}^{1/2,b}$, Å	γ_{app}	γ_{corr} $\sigma' = 1.0$	γ_{corr} $\sigma' = 1.5$
PS–PMMA in Toluene at 30 °C (Our Work[5,10])						
53B	192	170	142	1.28	1.16	1.11
63B30	292	249	368	1.38	0.81	0.70
63B50	270	249	200	1.18	1.08	1.03
63B70	253	249	136	1.03	1.00	0.98
54B	274	255	240	1.16	1.00	0.93
61B	620	628	330	0.98	0.94	0.91
55B	746	730	413	1.04	1.00	0.97
PS–PMMA 54B in Toluene at Different Temperatures (°C) (This Work)						
21.3	257	255	240	1.02	1.01	1.00
27.6	272	255	240	1.14	1.00	0.96
40.6	299	255	240	1.38	1.07	0.97
58.7	321	255	240	1.59	1.11	0.97
69.4	332	255	240	1.70	1.13	0.97
PS–PMMA BMM-313 in Toluene/Furfuryl Alcohol (Wt Ratio) at 30 °C (Utiyama et al.[9])						
100/0	394	349	343	1.28	1.10	1.02
80/20	439	338	365	1.69	1.32	1.22
60/40	374	298	384	1.58	1.11	0.98
39/61	332	234	399	2.01	1.08	0.96
PS–PI in Chlorobenzene at 35 °C (Prud'homme and Bywater[7])						
SI-a-6	279	292	304	0.91	1.21	1.44
SI-b-7	257	264	148	0.95	0.98	1.00

[a] PS–PMMA in toluene (30 °C) data were measured values, and others were calculated (see text). [b] Calculated values (see text); B = PMMA or PI.

content increases: The value of ν_{PMMA} reaches 0.010 in pure FAL.[9] In addition, the PS block becomes less expanded, while the PMMA block becomes more expanded, because FAL is a nonsolvent for PS but a good solvent for PMMA.[4,9] Hence the ratio of $\langle S^2\rangle_{PMMA}/\langle S^2\rangle_{PS}$ becomes larger with increasing FAL content, resulting in a larger necessary correction. The correction becomes as large as 100% (i.e., 2 for $\sigma' = 1.3$) at an FAL content about 60% where the largest value of $\gamma_{app} = \langle S^2\rangle_{app}/\langle S^2\rangle_{H\text{-}PS} = 2.0$ was in fact observed. The observed deviation of $\langle S^2\rangle_{app}$ from $\langle S^2\rangle_{H\text{-}PS}$ may be attributed almost entirely to the visibility of the PMMA block rather than to the expansion of the A block due to the heterocontact interactions.

The correction factor for PS–PMMA/TOL system also becomes quite large at high temperatures, mainly because the PMMA block becomes more easily visible. Figure 7 shows the variation of γ_{app} with temperature. At the highest temperature examined (about 70 °C) γ_{app} becomes as large as 1.7, while $\gamma_{app} = 1.0$ at about 20 °C. The corrected values of $\gamma = \langle S^2\rangle_{PS}/\langle S^2\rangle_{H\text{-}PS}$ are indicated by the solid half-lines in the figure. The upper and the lower ends of each half-line correspond to the assumption of $\sigma' = 1.0$ and 1.5, respectively.

The PS–PI/CLB system is interesting, since ν_{PI} is negative and hence the correction factors would be less than unity (see Figure 6). As seen in Table III the value of γ_{app} for sample SI-a-6 is smaller than unity, but becomes larger than unity after the correction.

All the results are visualized in Figures 8a and 8b. The data points scatter widely in the range $0.9 < \gamma_{app} < 2$ (Figure 8a), coming closer to $\gamma = 1$ after correction (Figure 8b). The determination of the mean-square radius of a homopolymer usually is accompanied with an error of ±10%. The largely distorted Zimm plot characteristic of the block copolymer systems investigated herein inevitably causes a larger error.[7-10] In addition, ν_B (B = PMMA or PI) is too small to determine with accuracy and can be in considerable error as well. In this respect the scattering of the corrected points in Figure 8b should probably be ascribed more to the experimental accuracy than to specific conformational properties. Taking the average, we have $\gamma = 1.06$ (for $\sigma' = 1.0$) or 1.01 (for $\sigma' = 1.5$).

With the assumption that $1.0 \leq \sigma' \leq 1.5$, the values of γ become very close to unity, not seriously depending on the choice of σ'. If we assume a larger σ' (say, $\sigma' = 2.2$), γ becomes even smaller than unity ($\gamma \sim 0.9$). This is unlikely. Thus we may conclude that the radii of the individual blocks are practically the same as those of the equivalent homopolymers in any case. This conclusion is the same as the one we obtained in the previous section. Here we should emphasize the following: This does not necessarily mean that the conformation of the individual blocks is the same as that of the corresponding homopolymers. The Monte Carlo results already suggested that the segment distribution would be somewhat more assymetrical. An answer to such a problem would come after a more rigorous examination of the particle scattering function.

Discussion

By analogy with homopolymer blends in solution, there would exist incompatible (repulsive) interactions between the dissimilar blocks within a block copolymer molecule. Obviously, due to such interactions the chain would assume a conformation in which the probability of the heterocontacts is smaller than in the absence of such interactions. Upon the recognizance of a real polymer chain which is a sequence of chemically bonded atoms, we can envisage two possible ways to reduce this probability. One would be to expand the individual blocks in a certain manner. The other would be to widen the angle ($R_A \wedge R_B$) on average (see eq 1b). The "random-coil" model places an emphasis on the former aspect, and the "segregation" model places an emphasis on the latter. In reality these phenomena would occur simultaneously (the computer simulation indicated that this is the case (see eq 7)),

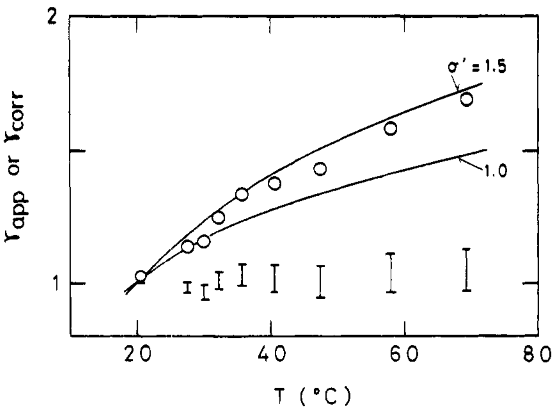

Figure 7. Plots of γ_{app} and γ_{corr} vs. temperature for PS–PMMA 54B in toluene: solid curves are the ratios $\langle S^2\rangle_{app}/\langle S^2\rangle_{PS}$ calculated from eq 11 with σ' as indicated in the figure; circles are measured γ_{app}; vertical half-lines are γ corrected with σ' varying fron 1.0 (upper end) to 1.5 (lower end).

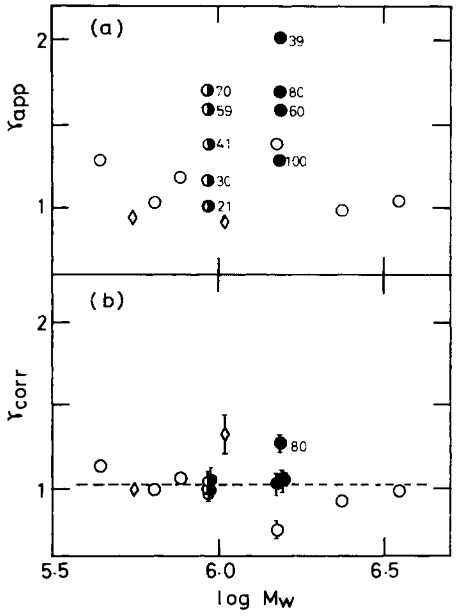

Figure 8. Plots of γ_{app} (a) and γ_{corr} (b) vs. M_w for PS–PMMA and PS–PI diblock copolymers: Open circles are PS–PMMA in toluene at 30 °C[5,10]; half-filled circles are PS–PMMA 54B in toluene at different temperature as indicated; filled circles are PS–PMMA BMM-313 in toluene/furfuryl alcohol mixture with a different toluene weight percent as indicated;[9] and squares are PS–PI in chlorobenzene at 35 °C.[7] The γ_{corr} values (b) were obtained by making corrections with $1.0 \leq \sigma' \leq 1.15$ (see text).

and the overall chain would end up a conformation somewhat more asymmetrical than homopolymer chains.

Nevertheless, the value of $\langle S^2\rangle_K$ is almost the same as that of $\langle S^2\rangle_{H\text{-}K}$. This conclusion commonly obtained by the computer simulation and the light-scattering analysis is of prime significance. The light-scattering apparent radius may now be given approximately by

$$\begin{aligned}\langle S^2\rangle_{app} &= \mu_A\langle S^2\rangle_{H\text{-}A} + \mu_B\langle S^2\rangle_{H\text{-}B} + \mu_A\mu_B\langle G^2\rangle \\ &= \mu_A(1 + 2\sigma\mu_B)\langle S^2\rangle_{H\text{-}A} + \mu_B(1 + 2\sigma\mu_A)\langle S^2\rangle_{H\text{-}B} \quad (15)\end{aligned}$$

Here $\langle S^2\rangle_{H\text{-}A}$ and $\langle S^2\rangle_{H\text{-}B}$ can be determined independently. Hence, the measurements of $\langle S^2\rangle_{app}$ in solvents having large μ's for the two blocks allow us to determine $\langle S^2\rangle$ or σ with a small (theoretical) ambiguity. As the computer simulation indicated, this ambiguity should be less than a few percent ($\leq$2%), which is well within the experimental ambiguities of $\langle S^2\rangle_{app}$ determination. This result would greatly simplify the analysis of light-scattering data of a (homogeneous) block copolymer. In the same light the mean-square radius of the overall chain may be given by eq 15 with its μ_A and μ_B replaced with x and y, respectively.

The parameter σ, by which the chain conformation appears to be best characterized, should definitely be smaller than the value 2.2 of our hypothetical "segregation" model. As the computer simulation indicated, it should range from unity to about 1.5, depending on the magnitudes of the A–B and the K–K interactions in the given environment. The analysis of the light-scattering data described in the last section implied that the σ cannot be so large as 2.2 (e.g., the assumption of σ' ($\simeq\sigma$) = 2.2 led to the unlikely conclusion that $\langle S^2\rangle_K < \langle S^2\rangle_{H\text{-}K}$). Its precise determination by the above-mentioned light-scattering method is left as a future problem.

Based on the above conclusions and by analogy with the Flory–Krigbaum model[26] on homopolymers, we propose a simple model for a diblock copolymer which consists of two Gaussian density bodies A and B (with the same dimensions as those of the corresponding homopolymers) separated by a mutual distance corresponding to σ. Our preliminary calculations based on this model indicate some interesting features of diblock copolymer solutions: The second virial coefficient A_2 becomes much smaller than that of the corresponding random copolymer when the A–B interactions are strong as compared with the K–K interactions. This mainly results from the fact that the centers of the A and B blocks are considerably separated from each other ($\sigma \geq 1$). When two such molecules come close, they rotate with each other to minimize the free energy of mixing, resulting in a small value of A_2. This is not the case with random copolymers. In fact the calculations indicate that rather sharp rotation occurs in the certain range of mutual distance. Our previous observations on the light-scattering behavior of PS–PMMA/TOL solutions suggested the formation of a certain ordered structure in the concentration region as low as 1%.[10] Even at this low concentration range the chains are expected to be overlapping with one another to a considerable extent. Then the structure formation might be closely related to the chain orientation implied above. These points will be discussed elsewhere in detail.[27]

In this article we have confined ourselves to diblock copolymers. Leng and Benoit[6] reported light-scattering data for PMMA–PS–PMMA triblock copolymers in benzene solutions, showing $\langle S^2\rangle_{app}$ considerably larger than $\langle S^2\rangle_{H\text{-}PS}$. In this solvent ν_{PMMA} is almost perfectly zero. Hence, γ_{app} should be very close to the true γ. On the other hand, the results for the PS–PMMA/benzene system[8] show that γ_{app} is very close to unity, which is consistent with the conclusion given in this article. These results imply that the behavior of triblock copolymers differ somewhat from those of diblock copolymers. Our preliminary light-scattering measurements on PMMA–PS–PMMA triblock copolymers and the Monte Carlo calculations support the above implication.[21]

Acknowledgment. We wish to thank Professors G. C. Berry and M. Kurata for kindly reading the manuscript and giving detailed comments. We are also indebted to the Staff of the Computer Laboratory of our Institute for improving our Fortran IV program.

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Sedimentation Equilibrium of Polymers in Good Solvents

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Received November 25, 1975

ABSTRACT: A method of interpretation of sedimentation equilibrium data is developed, which is designed for the analysis of nonideal solutions. Only one equilibrium experiment is needed for each sample. The effect of heterogeneity is studied theoretically. The method is verified by measurement of polystyrene fractions in benzene and ethyl acetate; the equilibrium photographs being evaluated automatically. The method yields useful molecular weights and virial coefficients for the narrow fractions which were studied. For broader distributions caution is indicated.

In biochemistry, sedimentation equilibrium is the most frequently used method for the measurement of molecular weight. It requires only a minimum amount of sample and yields the molecular weight with good accuracy. The success of the method may be ascribed to the fact that a typical solution of biochemical interest is usually rather ideal; moreover, the systems under study are usually monodisperse, at worst, oligodisperse. However, several procedures were developed[1,2] for treatment of slightly nonideal oligodisperse system. These procedures consisted of point by point analysis of an equilibrium pattern in a single equilibrium run: the nonideality was approximately eliminated by using so-called "ideal" molecular weight moments and the data were analyzed with respect to their oligodispersity. Green and McKay[3] used (without any derivation) a method based also on point by point analysis which evaluates and eliminates the nonideality for highly nonideal homogeneous systems. Actually, their method is based on ideas, which are developed more broadly in the theoretical part of this paper.

The character of typical polymer solutions is rather different from that of biochemical solutions. All synthetic polymers are polydisperse; the polydispersity even of so-called narrow fractions or living polymers is rather broad in the terms of a biochemist. On top of that, many polymer solutions of interest exhibit strong nonideality. The main theoretical and experimental effort was devoted to pseudo-ideal theta solutions, for which the nonideality effect is eliminated. Several methods were devised for measuring various averages of molecular weight or even the complete molecular weight distribution function. Some of them[4-6] use a single equilibrium run, the others combine data from several runs.[6-8] Some authors, e.g., Adams et al.,[9] offer methods on how to correct the experimental data for the nonideality and then proceed with the analysis of the distribution function. Their method is based on auxiliary measurements (as light scattering, osmotic pressure).

For the analysis of nonideal polydisperse solutions the methods offered[8,10-12] require a substantial number of equilibrium runs at different original concentrations and rotor velocities. Characteristically, only one experimental point is derived from each equilibrium run.

In this paper, a method of interpretation of the experimental data is developed, which is based on point by point analysis of a single equilibrium pattern. The method is useful for strongly nonideal solutions and is an extension of the method of Munk and Cox,[13] which is applicable for moderately nonideal systems. The characteristic feature of the present method is that it eliminates the effects of nonideality *not* by extrapolating the experimental data to zero concentration but by drawing a tangent to an appropriate form of the experimental curve. The tangent yields a well-defined average of the molecular weight at the point where the tangent was drawn. Thus, in principle the point-by-point molecular weight average may be calculated and an insight into the polydispersity could be obtained. However, for narrow fractions, the experimental error does not allow for such detailed treatment. A single value is derived for the mid-cell and is believed to be a characteristic value for the whole original sample.

The method was used for measurement of five polystyrene samples with narrow distributions of molecular weight in