Macromolecules 1981, *14*, 1104-1110

Intermolecular Interactions of Block Copolymers in Dilute Solutions

Tsunehisa Kimura and Michio Kurata*

Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan.

Received October 28, 1980

ABSTRACT: A theory of the second and third virial coefficients, A_2 and A_3, of block copolymer solutions is presented. Evaluation of these coefficients is performed mainly for equimolar diblock and triblock copolymers with a wide variety of segment interactions. It is shown that phase separation into dilute and concentrated solutions occurs only for triblock copolymers in solvents which are selective for the central block chains and that precipitation of the polymers occurs in other cases. When the polymer composition is shifted from an equimolar ratio, diblock copolymers also exhibit separation into two solution phases in solvents which are selective for the major component of the polymers, though the favorable condition is quite restricted.

Introduction

It is well-known that block copolymers form various types of "microdomain structure" in bulk, depending on the chain architecture, the segment interactions, and even the history which the polymers encountered during the course of formation of the bulk phase.[1] Phase separation in polymer solutions generally takes place at rather low concentrations of polymers due to the dissimilarity in the dimensions of solvent and solute molecules. Thus, we may hope that the evaluation of some lower members of the osmotic virial coefficients would provide useful information on the initial process of the domain formation of block copolymers.

In this paper, we develop a mean field theory of the second and third virial coefficients, A_2 and A_3, and perform calculations for AB diblock and ABA triblock copolymers with a wide variety of segment interactions. As far as we are aware, such calculations have not as yet been published, except for some perturbation calculations.[2,3]

Theory

1. Second Virial Coefficient. In mean field theory, the osmotic second virial coefficient A_2 of a copolymer with a given sequence of segments may be expressed as[4]

$$A_2 = \frac{N_{\mathrm{A}}}{2M^2} \int \left\{ 1 - \exp\left[-\frac{V(\mathbf{S}_{12})}{kT} \right] \right\} d\mathbf{S}_{12} \qquad (1)$$

$$\frac{V(\mathbf{S}_{12})}{kT} = \sum_{k_1=1}^{n} \sum_{k_2=1}^{n} \beta_{k_1k_2} \int P_{k_1}(\mathbf{S}) P_{k_2}(\mathbf{S} - \mathbf{S}_{12})\, d\mathbf{S} \qquad (2)$$

Here N_{A} is Avogadro's constant, M is the molar mass of the copolymer, n is the number of segments of one molecule, and $\mathbf{S}_{12}$ is the distance between the *geometric* centers of molecules 1 and 2. $P_{k_1}(\mathbf{S})$ in eq 2 represents the probability density that the k_1th segment of molecule 1 will be found at a point separated from the center of molecule 1 by a distance $\mathbf{S}$, $P_{k_2}(\mathbf{S} - \mathbf{S}_{12})$ represents the probability density that the k_2th segment of molecule 2 will be found at the same point as above which is separated from the center of molecule 2 by a distance $\mathbf{S} - \mathbf{S}_{12}$, and $\beta_{k_1k_2}$ is the interaction parameter (actually the binary cluster integral) of the segment contact of k_1 and k_2. Then $V(\mathbf{S}_{12})$ may be considered to be the mean intermolecular potential as a function of the distance $\mathbf{S}_{12}$. We note that in eq 2, the excluded-volume effect within each molecule should be incorporated in the form of the distribution functions P_{k_1} and P_{k_2}.

Now suppose the copolymer to be composed of several block chains B_p ($p = 1, 2, ..., N$) and denote the number of segments in the pth block by n_p. Hence $n = n_1 + n_2 + ... + n_N$. For simplicity, the bond length connecting adjacent segments is assumed to obey a Gaussian distribution with the mean-square length b^2, irrespective of block. Then in the hypothetical solvent where all the segment interactions vanish, the end-to-end distance of each block B_p also obeys a Gaussian distribution with the mean-square length $b^2 n_p$. In ordinary solvents, however, the mean-square end-to-end distance of block B_p is modified as $\alpha_p^2 b^2 n_p$ even at infinite dilution, due to the intramolecular segment interactions (the excluded-volume effect). The linear modification factor α_p could be either larger or smaller than unity, depending on the nature of solvent and the architecture (the n_p's) of the copolymer, but for simplicity we call α_p the linear *expansion* factor of block B_p.

The intramolecular segment interactions are classified into intrablock segment interactions and interblock segment interactions. If the number of blocks N in a copolymer is as small as two or three, the interblock interactions have a rather minor effect on the chain expansion as compared with the intrablock interactions.[5-7] Thus, we here assume that (A) the expansion factor for each block, α_p, is determined by the intrablock segment interactions alone. Furthermore, following the spirit of the uniform expansion approximation in homopolymer chain statistics, we assume that (B) the expansion α_p occurs uniformly throughout the block B_p.

These two assumptions allow us to write the distribution of the bond vector $\mathbf{r}_i$ in the form

$$\tau(\mathbf{r}_i) = [3/(2\pi\alpha_p^2 b^2)]^{3/2} \exp[-3\mathbf{r}_i^2/(2\alpha_p^2 b^2)] \qquad (3)$$

if the bond i belongs to block B_p. The distribution function for the distance $\mathbf{S}$ between the kth segment of the copolymer and the center of molecule, $P_k(\mathbf{S})$, is then written as

$$P_k(\mathbf{S}) = (3/2\pi\langle S_k^2\rangle)^{3/2} \exp(-3S^2/2\langle S_k^2\rangle) \qquad (4)$$

where $\langle S_k^2\rangle$ is the mean-square distance of the kth segment from the geometric center of molecule. Thus $\sum_k \mathbf{S}_k = \mathbf{0}$, irrespective of the disparity in segment mass. This quantity $\langle S_k^2\rangle$ can be expressed as

$$\langle S_k^2\rangle = b^2 \sum_{p=1}^{N} [\alpha_p^2 \sum_{l=m_{p-1}+1}^{m_p} \phi_{kl}^2] \qquad (5)$$

$$\phi_{kl} = H(k - l) + (l/n) - 1 \qquad (6)$$

where

$$m_p = n_1 + n_2 + ... + n_p \qquad \text{(hence } m_0 = 0,\ m_N = n) \qquad (7)$$

and $H(k - l)$ is a unit step function defined by

0024-9297/81/2214-1104$01.25/0

$$\begin{aligned} H(k-l) &= 1 \quad \text{for} \quad 1 \le l \le k-1 \\ &= 0 \quad \text{for} \quad k \le l \le n-1 \end{aligned} \tag{8}$$

Substitution of eq 4 into eq 2 and integration over **S** lead to an angle-independent potential

$$V(S_{12})/kT = 3^{3/2}\sum_{p=1}^{N}\sum_{q=1}^{N} z_{pq}\int_{f_{p-1}}^{f_p}\mathrm{d}x \int_{f_{q-1}}^{f_q}\mathrm{d}y \times [C(x) + C(y)]^{-3/2} \exp\{-9S_{12}^2/2[C(x) + C(y)]nb^2\} \tag{9}$$

where we put

$$x = k_1/n \qquad y = k_2/n \tag{10}$$

$$t_p = n_p/n \qquad f_p = t_1 + t_2 + \ldots + t_p \tag{11}$$

$$C(x) = 3\langle S_{k_1}^2\rangle/nb^2 \qquad C(y) = 3\langle S_{k_2}^2\rangle/nb^2 \tag{12}$$

$$z_{pq} = (3/2\pi b^2)^{3/2} n^{1/2} \beta_{k_1 k_2} \tag{13}$$

for

$$m_{p-1} + 1 \le k_1 \le m_p$$

and

$$m_{q-1} + 1 \le k_2 \le m_q$$

The explicit form of the function $C(x)$ is written as

$$C(x) = 3\alpha_p^2(x^2 - x - f_p^2 + f_p) + \sum_{u=1}^{N}\alpha_u^2(f_u^3 - f_{u-1}^3) - 3\sum_{u=p+1}^{N}\alpha_u^2(f_u^2 - f_{u-1}^2 - f_u + f_{u-1}) \tag{14}$$

for

$$f_{p-1} < x \le f_p$$

with $f_0 = 0$ and $f_N = 1$.

An N-block copolymer and solvent system may be specified by giving a set of parameters t_p (or f_p) and z_{pq} ($p, q = 1, 2, ..., N$). Thus if a theoretical equation of the end-to-end expansion factor $\alpha(z)$ for homopolymer chains is available over the entire range (including the negative range) of the excluded-volume parameter z, we can approximately evaluate α_p in eq 14 as

$$\alpha_p = \alpha(z_p) \tag{15a}$$

with

$$z_p = (n_p/n)^{1/2} z_{pp} = t_p^{1/2} z_{pp} \tag{15b}$$

where z_p represents the excluded-volume parameter for the pth block chain in the copolymer. For the purpose, we employ

$$\begin{aligned} \alpha(z) &= (1 + 1.41z)^{1/3} \quad &\text{for} \quad z \ge 0 \qquad &(16) \\ &= (1/\sqrt{3})|z|^{-3/4} \quad &\text{for} \quad -10 \le z \le -1 \qquad &(17) \end{aligned}$$

which were presented in our previous paper.[7] In the ranges $-1 < z < 0$ and $z < -10$, we evaluate α_p numerically by applying a Spline interpolation of the third degree to the theoretical values of $\alpha(z)$ given in the same paper. As is well-known, a number of approximate equations of $\alpha(z)$ have been published in the literature, but their applications are limited to the range of positive z by the nature of the approximations employed.

With α_p thus evaluated, eq 9 and 14 determine the mean intermolecular potential $V(S_{12})$, which is spherically symmetric around $S_{12} = 0$, and then numerical integration of eq 1 over S_{12} yields A_2.

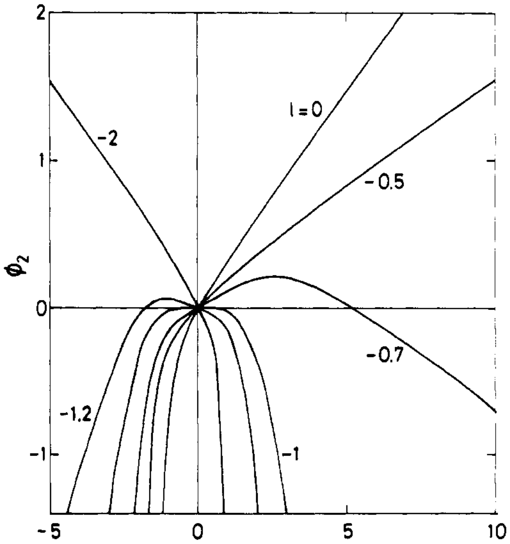

Figure 1. Second virial coefficient A_2 for equimolar diblock copolymer chains specified by $z_{AB} = 0$ and $z_{AA} = lz_{BB}$. ϕ_2 is defined by eq 22.

2. Third Virial Coefficient. With the angle-independent potential $V(S_{12})$ given by eq 9, the osmotic third virial coefficient A_3 may be written in the following forms:[4,8]

$$A_3 = (N_A^2/3M^3)\int\int f(\mathbf{S}_{12})f(\mathbf{S}_{13})f(\mathbf{S}_{23})\,\mathrm{d}\mathbf{S}_{12}\,\mathrm{d}\mathbf{S}_{13} \tag{18a}$$

$$A_3 = \frac{8\pi^2 N_A^2}{3M^3}\int\int\int f(S_{12})f(S_{13})f(S_{23})S_{12}S_{13}S_{23}\,\mathrm{d}S_{12}\,\mathrm{d}S_{13}\,\mathrm{d}S_{23} \tag{18b}$$

$$A_3 = \frac{8\pi^2 N_A^2}{3M^3}\int_0^\infty\int_0^\infty\int_0^\pi f(S_{12})f(S_{13})f(S_{23})S_{12}^2 S_{13}^2 \sin\theta\,\mathrm{d}S_{12}\,\mathrm{d}S_{13}\,\mathrm{d}\theta \tag{18c}$$

with

$$f(S_{ij}) = 1 - \exp[-V(S_{ij})/kT] \tag{19}$$

$$S_{23}^2 = S_{12}^2 + S_{13}^2 - 2S_{12}S_{13}\cos\theta \tag{20}$$

Here θ represents the angle between $\mathbf{S}_{12}$ and $\mathbf{S}_{13}$. The triple integral in eq 18b is to be performed over all possible values of S_{12}, S_{13}, and S_{23} which form a triangle. Numerical calculations of A_3 in this paper, however, were made according to eq 18c and 9.

Results and Discussion

1. Second Virial Coefficient of AB Diblock and ABA Triblock Copolymers with $z_{AB} = 0$. In this paper, we treat only equimolar block copolymers. Therefore, AB diblock copolymers are specified as $t_1 = t_2 = 0.5$ and ABA triblock copolymers as $t_1 = t_3 = 0.25$ and $t_2 = 0.5$. We begin with the case that $z_{AB} = 0$ and put

$$z_{AA} = lz_{BB} \tag{21}$$

This choice of excluded-volume parameters fits the assumption (A) employed in the present theory.

The results of A_2 obtained for diblock and triblock copolymers with various fixed values of l are shown in Figures 1 and 2, respectively, where ϕ_2 represents the dimensionless quantity defined by

$$A_2 = (N_A\langle R^2\rangle_0^{3/2}/M^2)\phi_2 \tag{22}$$

with the unperturbed mean-square end-to-end distance

$$\langle R^2\rangle_0 = b^2 n \tag{23}$$

In the case $l = 0$ or $z_{AA} = 0$, ϕ_2 for the diblock and triblock copolymers shows essentially the same behavior,

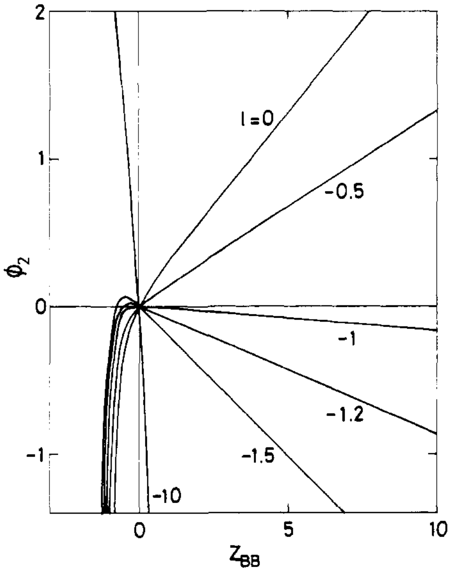

Figure 2. Second virial coefficient A_2 for equimolar triblock copolymer chains specified by $z_{AB} = 0$ and $z_{AA} = lz_{BB}$. ϕ_2 is defined by eq 22.

though the former gives slightly larger values over the entire region of z_{BB} than does the latter. ϕ_2 increases almost linearly with increasing z_{BB} in the region of positive z_{BB}, while it decreases rapidly with decreasing z_{BB} in the region of negative z_{BB}. We note that this behavior is qualitatively the same as that of homopolymer chains. A slight difference in ϕ_2 values exists between diblock and triblock copolymers. This is attributable to a difference between the mean-square radii of B-segment clouds, $\langle S_B^2 \rangle$, of these molecules, which are evaluated from eq 12 and 14 as

(i) diblock copolymers ($l = 0$)

$$\langle S_B^2 \rangle / b^2 n = \alpha_B^2/16 \quad \text{for} \quad \alpha_B \gg 1$$
$$= 1/48 \quad \text{for} \quad \alpha_B \ll 1 \qquad (24)$$

(ii) triblock copolymers ($l = 0$)

$$\langle S_B^2 \rangle / b^2 n = 3\alpha_B^2/64 \quad \text{for} \quad \alpha_B \gg 1$$
$$= 1/192 \quad \text{for} \quad \alpha_B \ll 1 \qquad (25)$$

The B-segment cloud in the diblock copolymer is more expanded over the entire region of z_{BB} as compared with the one in the triblock copolymer.

In the case $l = -1$ or $z_{AA} = -z_{BB}$, the ϕ_2 for diblock and triblock copolymers both display a maximum at $z_{BB} = 0$. There is, however, a notable difference in the shape of the ϕ_2 curves between these two polymers: ϕ_2 of the diblock copolymer shows a strong dependence on z_{BB} in both regions of positive and negative z_{BB}, while ϕ_2 of the triblock copolymer shows a strong dependence only in the region of negative z_{BB} and a rather weak dependence in the region of positive z_{BB}. These features of ϕ_2 are not essentially varied by moderate modification of the parameter l.

According to eq 12 and 14, the mean-square radii of A- and B-segment clouds are obtained as

(i) diblock copolymers

$$\langle S_A^2 \rangle / b^2 n = (\alpha_A^2/16) + (\alpha_B^2/48) \qquad (26a)$$

$$\langle S_B^2 \rangle / b^2 n = (\alpha_A^2/48) + (\alpha_B^2/16) \qquad (26b)$$

(ii) triblock copolymers

$$\langle S_A^2 \rangle / b^2 n = (3\alpha_A^2/64) + (13\alpha_B^2/192) \qquad (27a)$$

$$\langle S_B^2 \rangle / b^2 n = (\alpha_A^2/192) + (3\alpha_B^2/64) \qquad (27b)$$

Equations 26a,b indicate that the B-segment cloud in the diblock copolymer with $l < 0$ has a larger radius than does the A-segment cloud if $z_{BB} > 0$ and $\alpha_B > \alpha_A$ and a smaller radius if $z_{BB} < 0$ and $\alpha_B < \alpha_A$. In any case, the segments specified by a negative z parameter form the cloud with a smaller radius. Then it seems plausible that the intermolecular potential $V(S_{12})$ becomes negative at short distance and positive at long distance as long as z_{AA} and z_{BB} are of comparable magnitudes. On the contrary, eq 27a,b show that the B-segment cloud always has a smaller radius, irrespective of the sign of z_{BB}, than does the A-segment cloud. Thus, we may expect that the inner part of the intermolecular potential becomes negative or positive in accordance with the sign of z_{BB}, and, correspondingly, the outer parts become positive or negative.

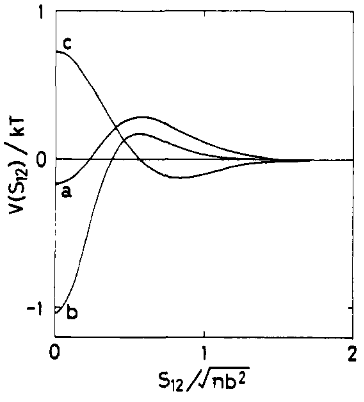

Figure 3. Mean interaction potential $V(S_{12})$ as a function of intermolecular distance S_{12}: (a) diblock copolymer with $l = -0.45$ and $z_{BB} = 3$; (b) triblock copolymer with $l = -2$ and $z_{BB} = -0.5$; (c) triblock copolymer with $l = -1.3$ and $z_{BB} = 3$.

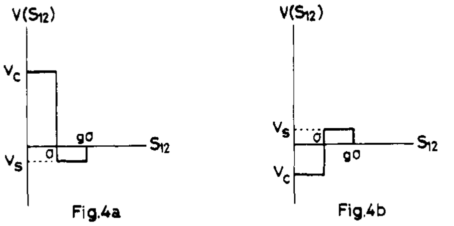

Figure 4. Modified square-well potential.

This conjecture on the intermolecular potential is supported by examples given in Figure 3, where curve a is for a diblock copolymer with $l = -0.45$ and $z_{BB} = 3$, curve b for a triblock copolymer with $l = -2$ and $z_{BB} = -0.5$, and curve c for another triblock copolymer with $l = -1.3$ and $z_{BB} = 3$. Such a potential consisting of negative inner and positive outer parts never appears in the case of ordinary low-molecular-weight substances and it gives rise to unique solution properties of block copolymers.

The curve for $l = -2.0$ in Figure 1 and the curve for l -10 in Figure 2 show positive ϕ_2 in the region of negative z_{BB}. The explanation of these curves will be given in the next section.

2. Modified Square-Well Potential. The intermolecular interaction potential $V(S_{12})$ for block copolymers may be approximated by a modified square-well potential schematically shown in Figure 4, where σ and V_c represent the radius and the energy of the core part and $g\sigma$ and V_s represent those of the skin part, respectively. We put

$$X = 1 - \exp(-V_c/kT) \qquad Y = 1 - \exp(-V_s/kT) \qquad (28)$$

The second and third virial coefficients for this potential are obtained as

$$A_2 = (2\pi N_A/3M^2)\sigma^3[X + (g^3 - 1)Y] \qquad (29)$$

and

$$A_3 = (\pi^2 N_A^2/18M^3)\sigma^6 G(g,X,Y) \qquad (30a)$$

with

$$G(g,X,Y) = 5X^3 + (g^6 - 18g^4 + 32g^3 - 15)X^2Y + (-2g^6 + 36g^4 - 32g^3 - 18g^2 + 16)XY^2 + (6g^6 - 18g^4 + 18g^2 - 6)Y^3 \qquad \text{for } g \le 2 \quad (30b)$$

$$G(g,X,Y) = 5X^3 + 17X^2Y + (32g^3 - 18g^2 - 48)XY^2 + (5g^6 - 32g^3 + 18g^2 + 26)Y^3 \qquad \text{for } g \ge 2 \quad (30c)$$

The derivation of these equations, though not reproduced here, is a simple extension of the well-known Kihara equations[9] for the original square-well potential, which corresponds to the case for $X = 1$.

We begin with homopolymer chains. In this case, our basic equations, eq 1, 2, and 4, become identical with those employed by Ishihara and Koyama;[10] hence we obtain the familar equation[11]

$$\phi_2 = \frac{1}{2}\left(\frac{2\pi}{3}\right)^{3/2}\alpha^3\left[\frac{1}{2.30}\ln\left(1 + \frac{2.30z}{\alpha^3}\right)\right] \quad (31)$$

$$\text{for } z \ge 0$$

In addition, we find that our numerical results for negative z are well approximated by

$$\phi_2 = -0.01\alpha^3 \exp(-5.9z/\alpha^3) \qquad \text{for } z < -0.6 \quad (32)$$

These features of ϕ_2 indicate that the parameters for the modified square-well potential are expressed as

$$\sigma/(b^2n)^{1/2} = c\alpha \quad (33a)$$

$$V_c/kT = c'z/\alpha^3 \qquad (\text{and } V_s = 0) \quad (33b)$$

where c and c' are constants. The combination of these equations with eq 16 and 17 predicts that X is practically independent of z and ϕ_2 is proportional to z in the region of positive z except in the vicinity of the origin and that V_c takes large negative values due to the effect of α^3 in the denominator and ϕ_2 behaves like eq 32 in the region of negative z.

In the case of the block copolymers with $\langle S_A{}^2\rangle > \langle S_B{}^2\rangle$ and $z_{AB} = 0$, the modified square-well potential may be specified as

$$\sigma/(b^2n)^{1/2} = c\alpha_B \quad (34a)$$

$$g = (\langle S_A{}^2\rangle/\langle S_B{}^2\rangle)^{1/2} \quad (34b)$$

$$V_c/kT = c'z_{BB}(b^2n/\langle S_B{}^2\rangle)^{3/2} + c''z_{AA}(b^2n/\langle S_A{}^2\rangle)^{3/2} \quad (34c)$$

$$V_s/kT = c'''z_{AA}(b^2n/\langle S_A{}^2\rangle)^{3/2} \quad (34d)$$

where the c's are all constants. Then the following predictions are derived:

(i) Diblock Copolymer with $z_{AA} > 0$ and $z_{BB} < 0$. The expansion factor α_A is considerably larger than α_B unless z_{BB} is nearly zero, and the core potential V_c is obtained, with the aid of eq 26b, as

$$V_c/kT = 64(3^{3/2}c' + lc'')(z_{BB}/\alpha_A{}^3) \quad (35)$$

In contrast to the homopolymer case, V_c is proportional to $z_{BB}/\alpha_A{}^3$ instead of $z_{BB}/\alpha_B{}^3$. V_c is negative unless the parameter l ($=z_{AA}/z_{BB}$) does not exceed a certain negative value. Under the conditions, the first term in eq 29 becomes dominant, and ϕ_2 decreases rapidly with decreasing z_{BB}. However, the slope of the ϕ_2 vs. z_{BB} curve is less steep in comparison with the corresponding slope for the homopolymer case. It is possible in the vicinity of $z_{BB} = 0$ for ϕ_2 to become positive due to the contribution from the Y term in eq 29. When a large negative value is assigned to l, V_c as given by eq 35 will become positive for negative z_{BB}. The curve for $l = -2$ in Figure 1 indicates this situation.

(ii) Triblock Copolymer with $z_{AA} > 0$ and $z_{BB} < 0$. The above features of ϕ_2 hold in this case. However, the dependence of ϕ_2 on z_{BB} is somewhat strengthened, as readily shown by eq 34c and 27b, and inversion of the sign of V_c occurs only at a very large negative value of l, say -10, as seen from Figure 2.

(iii) Triblock Copolymer with $z_{AA} < 0$ and $z_{BB} > 0$. An analysis similar to that above shows that the skin potential, V_s, is proportional to $z_{AA}/\alpha_B{}^3$, and hence to $lz_{BB}/\alpha_B{}^3$, except in the vicinity of $z_{BB} = 0$. The V_s rapidly attains a negative, constant value. The factor $X + (g^3 - 1)Y$ in eq 29 can be either positive or negative, depending upon the parameter value, but it is always a constant independent of z_{BB}. Thus, ϕ_2 is proportional to $\alpha_B{}^3$, and hence to z_{BB}, irrespective of the sign of ϕ_2.

3. Third Virial Coefficient and Two Types of Phase Separation in Solutions. The second virial coefficient, A_2, vanishes at the condition

$$X = -(g^3 - 1)Y \quad (36)$$

For the sake of convenience, we call this state the *apparent* Θ *state*. Then substituting eq 36 into eq 30, we obtain

$$A_3 = -(\pi^2N_A{}^2/18M^3)\sigma^6Y^3f(g) \quad (37a)$$

with

$$f(g) = g^3(-g^9 + 18g^7 - 27g^6 + 27g^3 - 18g^2 + 1) \qquad \text{for } 1 < g \le 2 \quad (37b)$$

$$f(g) = g^3(5g^6 - 5g^3 - 18g^2 + 1) \qquad \text{for } g > 2 \quad (37c)$$

Since $f(g)$ is positive for $g > 1$, we find that A_3 at the apparent Θ state is positive if $Y < 0$ or $X > 0$ and negative if $Y > 0$ or $X < 0$. The former case corresponds to the potential with positive V_c and negative V_s, and the latter case to that with negative V_c and positive V_s. Thus there appear two possible combinations of A_2 and A_3 in the vicinity of the apparent Θ state defined by $A_2 = 0$. These combinations are of positive A_2 and A_3 and of negative A_2 and positive A_3 in the case of polymers specified by positive V_c and negative V_s, and of positive A_2 and negative A_3 and of negative A_2 and A_3 in the case of polymers specified by negative V_c and positive V_s, respectively.

The osmotic pressure π can be written as

$$\pi/RT = C/M + A_2C^2 + A_3C^3 + \ldots \quad (38)$$

where R is the gas constant and C is the concentration in (polymer mass)/(unit volume of solution). We attempt to analyze the phase separation of the solution by considering terms up to A_3 in eq 38. π is a monotonously increasing function of C when A_2 and A_3 are both positive and no phase separation occurs. On the other hand, π can exhibit a pair of maxima and minima with increasing C when $A_2 < 0$ and $A_3 > 0$, and the solution separates into dilute and concentrated polymer phases in a certain range of C. The critical condition for this type of phase separation is determined by a set of equations

$$(\partial\pi/\partial C)_T = 0 \qquad (\partial^2\pi/\partial C^2)_T = 0 \qquad A_3 > 0 \quad (39)$$

which yields

$$A_3{}^*/M(A_2{}^*)^2 = 1/3 \qquad \text{and} \qquad C^* = -A_2{}^*/3A_3{}^* \quad (40)$$

Barker and co-workers[12] have calculated the virial coefficients for the square-well potential and also for the Lennard-Jones potential up to A_5 and shown that all of the higher coefficients, A_3 to A_5, are positive at the Boyle

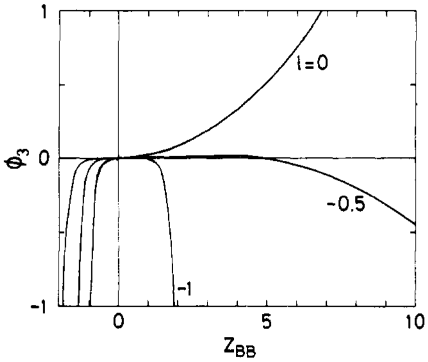

Figure 5. Third virial coefficient A_3 for equimolar diblock copolymers specified by $z_{AB} = 0$ and $z_{AA} = lz_{BB}$. ϕ_3 is defined by eq 41.

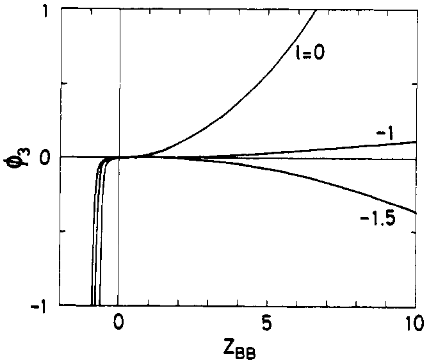

Figure 6. Third virial coefficient A_3 for equimolar triblock copolymer with $z_{AB} = 0$ and $z_{AA} = lz_{BB}$.

point, where $A_2 = 0$. Since the higher virial coefficients seem to be more strongly affected by the core part than the skin part of the potential, we may assume that they are all positive if $A_2 < 0$ and $A_3 > 0$. Then the above conjecture on the phase separation would not require any essential change by inclusion of higher virial coefficients.

When $A_2 > 0$ and $A_3 < 0$, π exhibits only a maximum at a certain concentration C^{**}, and afterward it decreases without limit with increasing C, making the solution unstable. Then the components should leave the solution at about a concentration higher than C^{**}. For the sake of convenience, we refer to this type of phase separation as "precipitation".

The stability of the "precipitated" polymer phase can not be ensured by the potentials employed in this paper. The hard-core potential for each polymer segment has to be introduced for the purpose. However, this is an extremely difficult task within the category of the mean field treatment. The force range of such a segment core must be of the order of 10^{-7} cm, which is practically zero as compared with the present scale of the intermolecular distance S_{12}. Thus, in this study, the stability of the precipitated polymer phase is simply introduced as an a priori postulate.

Now, returning to the diblock and triblock copolymers with $z_{AB} = 0$, we show some examples of A_3 as functions of z_{BB} in Figures 5 and 6, where l is defined by eq 21 and ϕ_3 by

$$A_3 = (N_A{}^2\langle R^2\rangle_0{}^3/M^3)\phi_3 \tag{41}$$

The shape of the illustrated curves can be interpreted, at least qualitatively, in terms of the modified square-well potentials, though not mentioned here.

Figures 7 and 8 give the phase diagrams for diblock and triblock copolymers, respectively, where the locus of the points for $A_2 = 0$ is shown by the solid line and that of $A_3 = 0$ by the dashed line. The lower area bounded by the solid line (or the dashed line) represents the region of positive A_2 (or A_3) in the left half of these figures, where $z_{BB} < 0$, while it represents the region of negative A_2 (or A_3) in the right half, where $z_{BB} > 0$. The upper pair of solid and dashed lines in each figure is for the equimolar copolymer, while the lower pair is for the polymers consisting of 0.4 parts of A and 0.6 parts of B, namely $t_1 = 0.4$ and $t_2 = 0.6$ in Figure 7 and $t_1 = t_3 = 0.2$ and $t_2 = 0.6$ in Figure 8, respectively.

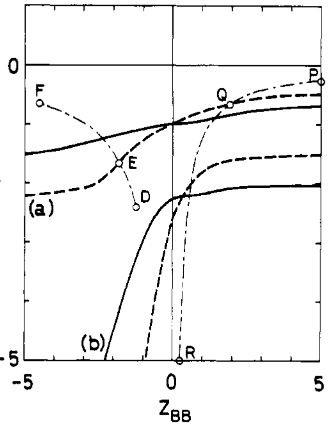

Figure 7. Phase diagram for diblock copolymers specified by (a) $t_1 = t_2 = 0.5$ and (b) $t_1 = 0.4$ and $t_2 = 0.6$. $z_{AB} = 0$ and l represents z_{AA}/z_{BB}. The lower area bounded by the solid line (or the dashed line) represents the region of positive A_2 (or A_3) for $z_{BB} < 0$, while it represents the region of negative A_2 (or A_3) for $z_{BB} > 0$.

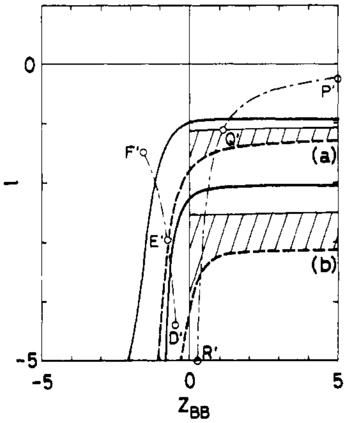

Figure 8. Phase diagram for triblock copolymers specified by (a) $t_1 = t_3 = 0.25$ and $t_2 = 0.5$ and by (b) $t_1 = t_3 = 0.2$ and $t_2 = 0.6$. $z_{AB} = 0$ and l represents z_{AA}/z_{BB}. The lower area bounded by the solid line (or the dashed line) represents the region of positive A_2 (or A_3) for $z_{BB} < 0$, while it represents the region of negative A_2 (or A_3) for $z_{BB} > 0$.

Suppose that one starts with point D in Figure 7, where the solvent condition is specified by $A_2 > 0$ and $A_3 > 0$ or, more precisely, by $z_{BB} = -1.25$ and $z_{AA} = -2.4z_{BB} = 3$. In this condition, the polymer solution is thermodynamically stable. If a second solvent which is neutral for block A but a precipitant for block B is added to the solution, the parameter z_{BB} decreases, leaving z_{AA} unchanged, and accordingly the solvent condition varies along the dash–dot line toward point F through point E. The polymer would precipitate from the solution at around point E. A similar process should be observed when the solvent condition is varied from point P toward point R through point Q; i.e., precipitation occurs at around point Q.

In the case of triblock copolymers shown in Figure 8, precipitation occurs at around point E′ if the solvent

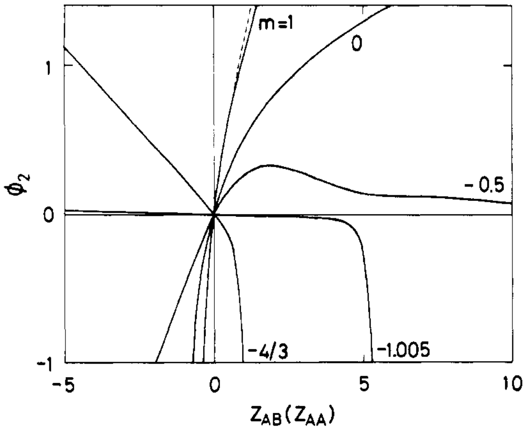

Figure 9. Second virial coefficient A_2 for diblock copolymers with various fixed values of m, which is defined as $z_{AA} = z_{BB} = mz_{AB}$.

condition is varied along the dash-dot line from point D′ to F′ and through E′. On the other hand, if the solvent condition is varied along P′Q′R′, phase separation into two solution phases occurs at around point Q′ where the conditions of eq 39 are fulfilled. The shaded area in Figure 8 represents the region bounded by eq 39 (almost horizontal line) and $A_3 = 0$ (dashed line).

In addition, we note that there is a small triangular area with $A_2 < 0$ and $A_3 > 0$ in the right half of Figure 7. Thus, if the solvent condition is varied through this area, the diblock copolymer solution may exhibit separation into two solution phases.

4. Effect of AB Interactions z_{AB}. We here study effects of interactions z_{AB} between unlike segments A and B on A_2. Let us start with the case of homopolymer A. ϕ_2 as a function of the excluded-volume parameter z_{AA} for this polymer can be obtained from eq 1 and 9, within the scope of the present model, either by putting $t_1 = 1$ or by putting $t_1 = t_2 = 0.5$ and $z_{AA} = z_{BB} = z_{AB}$. The results obtained are shown in Figure 9 by the dashed curve and the solid curve denoted by $m = 1$, respectively (see eq 42). In the former method, the block expansion factor α_p (actually α_A) in eq 15 is estimated at the excluded-volume parameter $z_p = z_{AA}$, while in the latter method, each α_p (actually α_A or α_B) is estimated at $z_p = (0.5)^{1/2}z_{AA}$. The discrepancy between these two curves is notable only for positive values of z_{AA} larger than unity. This fact seems to support that the effect of interblock segment interactions on the block expansion factor is not significant as expected.

On the basis of the above observation, we here assume, as before, that the interblock segment interactions do not affect the expansion of each individual block chain and study only the direct effect of inclusion of segment interaction z_{AB} on A_2 for various types of block copolymers by using eq 1 and 9. The results are shown in Figures 9–11.

Figure 9 shows ϕ_2 for equimolar AB diblock copolymers ($t_1 = t_2 = 0.5$), where we put

$$z_{AA} = z_{BB} = mz_{AB} \tag{42}$$

Under the condition that $z_{AA} = z_{BB}$, two segment clouds of A and B have the same average radius; hence the potential $V(S_{12})$ consists of a single region. Thus we may assign the modified square-well potential as

$$\sigma/(b^2n) = c\alpha_A \tag{43a}$$

$$V_c/kT = c'\bar{z}/\alpha_A{}^3 \qquad V_s = 0 \tag{43b}$$

where

$$\bar{z} = (m + 1)z_{AB}/2 \tag{44}$$

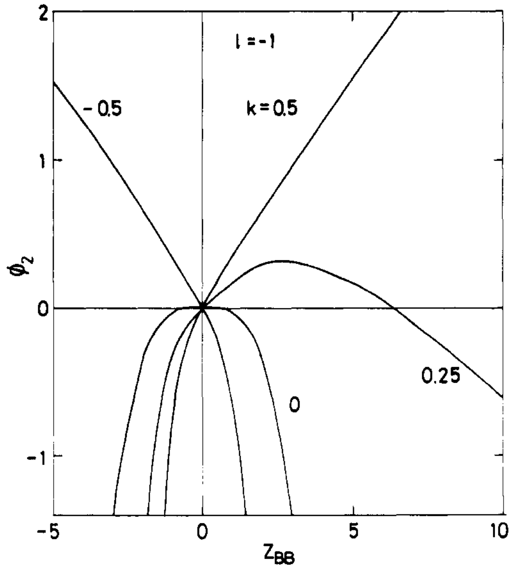

Figure 10. Second virial coefficient A_2 for diblock copolymers specified by $z_{AA} = -z_{BB}$ ($l = -1$) and $z_{AB} = kz_{BB}$.

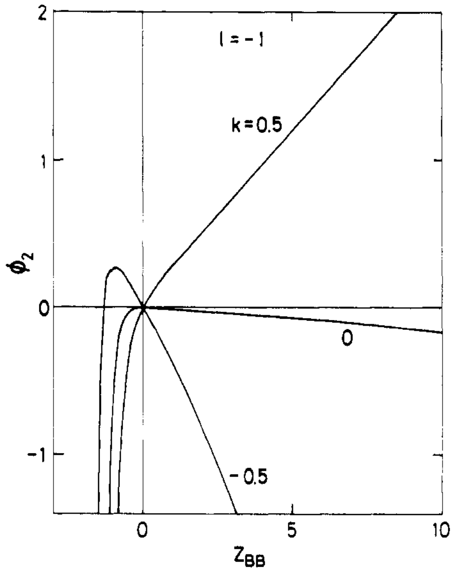

Figure 11. Second virial coefficient A_2 for triblock copolymers specified by $z_{AA} = -z_{BB}$ ($l = -1$) and $z_{AB} = kz_{BB}$.

The mean interaction parameter $\bar{z}$ as defined here is identical with the one which exercises the A_2 behavior of equimolar random copolymers. However, the potential given by eq 43a and 43b is different from that for the random copolymers: i.e., α_A for block copolymers is given by eq 15, while the corresponding factor $\bar{\alpha}$ for random copolymers is to be evaluated as $\bar{\alpha} = \alpha(\bar{z})$. Reflecting the difference in the potential, the ϕ_2 for block copolymers displays quite a different dependence on z_{AB} from that for random copolymers, which is always of the same form as the dashed curve for homopolymers, though with different scales of z_{AB}. As is seen from eq 29, 43a, and 43b, the quantity ϕ_2 for block copolymers is proportional to $\bar{z}$ for small values of $|z_{AB}|$, and afterward, ϕ_2 decreases slowly toward zero if $\bar{z} > 0$ and decreases very rapidly if $\bar{z} < 0$. When $m = -1$, all segment interactions cancel on the average, and ϕ_2 becomes identically zero.

Figures 10 and 11 illustrate effects of z_{AB} on the ϕ_2 behavior of equimolar diblock and triblock copolymers, respectively, where we put $z_{AA} = -z_{BB}$ and $z_{AB} = kz_{BB}$. Thus, the curves for $k = 0$ reproduce the curves for $l = -1$

in Figures 1 and 2. Inclusion of the z_{AB} terms in eq 9 raises or diminishes the potential energy level, so that the core–skin structure of $V(S_{12})$ is weakened or even destroyed according to the magnitude of k. Thus the effect of k on the systems of a fixed l has a resemblance to the effect of l on the systems of $k = 0$ shown in Figures 1 and 2.

As shown in the previous paper of this series, the repulsive interblock interaction, $z_{AB} > 0$, promotes the formation of a collapsed dumbbell form of the diblock copolymers if it is associated with negative intrablock interactions, $z_{AA} < 0$ and $z_{BB} < 0$. On the other hand, the attractive interblock interaction, $z_{AA} < 0$, promotes the formation of a collapsed ring form of the ABA triblock copolymers if z_{AB} is absent. The present theory based on the spherical potential given by eq 9 is insufficient for clarifying the behavior of A_2 in these states. Finally, we note that an analytical expression for $V(S_{12})$ obtainable at $S_{12} = 0$ is useful for a quick test of the sign of core potential.

References and Notes

(1) Noshay, A.; McGrath, J. E. "Block Copolymers"; Academic Press: New York, 1977.
(2) Sato, H.; Kamada, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2264.
(3) Sikora, A. *Makromol. Chem.* **1978**, *179*, 633.
(4) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(5) Tanaka, T.; Kotaka, T.; Inagaki, H. *Macromolecules* **1976**, *9*, 561.
(6) Bendler, J.; Solc, K.; Gobush, W. *Macromolecules* **1977**, *10*, 635.
(7) Kurata, M.; Kimura, T. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2133.
(8) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. "The Molecular Theory of Gases and Liquids"; Wiley: New York, 1954.
(9) Kihara, T. *Rev. Mod. Phys.* **1953**, *25*, 831. *Ibid.* **1955**, *27*, 412.
(10) Ishihara, A.; Koyama, R. *J. Chem. Phys.* **1956**, *25*, 712.
(11) Flory, P. J.; Krigbaum, W. R. *J. Chem. Phys.* **1950**, *18*, 1086. Orofino, T. A.; Flory, P. J. *Ibid.* **1957**, *26*, 1067.
(12) Barker, J. A.; Monaghan, J. J. *J. Chem. Phys.* **1962**, *36*, 2558, 2564. Barker, J. A.; Leonard, P. J.; Pompe, A. *Ibid.* **1966**, *44*, 4206.

Configurations and Dynamics of Real Chains. 2. Internal Viscosity

G. Allegra*

Istituto di Chimica del Politecnico, 20133 Milano, Italy

F. Ganazzoli

Scuola di Perfezionamento in Scienza dei Polimeri "G. Natta", Politecnico, 20133 Milano, Italy.

Received December 8, 1980

ABSTRACT: Intramolecular transmission of tensile force along a polymer chain can only occur via rotational rearrangements, which is the origin of internal viscosity. This is interpreted as the resistance to the propagation of configurational motions along the chain, caused by the rotational barriers around skeletal bonds. The relaxation mechanism occurs via traveling waves damping off as $e^{-t/\tau}$. Within the linear force approximation, each normal mode is characterized by two distinct relaxation times. The larger of them contains an internal viscosity contribution increasing with the normal mode coordinate, in essential agreement with what is currently assumed. A realistic, quadratic intramolecular potential is also incorporated in the theory, proceeding in analogy with the first paper of this series (Allegra, G.; Ganazzoli, F. *J. Chem. Phys.* 1981, *74*, 1310). With a suitable choice of the characteristic time τ_0 for bond-rotation relaxation, the complex modulus experimentally found for polystyrene is approximately reproduced. The dynamic structure factor departs in general from a single time exponential even more dramatically than in the absence of internal viscosity. Selecting a Q range where the actual stereochemical structure of the polymer comes into play ($0.1 \leq Q = 4\pi \sin(\theta/2)/\lambda \leq 0.4$ Å^{-1}) and ignoring the hydrodynamic interaction effects, we show that the approximate power law $t_{1/2}Q^{\beta}$ = constant is verified with $\beta \simeq 3$ for coherent scattering and with β between 2.4 and $\sim$3 for incoherent scattering, depending on the particular value chosen for τ_0 ($t_{1/2}$ = half-peak time width). Hence the suggestion proposed in the quoted paper that hydrodynamic interaction need not be invoked to explain a value of β close to 3 in this Q range is confirmed. The theory also predicts a Rouse-like spectrum of the relaxation times even in the ideal absence of external friction forces. Furthermore, in agreement with Fixman's computer simulation results, the incipient rate of chain relaxation is independent of internal viscosity.

Introduction

At sufficiently high frequencies of the alternating shear stress applied to a polymer solution, a peculiar behavior is observed which cannot be explained by the classical theories of polymer viscoelasticity.[1,2] In practice, the chains appear to stiffen, and a seemingly constant value of the component of the dynamic viscosity in phase with the velocity of deformation is observed through some frequency decades. This phenomenon is currently associated with the so-called "internal viscosity", but its molecular origins are still controversial. Kuhn and Kuhn[3] first suggested that it should be attributed to the dissipative effect connected with the rotational energy barriers surmounted during any configurational change; in analogy with Eyring's treatment of fluid viscosity, the faster the rate at which the energy barriers are crossed, the larger the extra force that is required. Cerf[4] and Peterlin[5] expressed in quantitative forms this plausible idea; although their mathematical formulation appeared to be quite successful in terms of numerical comparison with some experimental data,[6-8] it mainly rested on semiempirical criteria. More recently, Iwata,[9] Cerf,[10] and MacInnes[11] directed their attention to more sophisticated stochastic models. Bazua and Williams offered a detailed model of the rotational relaxation process,[12] while Allegra proposed an alternative nonequilibrium statistical mechanical approach where the hindered skeletal rotations are shown to slow down the propagation of configurational perturbations along the chain.[13]

While de Gennes suggests that intramolecular segment–segment friction may be the source of internal viscosity,[14] a still different approach is proposed by Adelman