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Theoretical Studies of the Second Virial Coefficient of the Copolymer Near the θ Temperature

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The osmotic second virial coefficients of random and block copolymers are calculated according to the perturbation theory. Evaluation is carried out to the double-contact approximation. The results show that the expressions for the osmotic second virial coefficients of random and block copolymers have different forms in their second term. The so-called "theta" temperature of the block copolymer at which the second virial coefficient vanishes, is found to be higher than that of the random copolymer. These results are compared with some existing experimental results. It is also suggested that the "theta" temperature of a copolymer having a distribution of the sequence length of two monomers is located between those of the random and two-block copolymers.

In recent years, studies of dilute polymer solutions of copolymers have been published by many authors, and the composition dependences of the unperturbed dimension, K, and of the excluded volume effect, B, have been discussed qualitatively. In order to characterize a copolymer, however, we must know not only its composition, but also the distributions of the sequence length of different monomers in the copolymer chain.

Some experimental studies[1,2] of these factors, utilizing an anionic polymerization technique, have given interesting results, but theoretical interpretations of these results are still too scanty. Recently, Froelich[1] calculated the expansion factor of the radius of gyration, α_R, for random and block copolymers near the θ temperature and showed that the former is more expanded. This calculation corresponds to the two limiting cases of distributions of the sequence length.

On the other hand, experimental results show that the temperature at which the osmotic second virial coefficient vanishes is different for the random and block copolymers; it may be expected that the solubility of a copolymer will be influenced by the distributions of the sequence length of the two monomers. Taking notice of this difference, we have calculated the second virial coefficient of random and block copolymers to the double-contact term according to the perturbation theory; these results will be compared with other experimental results.

Outline of Calculations

Consider a pearl-necklace model of a linear polymer chain and assume that the expansion of the polymer coil due to the volume effect occurs uniformly by a factor α. The second virial coefficient of the osmotic pressure is then written in the form:

$$A_2 = (N_A/V\cdot 2M^2)\int\cdots\int\{1-\exp(-V_{\text{inter}}/\boldsymbol{k}T)\} \times\left\{\prod_{i=1}^{n}(3/2\pi\alpha^2b^2)^{3/2}\exp(-3\boldsymbol{r}_i{}^2/2\alpha^2b^2)\mathrm{d}\boldsymbol{r}_i\right\}\mathrm{d}\boldsymbol{L}_{12} \tag{1}$$

where V is the volume of the solvent; M, the molecular weight of the polymer; V_{inter}, the mean potential of inter-molecular interaction between two polymer coils; $\boldsymbol{r}_i$, the vector connecting the ith to the $(i+1)$th segment; b, the segment length; $\boldsymbol{L}_{12}$, the vector connecting the first segment of the 1 molecule to that of the 2 molecule and α, the intra-molecular expansion factor. The remaining symbols have their usual meanings.

According to the general theory of Zimm[3] and Fixman,[4] the mean potential of inter-molecular interaction is assumed to be of a short-range nature and additive with respect to the pair interaction. Then, we have:

$$V_{\text{inter}}/\boldsymbol{k}T = \sum_{(\lambda\mu)}\beta_{\lambda\mu}\delta(L\lambda_1\mu_2) \tag{2}$$

where δ is the three-dimensional Dirac delta function peaked at $\boldsymbol{L}_{\lambda_1\mu_2}=0$; $\boldsymbol{L}_{\lambda_1\mu_2}$ are vectors connecting the λth segment of the 1 molecule to the μth segment of the 2 molecule, and $\beta_{\lambda\mu}$ is the binary cluster integral between the denoted segments. By substituting Eq. (2) in Eq. (1) and expanding the powers of β, we obtain:

$$A_2 = (N_A/2M^2)\Big[\sum_{(\lambda\mu)}\beta_{\lambda_1\mu_2}$$

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1) D. Froelich and H. Benoit, *Makromol. Chem.*, **92**, 224 (1966).

2) T. Kotaka, H. Ohnuma and Y. Murakami, *J. Phys. Chem.*, **70**, 4099 (1966).

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

4) M. Fixman, *ibid.*, **23**, 1656 (1955).

$$- \frac{1}{2}(3/2\pi\alpha^2 b^2)^{3/2} \sum_{(\lambda\mu)}\sum_{(\kappa\nu)} \beta_{\lambda_1\mu_2} \times \beta_{\kappa_1\nu_2}(|\nu - \mu| + |\kappa - \lambda|)^{-3/2} + \cdots\Big] \qquad (3)$$

In this paper, two types of copolymers consisting of two monomers, A and B, are considered. One is the random copolymer, in which the mole fraction of the A monomer is X. The other is the block copolymer, in which A segments are successively connected from the first to the Xnth, and B segments, from the $(Xn+1)$th to the nth.

In the case of the random copolymer, the probability of the denoted segment being an A segment or a B segment is only defined in a statistical sense. Thus, $\beta_{\lambda_1\mu_2}$ and $\beta_{\kappa_1\nu_2}$ in Eq. (3) are given:

$$X^2\beta_{AA} + (1 - X)^2\beta_{BB} + 2X(1 - X)\beta_{AB} \qquad (4)$$

The summation in Eq. (3) may be converted to integrals, straightforward integrations over λ, μ, κ and ν then yield:

$$A_2 = (N_A n^2/2M^2)[\beta' - (3/2\pi\alpha^2 b^2)^{3/2} n^{1/2} \cdot (32/15)(7 - 4\sqrt{2})\beta'^2 + \cdots] \qquad (5)$$

where β' is replaced by Eq. (4). The above equation is equivalent to the expression of the A_2 of the linear homopolymer.

In the case of the block copolymer, the calculations are somewhat more complicated. Since the first term in Eq. (3) comes from the single intermolecular contact, it is easily found that the first term is equivalent for random and block copolymers as long as the mole fraction, X, is kept constant.

In the second term in Eq. (3), which represents the double inter-molecular contact, $\beta_{\lambda_1\mu_2}$ and $\beta_{\kappa_1\nu_2}$ are β_{AA}, β_{BB}, or β_{AB} according to the location of the λ_1th, μ_2th, κ_1th, and ν_2th segments. Figure 1 gives a diagramatic representation of nine types of possible contact, where the cross symbol represents the location of the Xnth segment. Considering symmetry, we can put it that the (d)-type is equal to the (b)-type, the (g)-type, to the (c)-type, and the (h)-type, to the (f)-type. Furthermore, the (f)-type can be identified with the (b)-type if X is replaced by $(1-X)$.

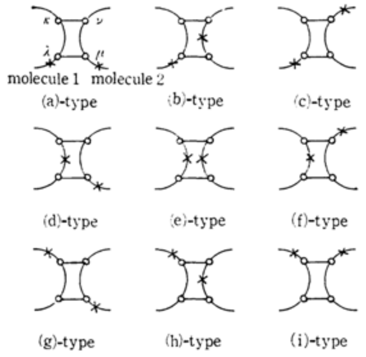

Fig. 1. Diagrams for double contact types.
The cross symbol represents Xnth segment and solid straight lines connect the contact segments.

Similarly, the sums in Eq. (3) may be converted to integrals; the integrations proceed about all types of Fig. 1. Finally, we obtain:

$$A_2 = (N_A n^2/2M^2)[\beta' - (3/2\pi\alpha^2 b^2)^{3/2} n^{1/2}\gamma + \cdots] \qquad (6)$$

with:

$$\begin{aligned}\gamma = {} & (32/15)(7 - 4\sqrt{2})\{X^{5/2}\beta^2{}_{AA} \\ & + (1 - X)^{5/2}\beta^2{}_{BB}\} + (32/15)\{(1 - X)^{3/2} \\ & \times (3X + 2) - 3X^{5/2} + 5X^{3/2} - 2\}\beta^2{}_{AB} \\ & + (16/15)[(1 + X)^2 + (2 - X)^{5/2} \\ & - (2\sqrt{2} - 1)\{X^{5/2} + (1 - X)^{5/2}\} \\ & - 2(\sqrt{2} + 1)]\beta_{AA}\beta_{BB} + (32/15) \\ & \times \{(8\sqrt{2} - 9)(1 - X)^{5/2} + 5(1 - X) \\ & \times (1 - X^{3/2}) - 2(2 - X)^{5/2} - 2X^{5/2} + 4\} \\ & \times \beta_{BB}\beta_{AB} + (32/15)[(8\sqrt{2} - 9)X^{5/2} \\ & + 5X\{1 - (1 - X)^{3/2}\} - 2(1 + X)^{5/2} \\ & - 2(1 - X)^{5/2} + 4]\beta_{AA}\beta_{AB} \end{aligned} \qquad (7)$$

In Eq. (6), β' is again replaced by Eq. (4).

Results and Discussion

The expansion of A_2 in powers of β takes different forms in the second term of the random and block copolymers. In the case of the random copolymer, when the intra-molecular excluded volume effect disappears, the second virial coefficient also vanishes, because the intra-molecular expansion factor, α, is only a function of β'.[1] On the other hand, that of the block copolymer is no longer expressed in terms of β' only; it is now a function of β_{AA}, β_{BB}, and β_{AB}. Thus, even if β_{AA}, β_{BB}, and β_{AB} are selected so as the expansion factor, α, of the block copolymer becomes unity, A_2 does not vanish generally. Therefore, we may predict that the temperature at which A_2 vanishes differs between block and random copolymers. For example, according to Froelich the temperature for the vanishing of A_2 in cyclohexanol is at 68.6°C for the random copolymer and at 81.6°C for a block copolymer which contains 0.5 mol of styrene and 0.5 mol of methyl methacrylate monomers. As the θ temperatures of polystyrene and polymethylmethacrylate in cyclohexanol are 83.5°C and 77.6°C respectively, the values of β_{AA} and β_{BB} are negative and β_{AB} may be positive at 68.6°C. In this special case, in Eq. (4) and Eq. (7), if $\beta_{AA} = \beta_{BB} = -\beta$ and $\beta_{AB} = \beta$, $\beta' = 0$ and $\gamma = 1.497\ \beta^2\ (>0)$. Thus near the θ temperature, the A_2 of the block copolymer is negative at the temperature at which the A_2 of the random copolymer vanishes. In other words, the θ temperature of the block copolymer is higher than that of the random copolymer. This is also qualitatively in agreement with some other experimental results.[2)]

The above calculations have been performed for a simplified model of copolymer; generally real samples of copolymers will have a much more complicated structure. The sequence lengths of A and B monomers, for example, may not be identical with each other. In such a copolymer, the temperature at which A_2 vanishes is influenced by the pistribution of the sequence lengths of A and B monomers. It is difficult to treat the effect of sequence length in a general form, but qualitatively it can be evaluated from the intra-molecular expansion.

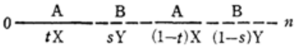

Fig. 2. Diagram for copolymer chain in which A and B segments are successively connected in sandwich with sequence length tX, sY, $(1-t)X$, and $(1-s)Y$ respectively. Solid lines and broken lines represent respectively A and B segments.

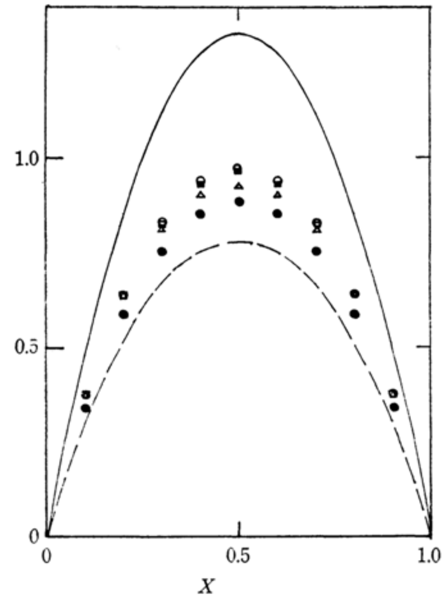

Fig. 3. Plots of α_L^2-1 *versus* X at several t, and s, values in the case of $Z_{AA}=Z_{BB}=0$ and $Z_{AB}=2$ where $Z=(3/2\pi b^2)^{3/2}n^{1/2}\beta$.
Solid line: random copolymer
Broken line: $t=s=1$
White circle: $t=s=1/2$
Filled circle: $t=3/4$, $s=1/4$
Square: $t=1/4$, $s=3/4$
Triangle: $t=s=1/4$ or $t=s=3/4$

Considering a copolymer (Fig. 2) in which A segments (mole fn. X) and B segments (mole fn. Y) are connected successively, sandwiched between the sequence lengths tX, sY, $(1-t)X$, and $(1-s)Y$, the expansion factor of the mean square end-to-end distance, α_L may be written in the form:

$$\langle L^2\rangle/\langle L^2\rangle_0=\alpha_L^2=$$
$$1+(4/3)(3/2\pi b^2)^{3/2}n^{1/2}\beta+\cdots$$

with:

$$\begin{aligned}\beta=\beta_{AA}\{&(tX)^{3/2}+(sY)^{3/2}+(X+sY)^{3/2}\\&+(X-tX)^{3/2}-(tX+sY)^{3/2}\\&-(X+sY-tX)^{3/2}\}+\beta_{BB}\{(sY)^{3/2}\\&+(1-tX)^{3/2}+(X-tX)^{3/2}+(Y-sY)^{3/2}\\&-(X+sY-tX)^{3/2}-(1-tX-sY)^{3/2}\}\\&+\beta_{AB}\{1+(tX+sY)^{3/2}\\&+2(X+sY-tX)^{3/2}+(1-tX-sY)^{3/2}\\&-(tX)^{3/2}-2(sY)^{3/2}-(X+sY)^{3/2}\\&-(1-tX)^{3/2}-2(X-tX)^{3/2}\\&-(Y-sY)^{3/2}\}\end{aligned}$$

In Fig. 3, α_L^2-1 values are plotted as a function of X at several t and s values. From Fig. 3, the expansion factors of the random and block copolymers are the two extremes while those of all other types of copolymers falling between them. It therefore seems reasonable to suggest that the temperature of any copolymer having a different sequence length at which A_2 vanishes is found between the two temperature limits of the random and block copolymers.

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