Molecular Dimensions of Block Copolymers in Solution

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First-order perturbation calculation was carried out concerning the mean-square radius of BAB triblock copolymers. General features of molecular dimensions of AB di- and BAB triblock copolymers in various solvents were discussed in relation to their parent homopolymers. Expressions describing the dimensions of A-subchain of each block copolymers were also given for the sake of their practical application to the light-scattering studies.

INTRODUCTION

The most characteristic feature of a block copolymer in solution results from interactions (of long range nature) between chemically different sequences composing the block copolymer chain. The fact that two different homopolymers are rather incompatible even in good solvents[1] allows us to expect that such interactions will be of repulsive nature, and this will lead to an expansion of the chain. The interactions as a whole should depend not only on the composition but also on the chain architecture, *i.e.*, the sequential arrangement of monomers along the chain.[2,3] It is the main purpose of this work to investigate the influences of the chain architecture upon the chain dimension for AB diblock and BAB triblock copolymers.

As to AB diblock copolymers, Froelich and Benoit[4] have carried out first-order perturbation calculation of the mean-square radius $\langle S^2 \rangle$ and evaluated the coefficients C's of a following rigourous expression for the expansion factor α in the proximity of the Θ state:

$$\alpha^2 = \langle S^2 \rangle / \langle S^2 \rangle_0 = 1 + C_1 Z_{AA} + C_2 Z_{BB} + C_3 Z_{AB} + \cdots \tag{1}$$

where $\langle S^2 \rangle_0$ is the mean-square radius in the absence of excluded volume effects. In the equation Z_{KL} (K and L denote either A or B) is defined by

$$Z_{KL} = (3/2\pi b^2)^{3/2} N^{1/2} X_{KL} \tag{2}$$

$$X_{KL} = \int [1 - \exp(-V_{KL}(r)/kT)] dr \tag{3}$$

where b^2 is the mean-square length of the segments, N the total number of the segments and V_{KL} the average potential of interaction between the segments K and L placed r apart. Our concern in this study is to give the coefficients C's for BAB triblock copolymer and make a brief discussion on the chain dimensions of block coplymers in various types of solvents.

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Although light-scattering measurements give us the direct knowledge of $\langle S^2 \rangle$ value for a homopolymer, they may fail to inform us of the true $\langle S^2 \rangle$ value for a block copolymer so far as the scattering power of each type of segments is different from one another.[5] On the other hand, it is less difficult to find such solvents that make either of the constituents invisible. Through measurements carried out in such solvents in which the sequences of type B, for example, are invisible, we can determine the value of $\langle S^2 \rangle_A$, the dimension of A-subchain affected by B-subchain(s). This should be of much help to the investigation of structural features of block copolymers.[6] Thus, for the sake of the practical application to the light-scattering study we will also give the expressions for $\langle S^2 \rangle_A$ for the two types of block copolymers mentioned above.

II. CALCULATIONS OF MEAN-SQUARE RADII

1. Basic Equations

Consider a linear chain, of any chain architecture, consisting of two types of segments A and B, each of which is governed by a Gaussian distribution. According to the perturbation theory generalized by Fixman,[7] the mean-square of the distance vector $\mathbf{r}_{ij}$ between two segments serially numbered i and j can be written as

$$\langle r_{ij}^2 \rangle = \langle r_{ij}^2 \rangle_0 - \sum_{k>l} \sum X_{KL} r_{ij}^2 [P(\mathbf{r}_{ij}, \mathbf{O}_{kl}) - P(\mathbf{r}_{ij})P(\mathbf{O}_{kl})]d\mathbf{r}_{ij} + \cdots \tag{4}$$

Here the subscript 'o' has the usual significance. $P(\mathbf{r}_{ij})$ is the probability density of the vector $\mathbf{r}_{ij}$ and $P(\mathbf{r}_{ij}, \mathbf{r}_{kl})$ is the bivariate probability density of the vectors $\mathbf{r}_{ij}$ and $\mathbf{r}_{kl}$, both calculated using random flight statistics ($\mathbf{O}_{kl}$ means $\mathbf{r}_{kl}=\mathbf{0}$). The excluded volume parameter X_{KL} defined by eq. (3) takes three values X_{AA}, X_{BB} and X_{AB}, corresponding to the types of the segment pairs k and l, namely, if both k and l are of type A, $X_{KL}=X_{AA}$, and so forth.

Application of the Wang-Uhlenbeck-Fixman theorem[7] to the function $P(\mathbf{r}_{ij}, \mathbf{r}_{kl})$ leads eq. (4) to

$$\langle r_{ij}^2 \rangle = \langle r_{ij}^2 \rangle_0 + (3/2\pi b^2)^{3/2} b^2 \sum_{k>l} \sum f_{kl}^2 (k-l)^{-5/2} X_{KL} + \cdots \tag{5}$$

Here it must be mentioned that we have assumed the mean-square length of all the segments to be equal to b^2, for the sake of simplicity (this will be discussed later). By this assumption the quantity $\langle r_{ij}^2 \rangle_0$ can be written simply as

$$\langle r_{ij}^2 \rangle_0 = |i-j|b^2 \tag{6}$$

The factor f_{kl} denotes the number of the segments common to the two sequences, one flanked by the segments i and j on either side, and the other by the segments k and l. The parameter X_{KL} takes again three values, corresponding to the locations of the segments k and l.

Summation of eq. (5) over all the segment pairs i and j involved in a specified sequence R which consists of a total of N_R segments generates the desired expression for R's mean-square radius $\langle S^2 \rangle_R$, in accordance with the general definition:

$$\langle S^2 \rangle_R = (1/N_R^2) \sum_{i>j}^{(R)} \sum \langle r_{ij}^2 \rangle \tag{7}$$

where the symbol (R) means both i and j belong to R. Obviously the overall dimension of the chain is given as

$$\langle S^2 \rangle = (1/N^2) \sum_{i>j} \sum \langle r_{ij}^2 \rangle \tag{8}$$

2. Mean-square Raius of BAB Triblock Copolymer

Consider a block copolymer chain with three subchains, one A-subchain consisting of N_1 segments of type A, and two B-subchains which flank the A-subchain on its either side, consisting of N_2 and N_3 segments of type B, respectively (see the following scheme). Calculation of the mean-square radius of this model chain by the use of eqs. (5) and
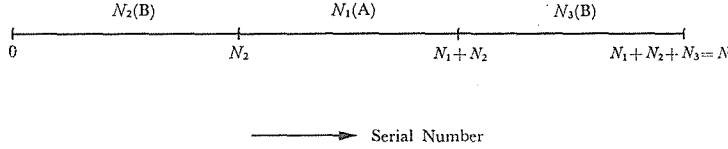
(8) needs to distinguish twenty-four cases (without symmetrical ones) corresponding to the various locations of the four segments i, j, k and l. They are somewhat confusing and troublesome, but straightforward.

Dividing the resultant expression for $\langle S^2 \rangle$ by $\langle S^2 \rangle_0$ derived by the use of eq. (6), we may calculate the coefficients C's in eq. (1) for BAB triblock copolymer as function of the segment compositions x_1, x_2 and x_3 as follows.

$$105C_1 = 134x_1^{7/2} + 392(x_2+x_3)x_1^{5/2} + 840x_2x_3x_1^{3/2} \tag{9a}$$

$$105C_2 = 134[1 + x_1^{7/2} + x_2^{7/2} + x_3^{7/2} - (x_1+x_2)^{7/2}]$$
$$+ 392[(x_2+x_3)x_1^{5/2} + (x_1+x_3)x_2^{5/2} + (x_1+x_2)x_3^{5/2} - x_2(x_1+x_3)^{5/2}$$
$$- x_3(x_1+x_2)^{5/2}] + 840x_2x_3x_1^{5/2} \tag{9b}$$

$$105C_3 = 134[(x_1+x_2)^{7/2} + (x_1+x_3)^{7/2} - (2x_1^{7/2} + x_2^{7/2} + x_3^{7/2})]$$
$$+ 392[x_2(x_1+x_3)^{5/2} + x_3(x_1+x_2)^{5/2} - 2(x_2+x_3)x_1^{5/2} - (x_1+x_3)x_2^{5/2}$$
$$- (x_1+x_2)x_3^{5/2}] + 1680x_2x_3x_1^{3/2} \tag{9c}$$

with

$$x_m = N_m/N, \ (m=1, \ 2 \ \text{and} \ 3) \ \text{and} N = N_1 + N_2 + N_3$$

We notice that the above equations for $x_3 = 0$ reduce to those earlier given by Froelich and Benoit[4] for AB diblock copolymer, which read

$$105C_1 = 134x_1^{7/2} + 392x_2x_1^{5/2} \tag{10a}$$

$$105C_2 = 134x_2^{7/2} + 392x_1x_2^{5/2} \tag{10b}$$

$$105C_3 = 134(1 - x_1^{7/2} - x_2^{7/2}) - 392x_1x_2(x_1^{3/2} + x_2^{3/2}) \tag{10c}$$

with

$$x_1 + x_2 = 1$$

3. Mean-square Radii of A-subchains

To begin with, we introduce a new quantity $(\alpha)_A^2$, which represents the ratio of the mean-square radius of A-subchain to that in the unperturbed state, $i. \ e.,$

$$(\alpha)_A^2 = \langle S^2 \rangle_A / \langle S^2 \rangle_{A,0} \tag{11}$$

For the sake of easy recognition, this factor should be written in the form,

$$(\alpha)_A^2 = 1 + C_1^* Z_{AA}^* + C_2^* Z_{BB}^* + C_3^* Z_{AB}^* + \cdots \tag{12}$$

where Z_{KL}^* (K and L=A or B) is defined by

$$Z_{KL}^* = (3/2\pi b^2)^{3/2} N_1^{1/2} X_{KL} = x_1^{1/2} Z_{KL} \tag{13}$$

with N_1 still being the number of the segments involved in A-subchain and $x_1 = N_1/N$.

As eqs. (7) and (8) indicate, no new calculations other than those already carried out are necessary in order to find the coefficients C^*'s for BAB triblock copolymer. All that must be done is to pick up the cases where both i and j belong to A-subchain, and sum them up.

Thus, for BAB triblock copolymer we have

$$105C_1^* = 134 \tag{14a}$$

$$105C_2^* = 70[1 + (1+y_1+y_2)^{-1/2} - (1+y_1)^{-1/2} - (1+y_2)^{-1/2}] \tag{14b}$$

$$\begin{aligned} 105C_3^* = &52 + 768(y_1^{7/2} + y_2^{7/2}) + 896(y_1^{5/2} + y_2^{5/2}) \\ &- 96[(1+y_1)^{7/2} + (1+y_2)^{7/2}] + 448[y_1(1+y_1)^{5/2} + y_2(1+y_2)^{5/2}] \\ &- 1120[y_1^2(1+y_1)^{3/2} + y_2^2(1+y_2)^{3/2} \\ &+ 70[(1+y_1)^{-1/2} + (1+y_2)^{-1/2}] \end{aligned} \tag{14c}$$

where

$$y_1 = x_2/x_1, \text{ and } y_2 = x_3/x_1$$

Again, eq. (14) for $x_3=0$, generates the corresponding expression for AB diblock copolymer, i. e.,

$$105C_1^* = 134 \tag{15a}$$

$$105C_2^* = 0 \tag{15b}$$

$$\begin{aligned} 105C_3^* = &26 + 768y^{7/2} + 896y^{5/2} - 96(1+y)^{7/2} + 448y(1+y)^{5/2} \\ &- 1120y^2(1+y)^{3/2} + 70(1+y)^{-1/2} \end{aligned} \tag{15c}$$

where

$$y = x_2/x_1$$

III. DISCUSSION

1. Overall Dimensions

First we examine the overall dimensions of AB di- and BAB triblock copolymers. For the sake of easy association with their parent homopolymers we rewrite eq. (1) in a following form:

$$\alpha^2 = 1 + [C_1 + (C_3/2)]Z_{AA} + [C_2 + (C_3/2)]Z_{BB} + C_3 \Delta Z_{AB} + \cdots \tag{16}$$

where

$$\Delta Z_{AB} = Z_{AB} - (Z_{AA} + Z_{BB})/2 = (3/2\pi b^2)^{3/2} N^{1/2} \Delta X_{AB} \tag{17}$$

$$\Delta X_{AB} = X_{AB} - (X_{AA} + X_{BB})/2$$

The well-known relation for homopolymers with small excluded volume effects,[7]

$$\alpha^2 = 1 + (134/105)Z + \cdots \tag{18}$$

is now applied to Z_{AA} and Z_{BB} in eq. (16), and we have

$$\alpha^2 = F_1\alpha_A^2 + F_2\alpha_B^2 + F_3\Delta Z_{AB} + \cdots \tag{19}$$

where α_K (K=A or B) denotes the expansion factor of the parent homopolymer consisting of N segments of type K and the coefficients F's are related to C's as

$$F_1 = (105/134)[C_1 + (C_3/2)]$$
$$F_2 = (105/134)[C_2 + (C_3/2)] \tag{20}$$
$$F_3 = C_3$$

Here we notice the obvious relation,

$$F_1 + F_2 = 1 \tag{21}$$

The quantitative usage of eq. (19) is, needless to say, limited to the cases where each of the parameter Z's is very small.

In order to get some quantitative information of the cases where Z's are large, we introduce the following two assumptions. One of them is that the expansion factor α be a function of a single variable $\langle Z \rangle$ which is written as

$$\langle Z \rangle = (105/134)(C_1 Z_{AA} + C_2 Z_{BB} + C_3 Z_{AB}) \tag{22}$$

and the other is that any change in α be identified with a uniform change in the mean-square length of every segment. These assumptions are as fully justified as in the case of homopolymers, if $Z_{AA} = Z_{BB} = Z_{AB}$. Otherwise, the first assumption would not be the case, and its validity should be tested by higher order perturbation calculation.

Under the above assumptions we may follow, for example, Fixman's procedure,[8] according to which the relation

$$\alpha^3 - 1 = (67/35)Z \tag{23}$$

was derived, and we have

$$\alpha^3 - 1 = (67/35)\langle Z \rangle \tag{24}$$

Through the last five equations the expansion factor of block copolymer is, again, related to those of the parent homopolymers, each consisting of N segments.

$$\alpha^3 = F_1\alpha_A^3 + F_2\alpha_B^3 + (3/2)F_3\Delta Z_{AB} \tag{25}$$

On the other hand, if we assume an approximated relation[9] between the hydrodynamic expansion factor α_η and Z

$$\alpha_\eta^3 - 1 = 1.55Z \tag{26}$$

for block copolymers, we have

$$\alpha_\eta^3 - 1 = 1.55\langle Z \rangle \tag{27}$$

Combining eqs. (22), (26) and (27), we find the following convenient relation:

$$[\eta] = F_1[\eta]_A + F_2[\eta]_B + 1.22[\eta]_0\Delta Z_{AB} \tag{28}$$

where $[\eta]$ and $[\eta]_0$ are the intrinsic viscosities of block copolymer at the perturbed and unperturbed state, respectively, and $[\eta]_A$ and $[\eta]_B$ are those of the parent homopolymers, each consisting of N segments of type A and B, respectively.

The numerical values of the coefficients F_1 ($=1-F_2$) and F_3 are plotted against the segment composition of type A for AB diblock and symmetrical BAB triblock copolymers in Fig. 1. In this figure it is particularly noticed that both F_1 and F_3 values for a triblock chain are considerably larger than those for a diblock chain in the region where $x_1 < 0.5$. The quanlitative features of these values can be roughly summarized as

$$F_1(\text{Triblock}) > x_1 > F_1(\text{Diblock}) \quad \text{if} \quad x_1 < 0.5$$
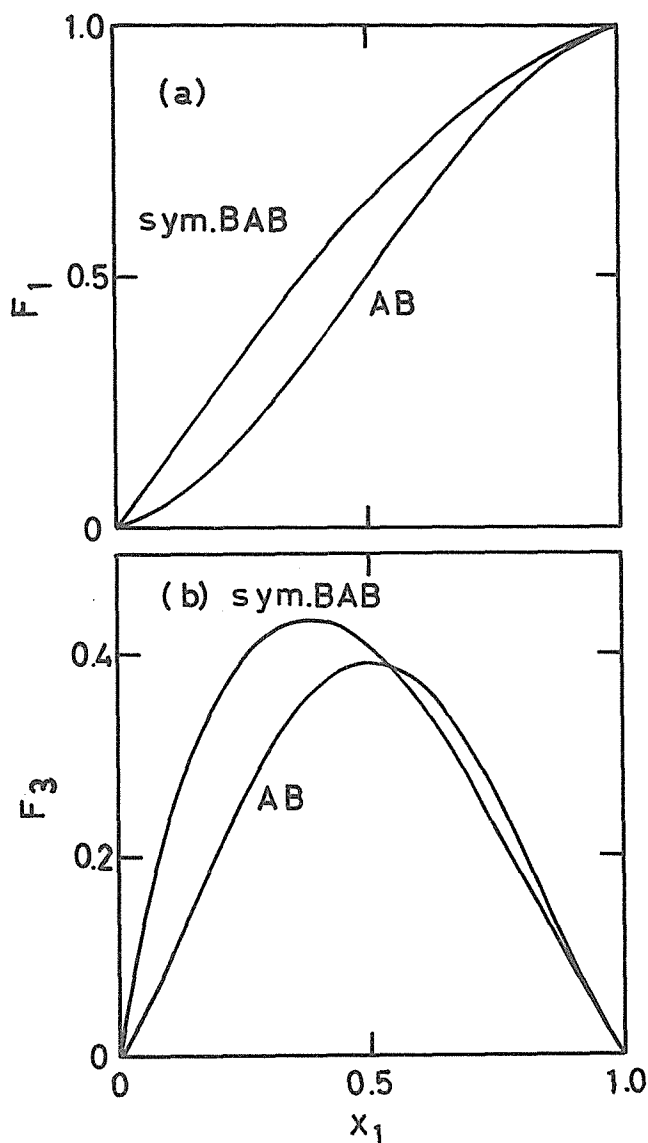$$F_1(\text{Triblock}) \simeq F_1(\text{Diblock}) > x_1 \quad \text{if} \quad x_1 > 0.5$$

and

Fig. 1. Plots of the coefficients, (a) F_1 ($=1-F_2$) and (b) F_3 against the A-segment composition x_1 for AB diblock and symmetrical BAB triblock copolymers as indicated (for the detail, see eqs. (19), (25) and (28)).

$$F_3(\text{Triblock}) > F_3(\text{Diblock}) \quad \text{if } x_1 < 0.5$$
$$F_3(\text{Triblock}) \simeq F_3(\text{Diblock}) \quad \text{if } x_1 > 0.5$$

By applying these general features of the coefficients to the equations given in this section, the following qualitative pictures might be drawn in comparison of the molecular dimensions of the two types of block copolymers: (1) A triblock chain will be more expanded if, $X_{AA} \geq X_{BB}$, and $x_1 < 0.5$, (2) A diblock chain will be more expanded if, $X_{AA} < X_{BB}$, $x_1 < 0.5$, and $\varDelta X \simeq 0$, and (3) there will be no significant differences between their molecular dimensions if $x_1 > 0.5$. Here it was assumed that $\varDelta X \geq 0$. This quantity is expected to reflect the incompatibility of the parent homopolymers in a given solvent, and there are some evidences to suppose it generally to be non-negative, its magnitude depending strongly on the solvent nature.[1,10] As is seen in Fig. 1b., the differences between the contribution of $\varDelta X$ terms to the overall dimensions of the two types of block copolymers would be trivial when $x_1 > 0.5$, while it would be considerably large when $x_1 < 0.5$.

2. Dimensions of A-subchains

As before, we first relate the expansion factor of A-subchain $(\alpha)_A$ to $\alpha_A{}^*$ and $\alpha_B{}^*$, which denote the expansion factors of homopolymers A and B, respectively, each consisting of N_1 segments. For the cases where the effects of volume exclusion are small (or, each of Z^*'s is small), eq. (12) can be written as

$$(\alpha)_A = \alpha_A{}^{*2} + G_1(\alpha_A{}^{*2} - 1) + G_2(\alpha_B{}^{*2} - 1) + (268/105)G_1 \varDelta Z_{AB}{}^* + \cdots \qquad (29)$$

where

$$\varDelta Z_{AB}{}^* = Z_{AB}{}^* - (Z_{AA}{}^* + Z_{BB}{}^*)/2 = (3/2\pi b^2)^{3/2} N_1{}^{1/2} \varDelta X_{AB} \qquad (30)$$

and

$$G_1 = (105/268)C_3{}^* \qquad (31)$$

$$G_2 = (105/134)[C_2{}^* + (C_3{}^*/2)] \qquad (31)$$

If we again accept the two assumtions similar to those given in the last section, we can show the following relation for the cases where Z^*'s are large:

$$(\alpha)_A{}^3 = \alpha_A{}^{*3} + G_1(\alpha_A{}^{*3} - 1) + G_2(\alpha_B{}^{*3} - 1) + (134/35)G_1 \varDelta Z_{AB}{}^* \qquad (32)$$

The numerical values of G_1 and G_2 for AB diblock and symmetrical BAB triblock copolymers are illustrated in Fig. 2. In these figures it should be noticed that both G_1 and G_2 have finite values at $x_1 = 0$, this suggesting that $(\alpha)_A$ value for an A-subchain flanked by extremely long B-subchain(s) will approach a finite value which is not so large.

All these results imply that if $\varDelta X$ is assumed to be non-negative, an A-subchain within a block copolymer chain would be, as a matter of course, more expanded than the corresponding homopolymer and such a deviation would be much larger in the case of triblock copolymers. For example, taking the cases where $\alpha_A{}^{*3} = \alpha_B{}^{*3} = 2$, $x_1 = 0.5$ and $\varDelta Z_{AB}{}^* = 0$, the ratio $(\alpha)_A{}^3/\alpha_A{}^{*3}$ for BAB triblock copolymer can be estimated by eq. (32) to be 1.14, while that for AB diblock copolymer is found to be 1.07.

Discussions given so far about the dimensions of block copolymers in good solvents are based on the two assumptions described in Sec. III-1. As pointed out there, they are as fully justified as in the case of homopolymers only when $X_{AA} = X_{BB} = X_{AB}$. There-
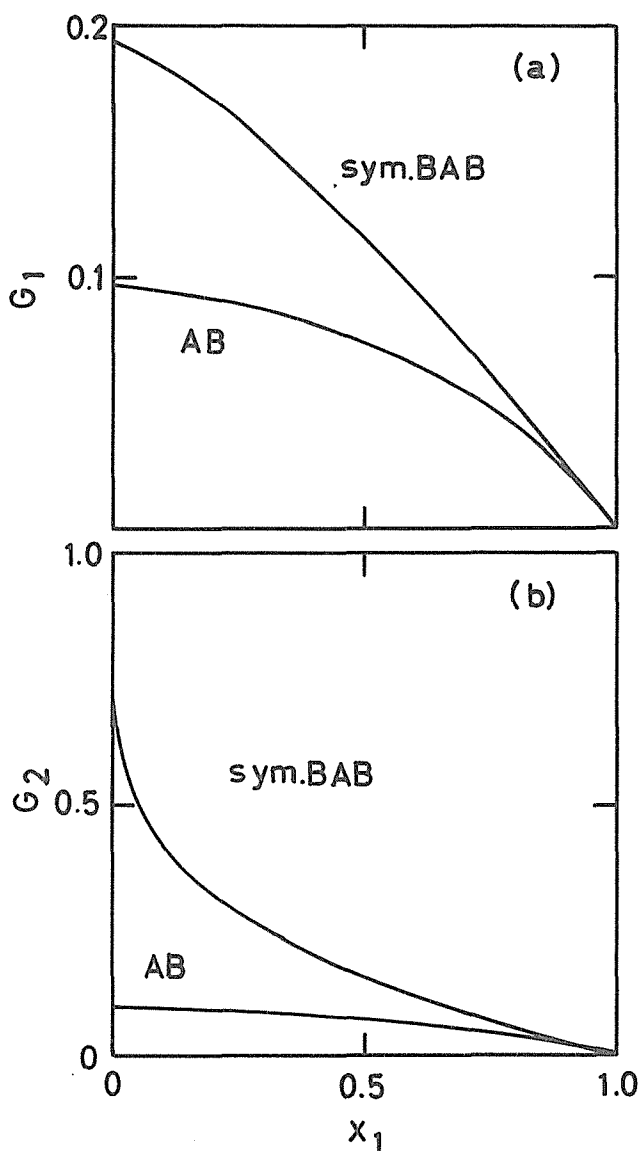
Fig. 2. Plots of the coefficients, (a) G_1 and (b) G_2 against the A-segment composition x_1 for AB diblock and symmetrical BAB triblock copolymers as indicated (for the detail, see eqs. (29) and (32)).

fore, the quantitative usage of eqs. (24), (25), (27), (28) and (32) should be confined to the cases, in which these quantities do not differ much from one another, and therefore, the parameter ΔX is relatively small. Otherwise, the expansion factor α may not be expressed by a single parameter $\langle Z \rangle$ defined by eq. (22), and it would become very difficult to describe quantitatively the dimensions of block copolymers on the basis of any procedure established for homopolymers. Moreover, when ΔX becomes very large, two different subchains within a molecule might exhibit a so-called phenomenon of intrachain phase separation to occupy some distinctly different domains in space.[11,12]

Obviously the above equations are not valid for a block copolymer molecule assuming such a conformation.

On the derivation of eq. (5), we have assumed the identical mean-square length for every segment. However some correction is necessary to apply it to the general cases in which the mean-square lengths of each type of segment are not identical, *i.e.*, $b_A{}^2 \neq b_B{}^2$. For such cases it might be reasonable to introduce a mean-square length of segment as defined, for example, by

$$b^2 = (b_A{}^2 + b_B{}^2)/2 \tag{33}$$

Then, further assumption is made that the following relations hold:

$$Nb^2 = (N_A + N_B)b^2 = N_A' b_A{}^2 + N_B' b_B{}^2 \tag{34}$$

and

$$N_A b^2 = N_A' b_A{}^2, \quad N_B b^2 = N_B' b_B{}^2 \tag{35}$$

where N_K and N_K' (K = A or B) are the total number of identical segments and co-monomers, respectively, both involved in K-subchain(s). By the above relations it is meant that the block copolymer chain is composed of N segments with identical mean-square length defined by eq. (33). It follows that the mole fraction of K-identical segments X_K is correlated to the mole fraction of K-comonomers x_K' by writing

$$x_K = N_K/N = x_K' b_K{}^2/(x_A' b_A{}^2 + x_B' b_B{}^2), \quad (K = A \text{ or } B) \tag{36}$$

The quantities $b_A{}^2$ and $b_B{}^2$ may be determined by investigating appropriately the parent homopolymers. Further it is noted that the newly introduced quantities x_K are reasonably identified with those defined earlier, *i.e.*, x_1, x_2 and so on.

In connection to the above treatment, it is much more realistic to convert the mean–square radius $\langle S^2 \rangle$ defined by Eq. (8) as that around the geometrical center to that around the center of mass. This is, especially, necessary if one concerns the problem of intrinsic viscosity. Such a mean-square radius may be generally be described by

$$\langle S^2 \rangle = (1/M^2) \sum_{i > j} \sum m_i m_j \langle r_{ij}{}^2 \rangle \tag{37}$$

where M is the molecular weight of block copolymer and m_i ($= m_A$ or m_B) is the mass of the segment i. Eq. (37) can be rewritten as

$$\langle S^2 \rangle = w_A{}^2 \langle S^2 \rangle_A + w_B{}^2 \langle S^2 \rangle_B + 2 w_A w_A \langle S^2 \rangle_{AB} \tag{38}$$

where w_K (K = A or B) is the weight fraction of K-segments, and $\langle S^2 \rangle_{AB}$ is obtainable from

$$\langle S^2 \rangle_{AB} = (1/N_A N_B) \sum_i^{(A)} \sum_j^{(B)} \langle r_{ij}{}^2 \rangle \tag{39}$$

However, there will be no significant difference between the mean-square radii defined by eq. (8) and eq. (36), so far as m_A and m_B are not largely different from one another.

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