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# A 'Segregated' Conformation Model of AB-Diblock Copolymers

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A hypothetical model representing the conformation of an AB-diblock copolymer chain was proposed. In the model the two blocks are spatially separated from each other by two parallel planes with the A–B junction point in between so as to form pure A, A–B intermixing and pure B phases. Dimensional parameters of the model were calculated on the basis of the random-flight statistics. It was found that the behavior of the model, which presumably constitute one extreme case of a real block copolymer chain, are qualitatively similar to those of our lattice-walk model proposed previously, and in a certain case they even show quantitative agreement.

## INTRODUCTION

On discussing the conformation of a block copolymer chain in dilute solution, one often refers to the so-called 'segregated' conformation as an alternative to the 'quasi-random coil' conformation, but apparently without clearly defining the model.[1] Here we propose a simple model of 'segregated' chain for an *AB*-diblock copolymer. Figure 1 schematically represents the model: The origin of an orthogonal coordinate

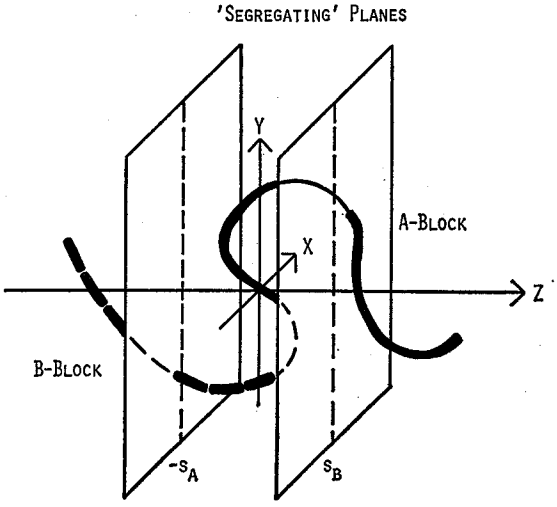


Fig. 1. Schematical representation of 'segregation' model. The *A–B* junction point is at $Z=0$. The *A*- and *B*-blocks are restricted from entering the regions $Z<-s_A$ and $Z>s_B$, respectively.

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$(X, Y, Z)$ is at the $A$–$B$ junction point. The $A$- and $B$-blocks, both obeying the random-flight statistics, are restricted from entering the regions $Z<-s_A$ and $Z>s_B$ ($s_A$ and $s_B \geq 0$), respectively, to form three phases; pure $A$ ($Z>s_B$), $A$–$B$ intermixing ($-s_A<Z<s_B$) and pure $B$ ($Z<-s_A$) phases. Such a model was implied by micro-domain structures of block copolymers in solid[2,3] and in concentrated solution.[4,5]

However we do not intend to propose the model as a plausible one which represents the conformation of a real block copolymer chain in dilute solution: The situation in dilute solution is quite different from those in solid or concentrated solution, where intermolecular interactions are predominantly important. We should rather emphasize that the model is utterly at variance with reality. Nevertheless, it is of certain significance to examine its statistical properties, since the random-flight model (without 'segregating' planes) and the present one would constitute the two extremes beyond which any real block copolymer chain would never exist. Moreover, analysis of the model should offer some basic information about the properties of individual block copolymer chains in bulk and in concentrated solution as well. The implications of the model have been utilized in our previous articles[6~8] for investigation of dilute block copolymer solutions.

**Statistics of Random-Flights near an Impermeable Plane**

Recently one of us[9] generalized the statistics[10~13,6] of random-flight chain which is bound on or near an impermeable, noninteracting plane with one end ('tail-like' chain) or both ends ('loop-like' chain). A tail-like chain[9] forms the basis of the present block copolymer model: Let $n+1$ be the number of segments (serially numbered from 0 to $n$) of a chain (chain size$=n$). The normalized probability density $P_n(Z_i, Z_j, Z_k, \ldots, Z_m, Z_n/Z_0)$ of finding a series of segments ($i<j<k<\cdots<m<n$) at respective distances $(Z_i, Z_j, Z_k, \ldots, Z_m, Z_n)$ from the plane with the first (0-th) segment being fixed at $Z_0$ ($\geq 0$) is given by

$$P_n(Z_i, Z_j, Z_k, \ldots, Z_m, Z_n/Z_0) = [\mathrm{Erf}\ (\beta_{0n}^{1/2} Z_0)]^{-1}(Q_{ij}Q_{jk}\cdots Q_{mn}) \tag{1}$$

$$Q_{pq} = (\beta_{pq}/\pi)^{1/2}\{\exp[-\beta_{pq}(Z_p - Z_q)^2] - \exp[-\beta_{pq}(Z_p + Z_q)^2]\} \tag{2}$$

$$\beta_{pq} = 3/[2(q-p)b^2],\ p<q \tag{3}$$

$$\mathrm{Erf}\ (x) = (2/\pi^{1/2})\int_0^x \exp(-t^2)\,dt \tag{4}$$

with $b^2$ being the mean-square segment length. When the position of the last ($n$-th) segment is not specified, $Q_{mn}$ in Eq. (1) can be replaced by Erf $(\beta_{mn}^{1/2} Z_m)$. The overall (normalized) distribution of segments $\rho_n(Z/Z_0)$ for such a chain is given by

$$\begin{aligned}\rho_n(Z/Z_0) &= (n+1)^{-1}\sum_i P_n(Z/Z_0) \\ &= [2\pi^{1/2}/\mathrm{Erf}\ (\beta^{1/2}Z_0)]\,[p_1\,\mathrm{Erf}\ (p_1) + p_2\,\mathrm{Erf}(p_2) - p_3\,\mathrm{Erf}\ (p_3) \\ &\quad - p_4\,\mathrm{Erf}\ (p_4) + \pi^{-1/2}(e^{-p_1^2} + e^{-p_2^2} - e^{-p_3^2} - e^{-p_4^2})] \\ &\quad p_1 = \beta^{1/2}|Z - Z_0|, \qquad p_2 = \beta^{1/2}(2Z + Z_0), \\ &\quad p_3 = \beta^{1/2}(Z + Z_0), \qquad p_4 = \beta^{1/2}(|Z - Z_0| + Z),\end{aligned} \tag{5}$$

$$\beta=\beta_{0n}=3/(2nb^2)$$

With Eqs. (1) and (5), we calculate various moments of the segment distribution, which are necessary to construct our block copolymer model.

The first and second moments $<Z_n>_{(0)}$ and $<Z_n^2>_{(0)}$ of the last segment about the first segment are respectively given by

$$<Z_n>_{(0)}=\int_0^\infty (Z_n-Z_0)P_n(Z_n/Z_0)\,dZ_n=Z_0\{[\mathrm{Erf}\ (\beta^{1/2}Z_0)]^{-1}-1\} \tag{6}$$

$$\lim_{Z_0\to 0}<Z_n>_{(0)}=(\pi/\beta)^{1/2}/2 \tag{6'}$$

and

$$\begin{aligned}<Z_n^2>_{(0)}&=\int_0^\infty (Z_n-Z_0)^2P_n(Z_n/Z_0)\,dZ_n\\&=(2\beta)^{-1}+2Z_0^2\{1-[\mathrm{Erf}(\beta^{1/2}Z_0)]^{-1}\}\\&\quad+Z_0/[(\pi\beta)^{1/2}\exp(\beta Z_0^2)\ \mathrm{Erf}\ (\beta^{1/2}Z_0)]\end{aligned} \tag{7}$$

$$\lim_{Z_0\to 0}<Z_n^2>_{(0)}=\beta^{-1} \tag{7'}$$

The first and second moments $<Z>_{(0)}$ and $<Z^2>_{(0)}$ of the segment distribution about the first segment are given by

$$<Z>_{(0)}=\int_0^\infty (Z-Z_0)\rho_n(Z/Z_0)\,dZ \tag{8}$$

$$\longrightarrow(3/8)\ (\pi/\beta)^{1/2},\ \text{as}\ Z_0\longrightarrow 0 \tag{8'}$$

$$<Z^2>_{(0)}=\int_0^\infty (Z-Z_0)^2\rho_n(Z/Z_0)\,dZ \tag{9}$$

$$\longrightarrow 7/(12\beta),\ \text{as}\ Z_0\longrightarrow 0 \tag{9'}$$

Because of their complexity, analytical results of the above integrations are not given here except those for $Z_0\to 0$. The second moment $<Z^2>_{(G)}$ of segment distribution about the center of mass is given by

$$<Z^2>_{(G)}=(n+1)^{-2}\sum_{i<j}\sum\int_0^\infty (Z_i-Z_j)^2P_n(Z_i,Z_j/Z_0)\,dZ_i\,dZ_j \tag{10}$$

Equation (10) has been calculated numerically by a Monte Carlo method.[9]

Table I lists the values of $<Z_n>_{(0)}$, $<Z_n^2>_{(0)}$, $<Z>_{(0)}$, $<Z^2>_{(0)}$ and $<Z^2>_{(G)}$ for various values of $Z_0$. Table II lists the corresponding values for 'loop-like' chains[9] just for the sake of comparison, although they are not necessary for the present purpose.

## Average Dimensions of 'Segregation' Model

The results of tail-like chains can be readily applied for our block copolymer model. Here we calculate various dimensional parameters of the model from the data given in Table I. We let $N_K$ be the number of $K$-type segments in a block copolymer chain, $b_k^2$ the mean-square length of $K$-type segment ($K=A$ or $B$), and $x=1-y=N_A/(N_A+N_B)$ the composition of the block copolymer chain.

The mean-square radius of gyration $<S^2>_K$ of the $K$-block ($K=A$ or $B$) is given as the sum of $<Z^2>_{(G),K}$ and the other two components $<X^2>_{(G),K}$ and $<Y^2>_{(G),K}$,

Table I. Various Moments of Segment Distribution for Tail-Like Chains[a]

| $\beta^{1/2}Z_0$ | $\beta^{1/2}<Z_n>_{(0)}$ | $\beta<Z_n^2>_{(0)}$ | $\beta^{1/2}<Z>_{(0)}$ | $\beta<Z^2>_{(0)}$ | $10\beta<Z^2>_{(G)}$ |
|---|---|---|---|---|---|
| 0 | 0.886 | 1.000 | 0.665 | 0.583 | 0.905 |
| 0.1 | 0.789 | 0.893 | 0.571 | 0.467 | 0.865 |
| 0.2 | 0.698 | 0.708 | 0.489 | 0.379 | 0.827 |
| 0.3 | 0.613 | 0.603 | 0.417 | 0.314 | 0.798 |
| 0.4 | 0.534 | 0.522 | 0.353 | 0.267 | 0.773 |
| 0.5 | 0.461 | 0.461 | 0.298 | 0.234 | 0.754 |
| 0.6 | 0.394 | 0.419 | 0.249 | 0.212 | 0.737 |
| 0.7 | 0.333 | 0.391 | 0.206 | 0.199 | 0.727 |
| 0.8 | 0.278 | 0.376 | 0.169 | 0.193 | 0.722 |
| 0.9 | 0.229 | 0.371 | 0.137 | 0.192 | 0.720 |
| 1.0 | 0.187 | 0.373 | 0.110 | 0.194 | 0.722 |
| 1.1 | 0.150 | 0.381 | 0.087 | 0.198 | 0.725 |
| 1.2 | 0.118 | 0.392 | 0.068 | 0.204 | 0.730 |
| 1.3 | 0.092 | 0.406 | 0.052 | 0.211 | 0.738 |
| 1.4 | 0.070 | 0.420 | 0.040 | 0.217 | 0.751 |
| 1.5 | 0.053 | 0.434 | 0.029 | 0.223 | 0.765 |
| 1.6 | 0.039 | 0.446 | 0.022 | 0.229 | 0.779 |
| 1.7 | 0.028 | 0.459 | 0.015 | 0.234 | 0.791 |
| 1.8 | 0.020 | 0.469 | 0.011 | 0.238 | 0.802 |
| 1.9 | 0.014 | 0.477 | 0.008 | 0.241 | 0.810 |
| 2.0 | 0.009 | 0.483 | 0.005 | 0.244 | 0.819 |
| 2.1 | 0.006 | 0.488 | 0.003 | 0.245 | 0.827 |
| 2.2 | 0.004 | 0.492 | 0.002 | 0.247 | 0.831 |
| 2.3 | 0.003 | 0.494 | 0.001 | 0.248 | 0.833 |
| $\infty$ | 0 | 0.5 | 0 | 0.25 | 0.833 |

(a) $\beta=3/(2nb^2)$; $Z_0$=normal to the surface distance of the first segment; $<Z_n>_{(0)}$ and $<Z_n^2>_{(0)}$=first and second moments of the last segment about the first segment; $<Z>_{(0)}$ and $<Z^2>_{(0)}$=first and second moments of segment distribution about the first segment; $<Z^2>_{(G)}$=second moment of segment distribution about the center of mass.

(b) Correct to $\pm 1\%$.

both being $N_K b_k^2/18$. Obviously $<Z^2>_{(G),K}$ is given by $<Z^2>_{(G)}$ of Eq. (10) with its $n$, $b$ and $Z_0$ being replaced by $N_K$ $b_K$ and $s_K$, respectively. The mean-square end-to-end distance $<R^2>_K$ of the $K$-block is obtained similarly from $<Z_n^2>_{(0)}$ of Eq. (7).

The (geometrical) mean-square radius of gyration $<S^2>$ of a block copolymer chain (or any copolymer chain) is given by

$$<S^2>=x^2<S^2>_A+y^2<S^2>_B+x\,y<S^2>_{AB} \tag{11}$$

$$<S^2>_{AB}=(N_A N_B)^{-1}\sum_i\sum_j<r_{ij}^2> \tag{12}$$

where $<r_{ij}^2>$ is the mean-square distance between the $i$- and $j$-th segments belonging to the $A$- and $B$-blocks, respectively. Obviously for the 'segregation' model the $Z$-component $<S_Z^2>_{AB}$ of $<S^2>_{AB}$ is given by

Table II. Various Moments of Segment Distribution for Loop-Like Chains[a]

| $\beta^{1/2}Z_0$ | $\beta^{1/2}\langle Z\rangle_{(0)}$ | $\beta\langle Z^2\rangle_{(0)}$ | $10\beta\langle Z^2\rangle_{(G)}$[b] |
|---|---|---|---|
| 0 | 0.443 | 0.2500 | 0.443 |
| 0.1 | 0.351 | 0.1764 | 0.417 |
| 0.2 | 0.274 | 0.1274 | 0.379 |
| 0.3 | 0.209 | 0.0964 | 0.368 |
| 0.4 | 0.155 | 0.0785 | 0.364 |
| 0.5 | 0.110 | 0.0701 | 0.366 |
| 0.6 | 0.075 | 0.0679 | 0.372 |
| 0.7 | 0.048 | 0.0694 | 0.381 |
| 0.8 | 0.029 | 0.0726 | 0.392 |
| 0.9 | 0.016 | 0.0760 | 0.402 |
| 1.0 | 0.008 | 0.0789 | 0.407 |
| 1.1 | 0.004 | 0.0809 | 0.413 |
| 1.2 | 0.002 | 0.0821 | 0.416 |
| 1.3 | 0.001 | 0.0828 | 0.417 |
| 1.4 | 0.000 | 0.0831 | 0.417 |
| $\infty$ | 0 | 0.0833 | 0.417 |

(a) Parameters are as in Table I ($Z_n=Z_0$).
(b) Correct to $\pm 1\%$.

$$\langle S_Z^2\rangle_{AB}=\langle Z^2\rangle_{(0),A}+\langle Z^2\rangle_{(0),B}+2\langle Z\rangle_{(0),A}\langle Z\rangle_{(0),B} \tag{13}$$

where $\langle Z\rangle_{(0),K}$ and $\langle Z^2\rangle_{(0),K}(K=A \text{ or } B)$ can be given, respectively, by $\langle Z\rangle_{(0)}$ of Eq. (8) and $\langle Z^2\rangle_{(0)}$ of Eq. (9). The other two components $\langle S_X^2\rangle_{AB}$ and $\langle S_Y^2\rangle_{AB}$ are both $(N_Ab_A^2+N_Bb_B^2)/6$. The mean-square distance $\langle G^2\rangle$ between the centers of mass of the two blocks is obtained from

$$\langle G^2\rangle=\langle S^2\rangle_{AB}-\langle S^2\rangle_A-\langle S^2\rangle_B \tag{14}$$

Similarly the mean-square end-to-end distance $\langle R^2\rangle$ of the whole chain is obtained from $\langle Z_n\rangle_{(0)}$ and $\langle Z_n^2\rangle_{(0)}$.

## Numerical Results and Discussion

Figure 2 shows the overall density distribution of segments for the 'segregation' model (cf. Eq. (5)). We have set $N_A=N_B=N$, $b_A=b_B=b$ and $s_A=s_B=s$. Hence, $2s$ is the thickness of the $A$–$B$ intermixing phase. When $s=0$, the $A$- and $B$-blocks are completely segregated in space by a plane. Thus we call it a 'complete segregation' model. While if $s\to\infty$, the model is no other than two random-flight chains connected at the ends: We call it a 'random-flight' model. Figure 2a is the distribution curve for the 'complete segregation' model ($s=0$). For small nonzero $s$, the curve exhibits three peaks (Figure 2b). For larger $s$, the distribution becomes a sigle-peaked curve approaching to that of the random-flight model, which of cource is equivalent to that of a random-flight chain of size $2N$ (Figure 2c).[9]

In Figure 3, the dimensional parameters are plotted against $s$ ($=s_A=s_B$), half the thickness of the intermixing phase. Again, we have set $N_A=N_B=N$ (or $x=y=1/2$) and $b_A=b_B=b$. As indicated in the figure the values are divided by the corresponding values for the random-flight model so that they all approach to unity

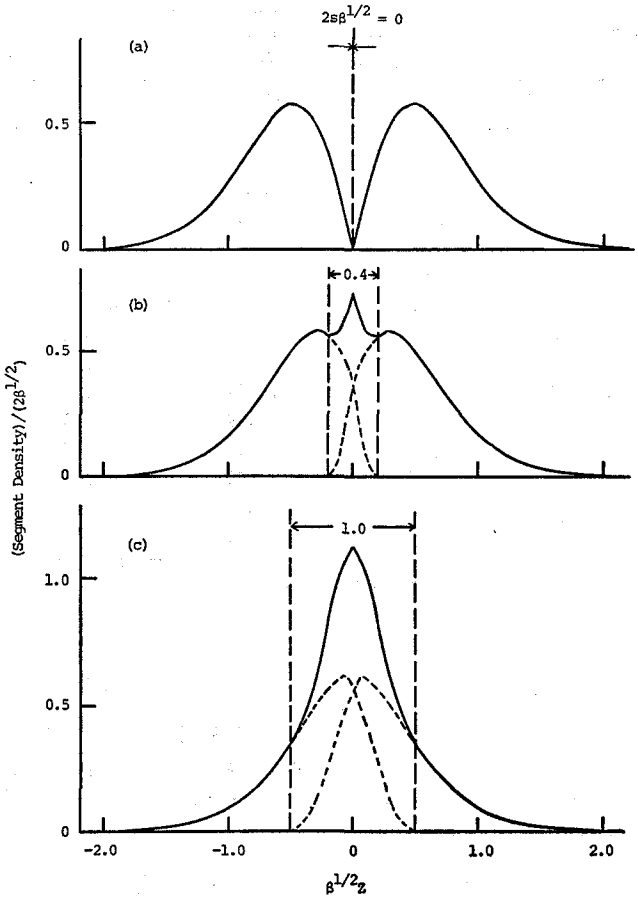


Fig. 2. Density distribution of segments in 'segregation' model with $N_A=N_B=N$, $b_A=b_B=b$ and $s_A=s_B=s$: The thickness of the $A$–$B$ intermixing phase $2s$ is (a) 0, (b) $0.4\beta^{-1/2}$ and (c) $1.0\beta^{-1/2}$; $\beta=3/(2Nb^2)$. Broken curves refer to individual blocks.

as $s$ goes to infinity. In view of microdomain structures in solid block copolymers,[2,3] it may be of little sense to consider an $s$ larger than, say 0.2 or $0.3(Nb^2)^{1/2}$. However, we have shown here the curves covering a wider range of $s$ just to clarify the behavior of the model. It is especially noteworthy that for small $s$ the ratio $\alpha_G^2(=\langle G^2\rangle/\langle G^2\rangle_f$, where throughout the paper subscript '$f$' refers to the random-flight model) is the largest of all, becoming as large as 2.54 for $s=0$. While the ratio $\alpha_K^2(=\langle S^2\rangle_K/\langle S^2\rangle_{K,f}$, $K=A$ or $B$) is close to unity over the entire range of $s$ (*i.e.*, $0.95_4\leq\alpha_K^2\leq 1.02_9$).[14] As $s$ approaches to zero, the two blocks obviously become more and more apart from each other as indicated by large $\alpha_G^2$, and at the same time, the density distribution of segments of individual blocks becomes more and more asymmetrical (see Figure 2). We note that $\alpha_K^2\sim 1.0$ for all $s$, while $\alpha_{RK}^2(=\langle R^2\rangle_K/\langle R^2\rangle_{K,f})\to 4/3$ as $s\to 0$ (cf. Figure 3). In this connection, our previous results of a Monte Carlo simulation on a lattice-walk model[8] are interesting: They showed that the lattice-walk model behaves much like the present model qualitatively, *i.e.*, $\alpha_G^2>\alpha_{RK}^2>\alpha_K^2\sim 1$.

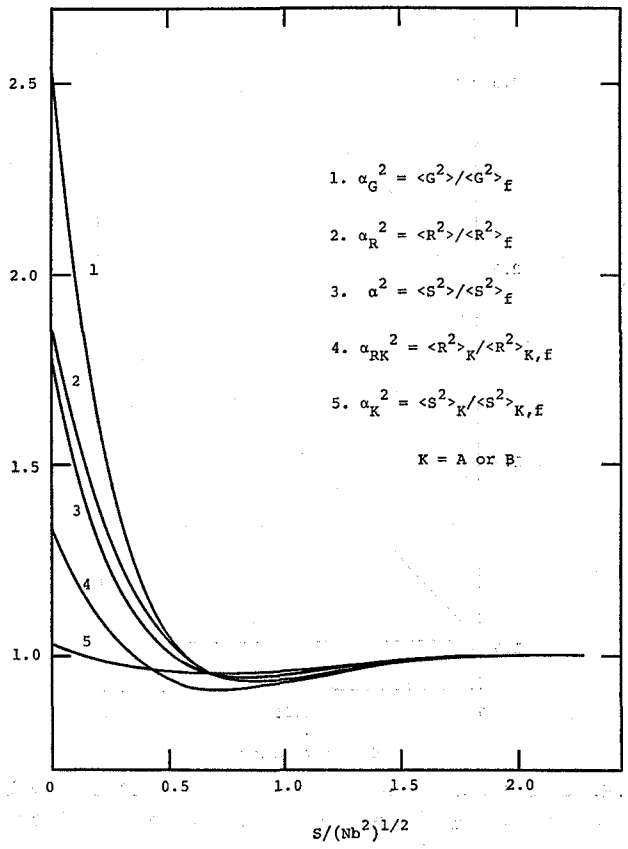


Fig. 3. Plots of dimensional parameters of 'segregation' model with $N_A=N_B=N$, $b_A=b_B=b$ and $s_A=s_B=s$ versus $s/(Nb^2)^{1/2}$; $\alpha$'s are as indicated in the figure.

By setting $s\sim(Nb^2)^{1/2}/4$, we see that the two models fit together almost quantitatively (as far as the dimensional parameters are concerned). This might be the indication that a real block copolymer chain assumes, in a certain occasion, a conformation which is close to the 'segregation' model. However, we still feel that the present model is unrealistic, because it is too artificial to set up segregating planes within a block copolymer chain (in dilute solution), and to use $s$ as a parameter representing the extent of segregation. It is more natural and less ambiguous to characterize the chain conformation by the dimensional parameters such as $\alpha_G^2$ and $\alpha_K^2$ rather than by the terms like 'segregation' or 'quasi-random coil'.[8]

In Figure 4, the ratios $\alpha^2$ are plotted against composition $x$ or $y$. Here we have set $s_A=s_B=0$ and $b_A=b_B=b$. Naturally the ratios $\alpha_K^2$ and $\alpha_{RK}^2$ are independent of $x$. It is noted that the variations of $\alpha_G^2$, $\alpha_R^2$ and $\alpha^2$ with $x$ (or $y$) are rather trivial, unless $x$ (or $y$) is small. This also coincides with the behavior of the lattice-walk model.[8]

Aside from the question of its reality, the present model is important in several aspects. For example, we can safely say that the $\alpha_G^2$ value 2.54 is the upper limit that a real block copolymer chain can hardly reach. Such information is useful indeed.[6~8,14] The model should become a better approximation to block copolymers

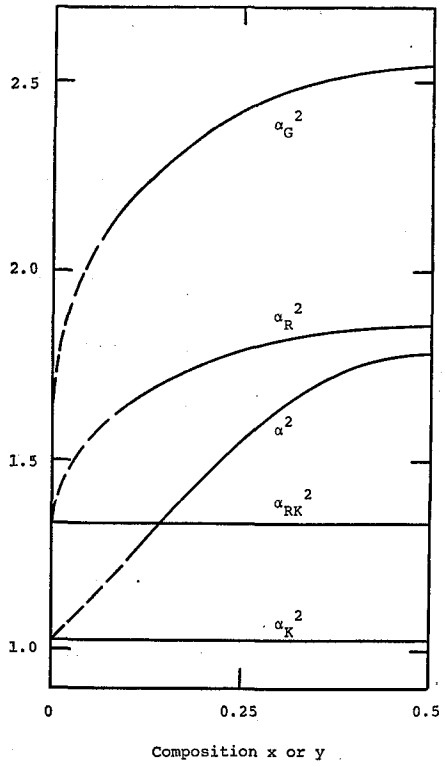


Fig. 4. Plots of dimensional parameters of 'segregation' model with $s_A=s_B=0$ and $b_A=b_B=b$ versus composition $x$ or $y$; $\alpha$'s are as in Figure 3.

in solid or concentrated solution. Due to the recent progress in experimental techniques, it will eventually become possible to investigate conformation of an individual block copolymer chain even in solid by, for example, neutron scattering method.[15]

Finally some words should be added about the excluded volume effects which we have neglected here. A perturbation calculation[9] indicates that the extent of expansion of a sidechain (block) due to the excluded-volume effects within itself is approximately equal to that of the homopolymer equivalent to the sidechain. This approximation should be valid as far as the *A–B* intermixing phase is narrow so that a sidechain of one kind is not much perturbed by the other and *vice versa.*

**ACKNOWLEDGMENT**

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## REFERENCES AND NOTES


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

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(14) In references 6–8, a 'segregation' model corresponding to the present model with $s=0$ was presented or referred to. This model is based on an approximately correct distribution equivalent to that of Meier[12,13] instead of the correct one given in references 9, 12 and here, thereby giving $\alpha_K^2=1.02$ and $\alpha_G^2=2.19$. These values are not far from the correct ones given here.

(15) A trial of such measurements was made using a styrene-butadiene diblock copolymer: T. Tanaka and G. Allen, unpublished experiments.