mayer et al.[8] also seem to indicate that the interactions between unlike monomer units are repulsive. They found the interaction parameter χ_1 of the binary S–MMA copolymers to be less than the weighted sum of homopolymer interaction parameters with the same pure solvent. Interpretation of this finding in terms of χ_{AB}, the parameter characterizing the interaction between monomer units A and B in a copolymer chain, leads to the conclusion that the interactions between S and MMA units are repulsive.

In the case of S–MMA copolymers at least, it appears that calculation of isolated chain conformational entropies and energies provides a molecular basis for understanding both the sequence distribution–T_g effects (a solid state property) and the dilute solution behavior of these copolymers.

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Biellipsoidal Model for AB Block Copolymers. Excluded Volume Effect in Isolated Molecules

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ABSTRACT: A new smooth density model is proposed to account for the intramolecular excluded volume effect in dilute solutions of AB block copolymers. Each block is approximated by an ellipsoidal Gaussian segment cloud which is allowed to interact with itself as well as its neighbor. The mean molecular properties, calculated by Monte Carlo method, are the overall mean square radius $\langle S^2 \rangle$, the mean square radii of the two blocks $\langle S_I^2 \rangle$, the mean square distance between the centers of mass of the blocks $\langle G^2 \rangle$, the mean square distances between the joint-segment and the centers of each block $\langle G_I^2 \rangle$ as well as the angle $\langle \theta \rangle$ between these two vectors, and the number of AB contacts N_{AB}. Applied to a homopolymer and to a block copolymer in a theta solvent for its blocks, the model agrees well with previously established theories. More complex cases studied include a block copolymer in a good solvent and a block copolymer in a preferential solvent. The model permits a unified view of both homopolymers and block copolymers. The molecular shape emerging from this model can be characterized as "arrowhead-like." The process of segregation is not unique to block copolymers. It is unlikely that it would result in a linear dumbbell conformation or in a spherically symmetrical core-in-shell conformation. The model is capable of reproducing the intramolecular transition. It is doubtful that AB repulsions increasing from zero alone could bring about a transition between the Gaussian and "segregated" conformations. The essential feature of the transition is a collapse caused by attractive forces, either a volume collapse of one or both blocks or an orientational collapse of the two blocks.

(I) Introduction

Until recently, progress in understanding the dilute solution behavior of block copolymers has been highly unsatisfactory, particularly for the following reasons:

(1) No theoretical basis was available to quantitatively explain the (often anomalous) experimental data. Therefore in many cases their interpretation has been confined to qualitative terms of either "segregated" or "pseudo-Gaussian" conformations which were considered as two distinct extreme cases.[2,3] The former one implies a bipolar geometry, with each block occupying a distinct region of space and almost no contact between the two blocks. Entropy loss in the segregated conformation is compensated for by a reduction in the number of energetically unfavorable heterocontacts A–B. On the other hand, a chain with the pseudo-Gaussian conformation is believed to have virtually the same conformation as a homopolymer, i.e., unaffected by the presence of A–B contacts. It is not surprising that the assumption of the existence of more or less only two distinct conformations then provoked discussions about a possible intramolecular transition from one to the other, in particular since some experimental data do suggest such a behavior.[4–7] It seems obvious that this is an over-simplification of the problem, since in reality the finite polymer chains can assume many other conformations between or beyond these two special cases which should be adequately taken into account. Furthermore, considerable controversy exists regarding the interpretation of data in terms of these two distinct conformations.[8,9]

(2) In the absence of any other theories, interpretations of experimental data have often been based[2a,3a] on the perturbation theory for the radius of gyration of block copolymer molecules worked out by Froelich and Benoit.[10] But it is well known from the homopolymer field[11] that the practical applicability of perturbation theory is severely limited to the very neighborhood of the theta point which, in most block copolymer systems, is far away from the experimental con-

ditions employed. Thus it is difficult to obtain valid interpretations in this way.

(3) In many papers a single-polymer approach has been adopted, i.e., the data on copolymers have been analyzed in a manner identical with that used for homopolymers with effective parameters assumed to be linear combinations of block parameters.[3b,10,12–14] The motivation probably rests with the perturbation results where such a method is valid, but in general this simple behavior cannot be expected. Similarly, attempts have been made to experimentally locate the theta temperature for the block copolymer system and to relate experimental data to it, as has been customarily done for homopolymers.[10,15,16] Yet the occurrence of a *true* theta system for block copolymers has to be extremely rare. For homopolymers, the theta state has been traditionally associated with the vanishing of the segment–segment binary cluster integral β.[11,17] Analogously, in a true theta system for block copolymers all three parameters β_{AA}, β_{BB}, and β_{AB} should become zero simultaneously which, because of the chemically different nature of the A and B units, is very unlikely at any temperature.

Often the above-cited authors recognized shortcomings in their treatments, yet were faced with the absence of practical alternatives.

The first nonperturbative statistical treatment of a single AB block copolymer molecule was given by Pouchlý, Živný, and Sikora (PZS).[18a] As a model of the copolymer molecule they took two spherical smooth-density segment clouds, joined them together (assuming that the probability density for an end segment of the block is no different from any other segment), and computed the mutual block interactions in the manner of Flory–Krigbaums' treatment for the second virial coefficient.[19a] The extent of block segregation (or interpenetration) was then measured by the number of AB contacts, N_{AB}. More recently[18b] they presented a perturbation theory for N_{AB} and an approximate closed form expression using the Casassa–Markovitz method.[19b] In both papers, N_{AB} was found to be a smooth function of excluded volume parameters with no indication of a sudden conformational transition.

Tanaka has examined several different models for block copolymer molecules.[20] The effect of repulsive forces between A and B units on the segment density distribution has been simulated by a random walk biased by the presence of an absorbing planar wall. He concludes that neither the Gaussian nor the completely segregated state accurately accounts for the properties of diblock copolymers of poly(methyl methacrylate) and polystyrene.

The only theory of block copolymers which indicates an intramolecular phase transition is due to Edwards.[21] Using a self-consistent-field method for the special case $\beta_{AB} = -\beta_{AA} = -\beta_{BB}$ he is able to show that at a certain "critical" value of the pseudopotential parameter (or the chain length) there suddenly appears a segregated dumbbell conformation which has a lower free energy than the original Gaussian, and hence is the stable form.

Recently Tanaka, Kotaka, and Inagaki (TKI)[22] have presented computer studies of AB block copolymer conformations. They generated random walks permitting self-intersections within each block, but excluding heterocontacts between the blocks. Introducing nearest neighbor interactions between AB segments, they follow the size and shape of the molecule as the interblock pseudopotential changes. Since intrablock interactions are not included, their results correspond to theta state conditions for each block. More general results have been reported by Birshtein, Skvortsov, and Sariban.[23]

It was our belief that some insight into this complex problem might be gained by applying the ellipsoidal model which yielded good results for homopolymers.[24] As compared to the similar smooth-density, but spherically symmetrical, model of PZS,[18a] our approach appears to be more realistic in respecting the strong asymmetry of each block as well as the high probability of finding the end segments near the tips of the cigar-shaped blocks. These two features permit a more rapid decrease in AB block overlap with changes in relative block orientations. On the other hand, our calculations require much less computer time than the more rigorous Monte Carlo calculations of TKI[22] therefore allowing us to investigate the copolymer behavior under general conditions.

In the next section we describe the biellipsoidal smooth-density model (BEM) for the AB block copolymer molecule. In section III the Monte Carlo method for computing mean values is outlined, followed by results and discussion in sections IV and V.

(II) The Biellipsoidal Model of a Block Copolymer Molecule (BEM)

Random-flight chains are often employed as models of polymer chains. The instantaneous segment density distribution of such a chain is not spherically symmetric, but more aptly described as ellipsoidal.[24–27] In the present study the individual polymer blocks are approximated by ellipsoidal clouds of segments. Each segment cloud is characterized by the ordered squared principal components of the radius of gyration, $L_1^2 \leq L_2^2 \leq L_3^2$, and by the coordinates (relative to the principal axes of inertia) of one end segment of the random-flight chain it represents. For the A block with components L_{A1}, L_{A2}, and L_{A3}, and its center of mass located at the origin of a fixed Cartesian system (see Figure 1), the segment density is assumed to have the form of a three-dimensional Gaussian

$$\rho_A(\Omega,\mathbf{x}|\mathbf{L}_A) = N_A(\pi^{-3}|\mathbf{D}_A|)^{1/2} \exp[-(\mathbf{Mx})^T\mathbf{D}_A(\mathbf{Mx})] \quad (1)$$

where N_A is the number of segments in the A block, Ω specifies the orientation of the principal axis of the A block with respect to the fixed frame as described by the rotation matrix $\mathbf{M}$ of Eulerian angles,[24] and $\mathbf{D}_A$ is the diagonal matrix, $(\mathbf{D}_A)_{ii} = (2L_{Ai}^2)^{-1}$, $i = 1, 2, 3$. To simulate the block copolymer molecule, two such segment clouds with principal components $\mathbf{L}_A$ and $\mathbf{L}_B$, and end vectors $\mathbf{G}_A$ and $\mathbf{G}_B$, are joined by their ends. As only relative orientations are important, it is convenient to align the Cartesian frame with the principal axes of the B block. Then the segment density for the B block is

$$\rho_B(0,\mathbf{G} - \mathbf{x}|\mathbf{L}_B) = N_B(\pi^{-3}|\mathbf{D}_B|)^{1/2} \exp[-(\mathbf{G} - \mathbf{x})^T\mathbf{D}_B(\mathbf{G} - \mathbf{x})] \quad (2)$$

where $\mathbf{G} = \mathbf{MG}_A - \mathbf{G}_B$, the vector between the centers of mass of the blocks, and N_B and $\mathbf{D}_B$ have meanings analogous to N_A and $\mathbf{D}_A$. Conformations corresponding to different block orientations can now be generated by varying Ω while the end vectors $\mathbf{G}_A$ and $\mathbf{G}_B$, fixed relative to the principal axes of the respective blocks, take care of keeping the block ends together.

A pseudopotential of mean force is adopted to account for block interactions. Three distinct contributions may be identified: V_{II}, I = A, B, result from interactions *within* individual blocks, and V_{AB} results from heterocontacts *between* different blocks. The pseudopotential V_{II}, corresponding to homopolymer self-interactions, is a generalization of the expression used for spherical smooth-density treatments[11]

$$V_{II}/kT = \tfrac{1}{2}\beta_{II}\int[\rho(\mathbf{x}|\mathbf{L}_I)]^2\,d\mathbf{x} \qquad (I = A, B) \qquad (3)$$

where β_{II} is the binary cluster integral for a pair of segments I. Using the ellipsoidal segment density of eq 1, the intrablock potential of eq 3 becomes[24]

$$V_{II}/kT = \beta_{II}N_I^2\pi^{-3/2}/(16L_{I1}L_{I2}L_{I3}) \qquad (I = A, B) \quad (4)$$

The important quantity affecting the conformation of the copolymer molecule is the heterosegment pseudopotential V_{AB}. In addition to depending on the sizes and shapes of the two blocks through $\mathbf{L}_A$ and $\mathbf{L}_B$, V_{AB} depends on their relative orientation Ω, as well as on the positions of the ends $\mathbf{G}_A$ and $\mathbf{G}_B$. By analogy with eq 3, the pseudopotential for the interactions between the A and B blocks is assumed to be

$$V_{AB}/kT = \beta_{AB}\int \rho_A(\Omega,\mathbf{x}|\mathbf{L}_A)\rho_B(0,\mathbf{G}-\mathbf{x}|\mathbf{L}_B)\,d\mathbf{x} \tag{5}$$

where β_{AB} is the binary cluster integral for a pair of segments A and B. Introducing the segment densities of eq 1 and 2, the integration in eq 5 yields[24]

$$\frac{V_{AB}}{kT} = N_A N_B \beta_{AB}\left(\frac{|\mathbf{D}_A||\mathbf{D}_B|}{\pi^3|\mathbf{A}|}\right)^{1/2} \exp[-\mathbf{G}^T\mathbf{P}\mathbf{G}] \tag{6}$$

where $\mathbf{A} = \mathbf{D}_B + \mathbf{M}^T\mathbf{D}_A\mathbf{M}$ and $\mathbf{P} = \mathbf{D}_B - \mathbf{D}_B{}^T\mathbf{A}^{-1}\mathbf{D}_B$.

Distance and composition variables can be serviceably redefined in terms of reduced quantities by introducing the segment length σ_I, the distance parameter R^2 equal to the average mean square end-to-end distance of a block in the theta state,

$$R^2 = (N_A\sigma_A{}^2 + N_B\sigma_B{}^2)/2 \tag{7a}$$

the composition variables x_A and x_B,

$$x_A = 1 - x_B = \tfrac{1}{2}N_A\sigma_A{}^2/R^2 \tag{7b}$$

and the reduced square principal components and end vectors

$$\Lambda_I = \mathbf{L}_I/(N_I\sigma_I{}^2)^{1/2} \tag{7c}$$

$$\Gamma_I = \mathbf{G}_I/(N_I\sigma_I{}^2)^{1/2} \tag{7d}$$

The relations between the various reduced and unreduced quantities of eq 6 then become

$$\mathbf{D}_I{}^r = R^2\mathbf{D}_I,\ (\mathbf{D}_I{}^r)_{ii} = (4x_I\Lambda_{Ii}{}^2)^{-1} \tag{7e}$$
$$I = A, B;\ i = 1, 2, 3$$

$$\mathbf{G}^r = R^{-1}\mathbf{G} = 2^{1/2}(x_A{}^{1/2}\mathbf{M}\boldsymbol{\Gamma}_A - x_B{}^{1/2}\boldsymbol{\Gamma}_B) \tag{7f}$$

$$\mathbf{A}^r = \mathbf{D}_B{}^r + \mathbf{M}^T\mathbf{D}_A{}^r\mathbf{M} \tag{7g}$$

$$\mathbf{P}^r = \mathbf{D}_B{}^r - \mathbf{D}_B{}^{rT}(\mathbf{A}^r)^{-1}\mathbf{D}_B{}^r \tag{7h}$$

In terms of reduced variables and "block" parameters Z_{IJ}, the intrablock potential is

$$V_{II}/kT = Z_{II}(2/3)^{3/2}(16\Lambda_{I1}\Lambda_{I2}\Lambda_{I3})^{-1} \qquad (I = A, B) \tag{8}$$

where $Z_{II} = [3/(2\pi\sigma_I{}^2)]^{3/2}\beta_{II}N_I{}^{1/2}$ as usual, while the heterocontact potential is given by

$$V_{AB}/kT = Z_{AB}(2/3)^{3/2} \times (|\mathbf{D}_A{}^r||\mathbf{D}_B{}^r|/|\mathbf{A}^r|)^{1/2}\exp(-\mathbf{G}^{rT}\mathbf{P}^r\mathbf{G}^r) \tag{9}$$

where the dimensionless parameter $Z_{AB} = [(3/(2\pi R^2)]^{3/2}\cdot N_A N_B \beta_{AB}$ has been introduced. Sometimes it will be convenient to use "molecular" parameters z_{IJ} referred to the entire molecule, where $z_{II} = Z_{II}(N/N_I)^{1/2}$, $z_{AB} = Z_{AB}N^2/(2^{3/2}N_A N_B)$, and $N = N_A + N_B$.

The complete pseudopotential V for the block copolymer molecule, consisting of the blocks of given dimensions and relative orientation, is obtained by combining contributions from inter- and intrablock segment contacts:

$$V/kT = (V_{AA} + V_{BB} + V_{AB})/kT \tag{10}$$

Mean values of molecular properties are then found by integration over all possible orientations and Monte Carlo averaging over the ensemble as described in the next section.

The present study is concerned with the "high molecular weight limit" of block copolymer behavior, where it can be assumed that the reduced quantities Λ_I and Γ_I are independent of the molecular weight of the blocks. The molecular weight M of the copolymer at a given block composition x_A thus affects only the z parameters which are proportional to $M^{1/2}$. On the other hand, a change in the relative block length x_A affects virtually all quantities defined in eq 7e–h, and thus requires a new set of calculations.

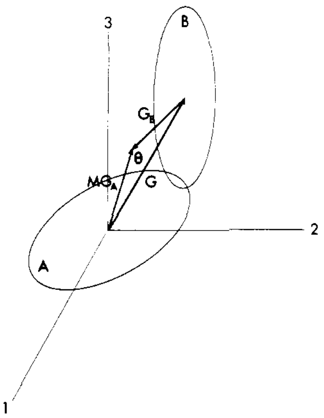

Figure 1. Biellipsoidal model (BEM) of the block copolymer molecule showing the vectors $\mathbf{MG}_A$ and $\mathbf{G}_B$ from the center of mass of each block to the joint, the vector $\mathbf{G}$ from the center of A to the center of B, and the angle θ between $\mathbf{MG}_A$ and $\mathbf{G}_B$.

(III) Monte Carlo Method

The size and shape distribution for the blocks of a copolymer molecule was approximated by a file of 10 000 random-flight chains generated on a simple six-choice cubic lattice. For each unrestricted walk of 480 steps, the reduced square principal components $\Lambda_i{}^2$, $i = 1, 2, 3$, were determined[24] and stored in a file, along with the reduced coordinates Γ of one chain end. From this file, pairs of chains were taken successively (starting with chains 1 and 10 000, followed by chains 2 and 9999, etc.) and assigned to blocks A and B, as well as to B and A. (This switching in assignment improved sampling at little cost in computer time.) For each allowed relative orientation Ω of the two selected chains, the pseudopotential V (eq 10) and the molecular properties of interest were computed. Boltzmann-weighted averages were then formed for the given pair by numerically integrating all quantities over all orientations Ω. Finally, ensemble averages were calculated by repeating the above process for many pairs of chains from the file.

Five groups of calculations, each consisting of 1000 pairs of chains, were made for given sets of triplets (z_{AA}, z_{BB}, z_{AB}) of z parameters, and the standard deviations were computed for each property from fluctuations in the five group averages, in the manner employed by McCrackin, Mazur, and Guttman.[28] The above mentioned way of selecting chain pairs ensures that each chain of the ensemble contributes once as an A block and once as a B block. Using the trapezoidal rule, the numerical integrations were performed over the intervals α,γ: $0 \rightarrow 2\pi$ and β: $0 \rightarrow \pi$, with increments of $\pi/2$ for α and γ and $\frac{1}{3}$ for $\cos\beta$. In two control calculations on 1000 pairs for triplets $z_{AA} = 3$, $z_{BB} = -0.5$, and z_{AB} growing from -1 to $+6$, the increments were reduced to $\pi/3$ and $\frac{1}{3}$ and to $\pi/2$ and $\frac{1}{6}$, respectively. In the interval $-0.4 \leq z_{AB} \leq +6$, the three-digit α^2 were not affected by these changes. Only for strongly negative z_{AB} were some differences observed, reaching the maximum of +1.4 and −5.2%, respectively, at $z_{AB} = -1$. Since this region is not expected to be quantitatively significant anyway, it appears that the originally chosen increments give satisfactory results.

A computation of this size for 15 z triplets requires about 60 h on the Hewlett-Packard System 2100.

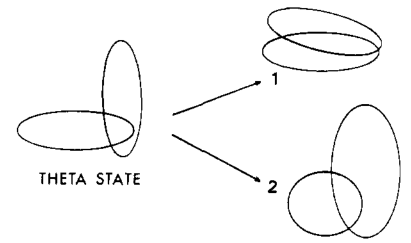

Figure 2. Illustration of the two basic mechanisms by which the copolymer molecule can react to the environment: (1) by changing the center of mass separation **G** and the orientation θ of the blocks; (2) by changing block size and shape.

(IV) Results

The principal alterations in conformation that a block copolymer molecule can undergo in the present model are: (1) changes in relative block orientation and separation; (2) changes in individual block sizes and shapes. These are illustrated in Figure 2. As solvent and temperature conditions vary, both mechanisms respond to produce the conformation of lowest free energy. The cooperative, and somewhat subtle, interplay between block conformations and the overall molecular conformation is followed by studying several key parameters.

The degree of AB block overlap can be described by the number of AB contacts N_{AB},[18] where in general

$$N_{\mathrm{AB}} = K\langle \rho_{\mathrm{A}}\rho_{\mathrm{B}} \rangle \qquad (11)$$

$$N_{\mathrm{II}} = \tfrac{1}{2}K\langle \rho_{\mathrm{I}}^2 \rangle$$

and K is a proportionality constant and the angular brackets denote a Boltzmann-weighted ensemble average computed for fixed values of the z parameters. Reduced values $N_{\mathrm{AB}}{}^*$ are reported here, relative to N_{AB} at theta conditions, i.e., $N_{\mathrm{AB}}{}^* = N_{\mathrm{AB}}(z_{\mathrm{AA}},z_{\mathrm{BB}},z_{\mathrm{AB}})/N_{\mathrm{AB}}(0,0,0)$.

The significant size parameters are the overall mean square radius of gyration $\langle S^2 \rangle$, individual radii $\langle S_{\mathrm{A}}{}^2 \rangle$ and $\langle S_{\mathrm{B}}{}^2 \rangle$ of the two blocks, and the mean square distance between their centers of mass $\langle G^2 \rangle$, all of which can be in principle determined from classical light-scattering measurements as well as by the more recent technique of low-angle elastic neutron scattering. Two other quantities of interest are the mean-square distances between the joint segment and the centers of mass of the two blocks, $\langle G_{\mathrm{A}}{}^2 \rangle$ and $\langle G_{\mathrm{B}}{}^2 \rangle$. These properties are tabulated in terms of expansion coefficients α^2 related to the true theta state, and calculated as

$$\alpha_{\mathrm{A}}{}^2 = \frac{\langle S_{\mathrm{A}}{}^2(z_{\mathrm{AA}},z_{\mathrm{BB}},z_{\mathrm{AB}}) \rangle}{\langle S_{\mathrm{A}}{}^2(0,z_{\mathrm{BB}},0) \rangle} \qquad (12a)$$

$$\alpha_{\mathrm{GA}}{}^2 = \frac{\langle G_{\mathrm{A}}{}^2(z_{\mathrm{AA}},z_{\mathrm{BB}},z_{\mathrm{AB}}) \rangle}{\langle G_{\mathrm{A}}{}^2(0,z_{\mathrm{BB}},0) \rangle} \qquad (12b)$$

$$\alpha_{\mathrm{G}}{}^2 = \frac{\langle G^2(z_{\mathrm{AA}},z_{\mathrm{BB}},z_{\mathrm{AB}}) \rangle}{\langle G^2(z_{\mathrm{AA}},z_{\mathrm{BB}},0) \rangle} \frac{\langle G_{\mathrm{A}}{}^2(z_{\mathrm{AA}},0,0) + G_{\mathrm{B}}{}^2(0,z_{\mathrm{BB}},0) \rangle}{\langle G_{\mathrm{A}}{}^2(0,0,0) + G_{\mathrm{B}}{}^2(0,0,0) \rangle} \qquad (12c)$$

$$\alpha^2 \equiv \frac{\langle S^2 \rangle}{\langle S^2 \rangle_0} = \frac{x_{\mathrm{A}}w_{\mathrm{A}}\alpha_{\mathrm{A}}{}^2 + x_{\mathrm{B}}w_{\mathrm{B}}\alpha_{\mathrm{B}}{}^2 + 2w_{\mathrm{A}}w_{\mathrm{B}}\alpha_{\mathrm{G}}{}^2}{x_{\mathrm{A}}w_{\mathrm{A}} + x_{\mathrm{B}}w_{\mathrm{B}} + 2w_{\mathrm{A}}w_{\mathrm{B}}} \qquad (12d)$$

where w_{I} is the weight fraction of I block. Also given are parameters γ_{I} and σ introduced by TKI,[22] which conveniently compare the dimensions of each block as well as of the molecule with the dimensions of homopolymer molecules under the same conditions of solvent and temperature, thus partly isolating the effect of AB interactions from AA and BB:

$$\gamma_{\mathrm{A}} = \langle S_{\mathrm{A}}{}^2(z_{\mathrm{AA}},z_{\mathrm{BB}},z_{\mathrm{AB}}) \rangle / \langle S_{\mathrm{HA}}{}^2 \rangle \qquad (13a)$$

$$\sigma = \tfrac{1}{2}\langle G^2(z_{\mathrm{AA}},z_{\mathrm{BB}},z_{\mathrm{AB}}) \rangle / (\langle S_{\mathrm{HA}}{}^2 \rangle + \langle S_{\mathrm{HB}}{}^2 \rangle) \qquad (13b)$$

$$\langle S_{\mathrm{HA}}{}^2 \rangle \equiv \langle S_{\mathrm{A}}{}^2(z_{\mathrm{AA}},z_{\mathrm{BB}},0) \rangle \qquad (13c)$$

where $\langle S_{\mathrm{HA}}{}^2 \rangle$ is the mean square radius of a homopolymer molecule identical with the A block and exposed to the same environment as the copolymer molecule. It is apparent that all of the quantities defined by eq 12a–13b equal unity at the theta state.

The peculiar way used to compute these parameters has been necessitated by difficulties encountered in sampling pairs of blocks out of our ensemble of 10^4 chains. For the single ellipsoid model (SEM), the complete sample is easily obtained by averaging over 10^4 single ellipsoids, but it is practically impossible to do the same for BEM in general; this would require averaging over 10^8 possible pairs, each for 96 different orientations. As can be expected, the sampling of only 10^4 pairs, i.e., 0.01% of the total, leads to results which are biased. The immediate cause of the bias is the presence of two weighting factors for homointeractions, affecting each other even for $z_{\mathrm{AB}} = 0$ where the two blocks should behave independently. Thus it is found that, $\langle S_{\mathrm{A}}{}^2(z_{\mathrm{AA}},z_{\mathrm{BB}},0) \rangle \neq \langle S_{\mathrm{A}}{}^2(z_{\mathrm{AA}},0,0) \rangle$, although in a complete sample these two quantities would obviously be identical. Of these two values, the latter one is unbiased (and is equivalent to the result obtained by SEM) since the weighting factor for the B block is unity. The difference between the two is negligible if $|z_{\mathrm{BB}}|$ is small but reaches an unpleasant level for higher $|z_{\mathrm{BB}}|$ (amounting, e.g., to 6% for $z_{\mathrm{AA}} = 0$ and $z_{\mathrm{BB}} = 3$). Since this is strictly due to sampling and not to the incompleteness of the ensemble or a failing of the model itself, it is legitimate and, in fact, desirable to attempt to reduce the bias. In the case of block properties related to the theta state, $\alpha_{\mathrm{A}}{}^2$ and $\alpha_{\mathrm{GA}}{}^2$ (eq 12a and 12b), the distortion is diminished simply by employing for the calculation of the denominator the similarly biased triplet $(0,z_{\mathrm{BB}},0)$ rather than the true theta state $(0,0,0)$. Analogously, we use the triplet $(z_{\mathrm{AA}},z_{\mathrm{BB}},0)$ for calculating the size of isolated blocks $\langle S_{\mathrm{HI}}{}^2 \rangle$ needed for γ_{I} and σ. Formula 12c for $\alpha_{\mathrm{G}}{}^2$ utilizes the general relation

$$\langle G^2 \rangle = \langle G_{\mathrm{A}}{}^2 \rangle + \langle G_{\mathrm{B}}{}^2 \rangle - 2\langle G_{\mathrm{A}}G_{\mathrm{B}}\cos\theta \rangle \qquad (14)$$

where the last term drops out for $z_{\mathrm{AB}} = 0$. Finally, eq 12d for expansion coefficient of the overall mean square radius, α^2, is derived from

$$\langle S^2 \rangle = w_{\mathrm{A}}\langle S_{\mathrm{A}}{}^2 \rangle + w_{\mathrm{B}}\langle S_{\mathrm{B}}{}^2 \rangle + w_{\mathrm{A}}w_{\mathrm{B}}\langle G^2 \rangle \qquad (15)$$

The relative block orientation is indicated by the angle θ between the vectors connecting the joined ends of the two blocks with their centers of mass (see Figure 1). Because of the high probability of finding the block ends at the tips of the respective ellipsoids,[29] the block copolymer molecule in the present model can "open" and "close" (segregate and overlap) like a pocketknife. At the theta state, where all orientations are equally probable, $\langle \cos\theta \rangle = 0$, i.e., on the average, $\theta = 90°$ (the initial state in Figure 2). Negative z_{AB} tends to emphasize overlapped conformations with $\langle \cos\theta \rangle > 0$ (state 1 in Figure 2), while positive z_{AB} causes the structure to open ($\langle \cos\theta \rangle < 0$, Figure 1). These qualitative reflections alone lead to the conclusion that the conformation of a diblock at the theta state is to a large extent segregated. The same conclusion has been reached on a quantitative basis by TKI[22] as well as in the present paper.

In this work the conformations of 50/50 block copolymer molecules ($N_{\mathrm{A}} = N_{\mathrm{B}}$, $x_{\mathrm{A}} = x_{\mathrm{B}}$) have been studied for a variety of solvent–temperature conditions likely to be encountered in practice. Presently, experimental values of the parameter z_{AB} are not available, though in principle they may be found from dilute solution studies of polymer mixtures. The range of z_{AB} in the calculations is taken the same as that of z_{AA} and z_{BB}. The range of z's also includes negative values. Although we are aware of little significance of the numerical values of

Table I
Expansion of a Homopolymer Molecule Using the BEM[a] (*z,z,z*)

z	α_{YT}^2	α^2	α_I^2	α_{GI}^2	α_G^2	γ_I	σ	$\langle\cos\theta\rangle$	N_{AB}^*
−1		0.21 ± 0.01	0.37 ± 0.03	0.79 ± 0.14	0.05 ± 0.04	1.19	0.15	0.98	19.4
−0.5		0.23 ± 0.02	0.41 ± 0.02	0.68 ± 0.11	0.06 ± 0.06	1.12	0.18	0.94	18.1
−0.25		0.42 ± 0.05	0.51 ± 0.04	0.46 ± 0.04	0.33 ± 0.06	0.82	0.49	0.45	7.62
−0.1	0.84	0.84 ± 0.01	0.87 ± 0.01	0.85 ± 0.02	0.81 ± 0.02	0.98	0.90	0.06	1.64
0	1.00	1.00 ± 0.01	1.00 ± 0.01	1.00 ± 0.01	1.00 ± 0.01	1.00	0.99	0.00	1.00
0.5	1.41	1.44 ± 0.01	1.36 ± 0.02	1.43 ± 0.02	1.53 ± 0.01	1.02	1.14	−0.10	0.36
1	1.67	1.71 ± 0.03	1.58 ± 0.03	1.69 ± 0.03	1.84 ± 0.03	1.02	1.19	−0.14	0.23
2	2.04	2.06 ± 0.07	1.89 ± 0.06	2.05 ± 0.09	2.23 ± 0.08	1.02	1.24	−0.17	0.13
3	2.32	2.27 ± 0.10	2.08 ± 0.10	2.27 ± 0.14	2.47 ± 0.12	1.01	1.27	−0.19	0.09
6	2.96	2.56 ± 0.17	2.31 ± 0.18	2.45 ± 0.21	2.81 ± 0.19	1.00	1.29	−0.23	0.06

[a] The standard deviations listed in the tables were computed as described in section III. They are rounded off to the nearest hundredth.

variables at the plateaus which occur for strongly negative z's, it is an added reassurance to see that a smooth-density model is capable of producing sharp conformational changes similar to the "gas–liquid" transition, or "collapse" of the coil, predicted[28,30,31] and recently observed[32,33] by several authors. Two comments seem appropriate at this point: (a) The concept of a "collapsed" state for an isolated polymer molecule is not devoid of physical interest. Although the majority of the molecules may be in an associated state (e.g., the concentrated phase of the polymer solution in the case of homopolymers, or micelles in the case of block copolymers) a small portion of material will always exist as isolated molecules. (b) An accurate picture of the transition region cannot be expected from Monte Carlo techniques, just as such methods do not yield precise results for either the gas–liquid or liquid–solid transitions in systems of simple molecules.[34] The finite sampling of configuration space, as well as the deficiencies of the ensemble, preclude seeing the discontinuous changes an exact treatment would produce. It also seems likely that a truly sharp transition would only occur for an infinite molecular weight molecule. It is rather expected that the single state regions far from the transition are adequately depicted, and that the transition itself can be identified by rapid changes in polymer properties, along with enhanced fluctuations in these properties.

In many approximate theories of homopolymer solutions, the pseudopotential of eq 3 is premultiplied by an adjustment constant which takes care of matching the approximate results with those of the exact first-order perturbation theory for small z.[11,35] Since there is no reason to expect that both the intra- and interblock interactions are approximated equally in the present treatment, we determined two kinds of constants C_{AA} ($=C_{BB}$) and C_{AB}, to be used in eq 3 and 5, respectively. They were calculated by comparing certain ensemble averages (see ref 24 for C_{AA}) with the perturbation theory of Froelich and Benoit.[10] It was pleasing to discover that the two constants differed by only 1% and were in equally good agreement with the value given in our previous study of homopolymer solutions.[24] Hence, in all reported calculations the pseudopotential of eq 10 was premultiplied by a single adjustment constant $C = 0.95$.

(A) Homopolymer ($z_{AA} = z_{BB} = z_{AB}$). To assess the reliability of the model and calculation method, we first examine the BEM for a homopolymer. In this case the homopolymer molecule is mentally divided into two halves, each of which is then approximated by an ellipsoidal segment cloud, and the interaction of these two identical blocks is computed. A priori, it seemed that the BEM should be a better model for the homopolymer than was the single ellipsoid model (SEM)[24] since it represents the right step in a hypothetical hierarchy of models, the final member of which would be the case where each segment of the macromolecule is approximated by an ellipsoid.

It is apparent from the definitions of the Z's employed in this paper (see immediately following eq 8 and 9) that for a homopolymer

$$Z_{II} = x_I^{1/2}z \qquad (I = A, B) \tag{16a}$$

$$Z_{AB} = 2^{3/2}x_Ax_Bz \tag{16b}$$

where z is the commonly used parameter for the entire homopolymer molecule. Thus, in general, the three Z parameters will not be the same. Only for our particular choice of $x_I = 1/2$ do all three parameters in eq 16 become identical, namely equal to $z/2^{1/2}$. To facilitate comparison with the results of homopolymer theories, our homopolymer data are reported as a function of z, rather than of $Z_{IJ} = z/2^{1/2}$. Correspondingly, parameters $z_{IJ} = 2^{1/2}Z_{IJ}$, I, J = A, B, will be used for tabulating the block copolymer results as well.

The expansion factor α^2 for the mean square radius of a single polymer chain has been frequently studied, and the various theoretical formulas advanced are summarized by Yamakawa.[11] To date, the available data seem to be closely fitted by the formula of Yamakawa–Tanaka (YT).[36] Expansion coefficients α^2 calculated from BEM are compared with those of YT theory in Table I. In the range $-0.1 \leq z \leq 3$ the results differ by less than 3%, while for larger z the negative deviations in α^2 observed for BEM grow stronger. For instance, for $z = 6$, $\alpha_{YT}^2 = 2.96$ whereas $\alpha_{BEM}^2 = 2.56 \pm 0.17$, i.e., the BEM yields a value 13% lower than predicted by YT. We might recall that in this respect SEM performed better in a wider range of z's.[24] This is confirmed with the present ensemble for which SEM gives $\alpha_{SEM}^2 = 2.82 \pm 0.20$ at $z = 6$ (cf. Table II). There are several possible reasons for the observed "failure" of BEM at large z:

(1) It may be inherent to BEM in its present form, caused by misrepresenting the amount of interaction in the very open structures (with large angle θ) through employment of a segment density which could be inadequate at the ends of the ellipsoids. Some indirect indication for this view comes from recent studies of the segment density distribution along the principal axes of inertia in both excluded volume[37] and self-intersecting chains.[38] It has been found that the segment density distribution along the longest principal axis is fairly uniform, resembling a step function rather than a Gaussian, in contrast to the two other principal directions where a Gaussian appears a reasonable approximation.

(2) The failure may be due to increased difficulty of efficient sampling for BEM at extreme z's. For instance, in the SEM at high z, the most expanded chains of the ensemble always have the opportunity to contribute to the computed average since the averaging is done over the entire ensemble. On the

Table II
Expansion of a Homopolymer Molecule Using the Single Ellipsoid Model

z	α^2	α_R^2	α_{G1}^2	$\overline{\alpha_{GI}^2}$	$\langle \cos \phi \rangle$[a]
−1	0.20	0.42	0.37	0.38	−0.51
−0.5	0.20	0.36	0.40	0.36	−0.28
−0.25	0.38	0.40	0.47	0.40	−0.17
−0.1	0.85	0.83	0.85	0.85	−0.38
0	1.00	1.00	1.00	1.00	−0.44
0.5	1.44	1.49	1.43	1.43	−0.53
1	1.70	1.78	1.68	1.69	−0.55
2	2.08	2.16	1.97	2.03	−0.58
3	2.35	2.44	2.13	2.27	−0.61
6	2.82	2.92	2.37	2.63	−0.65

[a] The symbol ϕ denotes the angle between the vectors connecting the center of mass with each of the two ends. The faster growth for $z > 0$ of α_R^2 as compared to α_{GI}^2 is accounted for by the increase in $\langle \phi \rangle$.

other hand, in order to have correspondingly expanded molecules represented in the BEM sample of 5000 pairs, it is almost necessary that some pairs consist of *two* highly expanded blocks. Unfortunately, the probability of selecting such a pair from the $10^4 \times 10^4$ possibilities is very small, and strongly expanded chains are likely to be underrepresented in the present sample. Analogous remarks apply to the region of collapsed chains at negative z's. To assess the importance of this factor, we added to the original sample of 5000 random pairs of chains (where each chain was different from each other) 2000 extra pairs, each of which consisted of two identical chains. These identical pairs were selected from an ordered file containing the original 10 000 chains arranged according to their volumes, $\Lambda_1\Lambda_2\Lambda_3$. In particular, the first 1000 chains were taken from the beginning of the file and paired with themselves (thus containing small chains important for $z < -0.1$) and the second thousand chains taken from the end of the ordered file (containing the highly expanded chains contributing at high z). The rest of the ordered file was ignored since the remaining 8000 identical pairs turned out to be unimportant for the averages in any region of z. In addition to the usual weighting of each pair by its Boltzmann factor, the identical pairs were assigned the statistical weight of 10^{-4} each, to account for the very special, one out of 10^4, chance of selecting the second member of a pair identical with the first. In the intermediate range of z, the identical pairs do not alter the previous results because of their low statistical weight. However, they do affect the results in both extreme regions, shifting the values of α^2 closer to the YT curve at high z, and making the collapse of the coil sharper and deeper at negative z. Although this method of enriching the wings of the ensemble is rather artificial, the results suggest that some kind of importance sampling would be highly desirable and beneficial.

(3) Finally, we examined the behavior of end segments in our ensemble using SEM since the ends play a crucial role in the BEM. It is seen from Table II that the expansion of the end-to-end distance, α_R^2, is indeed stronger than that of the mean square radius, α^2, and their ratio approaches a constant (for $z > 1$, $\alpha^2/\alpha_R^2 \simeq 0.96$, compared to the Domb–Barrett[39] estimate of $\simeq$0.93 for very high z). On the other hand, the expansion of the distance between the center of mass and the end used for BEM, α_{G1}^2, is approximately the same as α^2 only for $-0.1 \leq z \leq 1$, while for $z > 1$ it grows more slowly, with the difference reaching 15% for $z = 4$. This is at variance with Monte Carlo data on self-avoiding walks of Wall and Hioe[40] which yields a limiting ratio $\lim_{N\to\infty} \alpha^2/\alpha_{G1}^2 = 0.98 \pm 0.01$, and suggests that our G_1 expands too slowly. At least in part, the slow growth of G_1 must reflect sample fluctuations since the other end's distance, G_2, happens to expand faster, and the average expansion coefficient, $\overline{\alpha_{Gi}^2}$, deviates from α^2 less than α_{G1}^2. Nevertheless, the slow growth of G_1 must contribute to the slow expansion of the overall mean square radius observed with the BEM data of Table I.

As z falls below zero α^2 drops sharply, with a point of inflection in the range $-0.25 \leq z \leq -0.1$, and levels off for $z < -0.5$. This behavior is reminiscent of Monte Carlo results for excluded volume chains and is associated with a collapse of the coil to a dense particle.[30,32] Formal indications of such a "transition" are also contained in the Flory theory[31,41] and the YT theory[36] which predict for it $z_F^* \simeq -0.146$, $\alpha_F^{*2} \simeq 0.6$, and $z_{YT}^* \simeq -0.166$, $\alpha_{YT}^{*2} \simeq 0.54$, respectively, although in view of the mathematical approximations made α^2 is not defined in either case for $z < z^*$. It is obvious that within the framework of the two-parameter theory employed here (where $z \propto \beta M^{1/2}$), the rate of change at the transition becomes sharper with growing molecular weight M of the polymer when α^2 is plotted against β (which characterizes the solvent, temperature, and kind of polymer) rather than against z. Hence, in the limit for $M \to \infty$ a true phase transition[32] will occur at the theta point (i.e., for $\beta \to -0$). Sample fluctuations are found to pass through a maximum in the range $-0.25 < z < -0.1$ as is expected if the system is passing through a transition. Also observed is a minimum in the fluctuations near the theta point as has previously been reported and discussed for calculations with excluded volume chains.[28]

The reduced number of contacts N_{AB}^*, all expansion coefficients except α_{G1}^2, as well as $\langle \cos \theta \rangle$ follow the expected monotonic dependences, although the magnitude of the changes is in some cases surprising. At $z = -1.0$, the two halves of the polymer are practically overlapped ($\alpha_G^2 = 0.05$, $\langle \theta \rangle = 11°$). Upon increasing z the sharpest changes again occur in the transition region, $-0.25 \leq z \leq -0.1$, with the molecule then passing through the Gaussian conformation at $z = 0$ ($\alpha_G^2 = 1.00$, $\langle \theta \rangle = 90°$) and finally approaching what might be called a segregated conformation at $z = 6$ ($\alpha_G^2 = 2.81$, $\langle \theta \rangle = 103°$). Over the entire range N_{AB}^* decreases by an impressive factor of $\simeq$300. The location of the Gaussian conformation ($z = 0$) on the "segregated" side of the transition, as well as the low value of the relative number of AB contacts, $\upsilon_{AB} = N_{AB}/(N_{AA} + N_{BB} + N_{AB})$, at the theta point, $\upsilon_{AB} = 0.09$, support the view that the Gaussian conformation is to a considerable extent segregated. This is also reflected in the very asymmetric $\langle \cos \theta \rangle$ vs. z dependence. Once the molecule assumes the Gaussian conformation ($\langle \theta \rangle = 90°$), it has very little energy to gain in a high-z medium by further increasing the angle θ since there are not many AB contacts anyway (hence, $\langle \theta \rangle \simeq 103°$ at $z = 6$). On the other hand, it may gain a great amount of energy by going to the overlapped conformation in the medium with strongly negative z ($\langle \theta \rangle \simeq 11°$ for $z = -1$). All this suggests that in the case of block copolymers it is misleading to speak of a transition between a pseudo-Gaussian and a segregated conformation. Any transition starting from the pseudo-Gaussian conformation has to involve some kind of collapse or condensation, whether it be the collapse of only one of the blocks (in a poor solvent for that block) or an orientational collapse (which will happen for strongly negative z_{AB}) combined with a volume collapse of one or both blocks. Additional segregation may (as in the case of Edward's transition[21]) or may not (as in the "homopolymer" case just discussed) occur during a transition (depending on the direction z_{AB} changes), but a collapse is essential.

Next we examine effects exerted by one block of the homopolymer on the other. Near the theta point, where both blocks are partly overlapped, size perturbation is achieved easily, and hence we see $(d\gamma_I/dz) > 0$ (by undergoing a supplemental expansion beyond that which normally occurs in the given good solvent, each block reduces its own segment density, thereby also reducing the repulsive "heterocontacts"). For $z < 0$, the parameter γ_I passes through a minimum and eventually becomes larger than unity. Strong overlap occurs in this region (at $z = -0.5$, $\alpha_G^2 \simeq 0.06$ and $\langle\theta\rangle \simeq 20°$) and achieves a high segment density with better efficiency and less entropic expense than block shrinking alone (recall that in the lower range of radii of gyration, their density distribution drops to zero very quickly[11]). Thus the need for block shrinking is relaxed. In good agreement with the TKI's estimate for positive z, γ_I never exceeds 1.02, i.e., stays very close to one. The explanation has been offered in their paper.[22] The slight maximum in γ_I observed for positive z may not be real, considering the rapid increase in errors with growing z. The parameter σ levels off at $\simeq 1.29$ which is again in good agreement with TKI's estimate of σ in very good solvents being in the range $1.16 < \sigma < 1.43$, perhaps $\sigma \simeq 1.25$. It is also observed that in a good solvent ($z \geq 1$), the expansion of the mean square distance between the joint segment and the center of mass of a block, α_{GI}^2, is greater by 6–8% than the expansion of the block mean square radius, α_I^2, while in an isolated coil the two corresponding quantities α_{GI}^2 and α^2 (cf. Table II) are about equal or even $\alpha_{GI}^2 < \alpha^2$. This clearly indicates the pulling effect each block exercises on the end segment of the other. The minimum of α_{GI}^2 observed in the region where strong overlap begins ($\langle\cos\theta\rangle \simeq 0.9$) resembles the behavior of γ_I and comes about for the same reason. Comparing now the four expansion coefficients introduced in BEM, we have for $z > 0$ consistently $\alpha_G^2 > \alpha_{GI}^2 > \alpha_I^2$, with the overall coefficient α^2 being intermediate in magnitude. The distance between the center of mass of a block and the joint segment, $\langle G_I^2\rangle$, grows faster than the square radius of a block since it is statistically easier just to pull out the end of a block than to swell the whole coil. On the other hand, the distance between the centers of mass of the two blocks grows even faster than $\langle G_I^2\rangle$ since it is also helped by the increasing angle $\langle\theta\rangle$.

It can be concluded that the quantitative agreement of the BEM with previous work on homopolymers is satisfactory (within a few percent for $z < 3$), providing justification for use of this model in the more complex case of block copolymers. In the following sections, we examine the excluded volume effect in block copolymers for several typical situations. In each case the intrablock interactions are fixed at values corresponding either to a poor solvent ($z_{II} = 0$) or to a good solvent ($z_{II} = 3$) while the heterocontact interactions are varied ($-1 \leq z_{AB} \leq 6$).

(B) Copolymer with Both Blocks in the Theta State ($\mathbf{0,0,z_{AB}}$). Although the assumption of two chemically different blocks being simultaneously in the theta state is physically somewhat unreal, this is the only case where the excluded volume problem has been studied in detail by other than perturbative methods.[22] The results for BEM are shown in Table III. It is worth mentioning that TKI's data[22] for zero neighbor–neighbor interactions ($\alpha^2 = 1.22$, $\sigma = 1.43$, $\gamma_I = 1.02$) are pleasantly close to our values of 1.24, 1.42, and 1.05, respectively, for $z \simeq 1.8$, i.e., these two different models are capable of exhibiting an equal degree of segregation at practically the same overall swelling. The somewhat greater expansion of individual blocks, γ_I, observed with BEM is probably due to the inability of this model to localize the swelling effect of heterocontacts to the region of the overlap. On the other hand, it is consistent that the present limiting value of γ_I is greater than 1.02 found for the homopolymer since the unperturbed blocks are affected by the AB interactions more easily than the perturbed ones. The main conclusion of TKI is confirmed: for $z_{AB} > 0$, AB interactions have very little effect on the size and shape of individual blocks; the latter remain unperturbed within several percent. The principal mechanism for overall swelling is thus the change in the relative position and orientation of the two blocks exemplified by growing α_{GI}^2, $\langle\theta\rangle$, and α_G^2. Because of missing z_{II} interactions and hence relatively low expansion of the blocks, α_{GI}^2 is considerably smaller than in the previous case of the homopolymer (e.g., 1.26 vs. 2.27 for $z_{AB} = 3$). This lack of positional segregation then enhances the orientational segregation as measured by $\langle\theta\rangle$, but not enough to keep α_G^2 at high values shown by the homopolymer. On the other hand, the quantity σ which indicates the effect of AB interactions on the distance between block centers is greater in the present case than for homopolymers. Also the pulling effect on the joint segment is more distinct (cf. α_I^2 vs. α_{GI}^2 in Table III).

In the negative region, the sharpest change in α^2 occurs in the interval $-0.6 < z_{AB} < -0.4$, i.e., later than in the homopolymer. This is reasonable since in the latter case the collapse of blocks is induced directly by negative z_{II}'s, and hence the transition takes place at less attractive energies. On the other hand, in the present case of $z_{II} = 0$, the collapse of individual blocks (note the sharp decline in γ_I) is provoked only indirectly by the molecule trying to attain as many AB contacts as possible.

The agreement with the smooth density model of PZS[18a] is less satisfactory; their value for the relative number of AB contacts at $z_{AB} = 0$, $\nu_{AB} \simeq 0.31$, is more than three times higher than ours, $\nu_{AB} \simeq 0.09$. This discrepancy is probably due to the approximation employed in their model for the end-segment density distribution, resulting in the blocks being joined too closely. It can be shown, for instance, that for their model at the theta point and $x_I = \frac{1}{2}$ the reduced overall radius of gyration, $\langle S^2\rangle/N_I\sigma_I^2$, is only $\frac{1}{4}$ instead of $\frac{1}{3}$, and the reduced mean square distance between the centers of mass of the two blocks, $\langle G^{r2}\rangle$, is $\frac{1}{3}$ rather than $\frac{2}{3}$. It is interesting that even with less AB contact, the BEM yields a faster change of N_{AB}^* with z_{AB} than the smooth-density model of PZS. On the other hand, our dependence at $z_{AB} = 0$ is not as steep as predicted by the perturbation theory.[18b] At the theta point, BEM gives the derivative $\partial(\ln N_{AB})/\partial(z_{AB}) \simeq -2.35$, compared to the PZS value -1.63, and the exact value -2.92. It is our feeling that the PZS model could be greatly improved by utilizing a more realistic end segment distribution, while at the same time keeping its most attractive feature, simplicity. On the other hand, it should be realized that the assumption of $\langle S_I^2\rangle$ being independent of z_{AB}, although reasonably good for $z_{AB} > 0$, will always lead to an underestimation of the magnitude of conformational changes in the transition region (for $z_{AB} < 0$) since it precludes any effect z_{AB} might have on the size of the blocks (cf. Table III).

(C) Copolymer in Good Solvent for Both Blocks ($\mathbf{3,3,z_{AB}}$). When both blocks are in a good solvent environment, the reduced segment densities cause the numbers of contacts, N_{AA}, N_{BB}, and N_{AB}, to decrease with a resulting loss in the ability of z_{AB} to significantly influence the copolymer conformation. In Table IV are the copolymer properties computed for $z_{AA} = z_{BB} = 3$, and $-1 \leq z_{AB} \leq 6$. Throughout the examined range, the overall mean square radius changes by only about 40% whereas in the case of theta solvent for both blocks, $\langle S^2\rangle$ changed by a factor of 6. The individual block dimensions are virtually unaffected by z_{AB} (i.e., γ_I stays very close to one even for $z_{AB} < 0$) so that the growth in $\langle S^2\rangle$ is almost entirely due to the $\simeq$90% increase in $\langle G^2\rangle$. Also changes in $\langle G_I^2\rangle$ and $\langle\cos\theta\rangle$ are less pronounced than in any other case. The amount of AB contact is indeed very low; even when the blocks are most compatible ($z_{AB} = -1$), N_{AB}^* is less than for the true theta state, (0,0,0). The parameter z_{AB} would have to be unusually negative to ever accomplish an overlapping conformation (for $z_{AB} = -1$, $\langle\theta\rangle$ is still only 75°). For practical purposes, we believe that it is virtually impossible to have an intramolecular transition in a solvent which is good for both blocks.

Two reasons can be advanced for the observed insensitivity

Table III
Expansion of a Copolymer Molecule in a Theta Solvent for Both Blocks[a] $(0,0,z_{AB})$

z_{AB}	α^2	$\alpha_I^2 \equiv \gamma_I$	α_{GI}^2	$\alpha_G^2 \equiv \sigma$	$\langle\cos\theta\rangle$	N_{AB}^*
−1	0.21	0.39	0.24	0.03	0.93	18.1
−0.6	0.35	0.56	0.38	0.14	0.76	11.6
−0.4	0.67	0.82	0.70	0.51	0.39	4.62
−0.2	0.89	0.95	0.91	0.82	0.13	1.81
0	1.00	1.00	1.00	1.00	0.00	1.00
0.4	1.11	1.03	1.09	1.17	−0.12	0.51
1	1.18	1.05	1.16	1.31	−0.19	0.30
2	1.25	1.05	1.22	1.44	−0.25	0.19
3	1.29	1.06	1.26	1.51	−0.28	0.14
5	1.34	1.06	1.30	1.61	−0.31	0.09

[a] For $z_{AB} \geq -0.2$, errors in α^2, α_I^2, α_{GI}^2, and α_G^2 are all less than or equal to 0.01.

Table IV
Expansion of a Copolymer Molecule in a Good Solvent for Both Blocks[a] $(3,3,z_{AB})$

z_{AB}	α^2	α_I^2	α_{GI}^2	α_G^2	γ_I	σ	$\langle\cos\theta\rangle$	N_{AB}^*
−1	1.69	1.98	1.93	1.41	0.96	0.72	0.26	0.78
−0.6	1.86	2.02	2.03	1.69	0.98	0.87	0.12	0.51
−0.4	1.92	2.03	2.07	1.80	0.99	0.93	0.07	0.42
−0.2	1.97	2.04	2.09	1.90	1.00	0.98	0.03	0.35
0	2.01	2.05	2.12	1.98	1.00	1.02	0.00	0.30
0.4	2.08	2.06	2.16	2.10	1.01	1.08	−0.05	0.23
1	2.15	2.07	2.20	2.23	1.01	1.15	−0.10	0.17
2	2.23	2.08	2.24	2.38	1.01	1.22	−0.16	0.12
3	2.27	2.08	2.27	2.47	1.01	1.27	−0.19	0.09
6	2.36	2.08	2.33	2.64	1.02	1.36	−0.25	0.06

[a] Errors are virtually constant over the entire range of z_{AB}, amounting approximately to 0.10 for α^2 and α_I^2 and 0.12 to 0.14 for α_{GI}^2 and α_G^2.

of the molecular conformation to changes in AB interactions. The first, mentioned above, is that the effectiveness of the perturbing block through which the interactions come, as well as the susceptibility of the perturbed block, are reduced by their own low densities. Second, the blocks themselves are far from the transition region where their internal conformations are most labile, and hence most readily influenced by external perturbations. The nearer each block is to its own conformational transition, the more sensitive it is to perturbations from the other block (and from the surroundings).

(D) Copolymer in a Preferential Solvent $(3,0,z_{AB})$. In the chosen example, the solvent is good for the block A but is poor for the block B. As might be expected, the sensitivity of the overall dimensions to the parameter z_{AB} is here (see Table V) intermediate to the previous two cases. It is higher than for a copolymer in a good solvent (case C) but still considerably lower than for a copolymer in a theta solvent for both blocks (case B). Over the entire range of z_{AB}'s, the mean square radius increases by about 90% while the distance between centers of mass of the two blocks grows by more than a factor of 3.

The perturbation of the size of each block due to the presence of the other is again relatively small and fits the anticipated behavior. The individual blocks shrink below their isolated dimensions when they are compatible ($z_{AB} < 0$) so as to achieve a greater amount of heterosegment contact. This is reflected in the parameters γ_A and γ_B falling below one, just as in the other cases. When the blocks are incompatible ($z_{AB} > 0$), both swell beyond their isolated dimensions in the same solvent. In this way they reduce heterosegment contact and minimize repulsive interactions with the neighboring block. For the reasons cited in the previous example, block A (in good solvent) is perturbed somewhat more by the relatively dense block B in the present case than by an expanded block in case C (cf. γ_A's of Tables V and IV). On the other hand, block B (in theta solvent) is perturbed less by an expanded block A than by a shrunken block in a theta solvent in case B. The differences are negligible for positive z_{AB} but they become significant in the negative region. It is much more difficult to induce, by means of negative z_{AB}, the orientational collapse and the collapse of the B block here than it was in the case of theta solvent for both blocks. This observation suggests an interesting new aspect of solution behavior in preferential-solvent systems when $z_{AB} < 0$. The poorly soluble block B is kept from "precipitating", not only by the trivial strong expansion and solvation of the A block, but also indirectly by the relaxing effect the A block exercises on the urge of the B block to collapse due to $z_{AB} < 0$ (cf. γ_B's of Tables V and II for $z_{AB} < 0$). This also means that in the presence of an expanded A block the tendency of a B block to associate will be weaker than one would normally expect.

The data of Table V also serve to illustrate our concern about imprecise usage of theta terminology for block copolymers. If one defined theta conditions, for instance, in terms of $\langle S^2\rangle$, one would have to conclude that the molecule is approximately in its theta state at $(3,0,-1)$ where $\alpha^2 \simeq 1$. In fact, however, the molecular conformation under these conditions is highly nonrandom. The A block is expanded by about 80% above its theta dimensions, while the size of the B block is about 15% smaller. The two blocks also show considerably more overlap than at true theta conditions: N_{AB}^* is higher by a factor of 2.5, the center of mass distance between the two blocks is only ⅔ of the ideal value, and $\langle\theta\rangle \simeq 60°$. The strongly expanded A block has to be overlapped with the B block to produce a chain of "unperturbed" size. On the other hand, if one uses another property to define the theta point, one usually arrives at a different triplet (e.g., $\alpha_G^2 \simeq 1$ for $z_{AB} = -0.75$). While the possibility of two different "theta points" is generally recognized, it is apparent from our data (in Table V as well as other unreported results) that the proximity of two

Table V
Expansion of a Copolymer Molecule in a Preferential Solvent[a] (3,0,z_{AB})

z_{AB}	α^2	$\alpha_A{}^2$	$\alpha_B{}^2$	$\alpha_{GA}{}^2$	$\alpha_{GB}{}^2$	$\alpha_G{}^2$	γ_A	γ_B	σ	$\langle\cos\theta\rangle$	N_{AB}*
−1	1.00	1.80	0.84	1.41	0.79	0.68	0.85	0.84	0.43	0.48	2.57
−0.5	1.36	2.05	0.96	1.81	0.93	1.21	0.97	0.96	0.77	0.16	0.93
−0.25	1.45	2.09	0.98	1.91	0.97	1.37	0.99	0.98	0.87	0.07	0.66
−0.1	1.50	2.11	0.99	1.95	0.99	1.44	1.00	0.99	0.92	0.02	0.55
0	1.52	2.11	1.00	1.98	1.00	1.49	1.00	1.00	0.95	0.00	0.50
0.5	1.62	2.14	1.02	2.06	1.05	1.65	1.01	1.02	1.05	−0.08	0.33
1	1.68	2.15	1.03	2.11	1.09	1.76	1.02	1.03	1.12	−0.14	0.25
2	1.75	2.16	1.05	2.18	1.14	1.90	1.02	1.05	1.21	−0.20	0.17
3	1.80	2.17	1.06	2.22	1.18	2.00	1.03	1.06	1.27	−0.23	0.13
6	1.89	2.18	1.07	2.29	1.24	2.16	1.03	1.07	1.37	−0.28	0.08

[a] Errors are almost constant over the entire range of z_{AB}, about 0.04 to 0.05 for α^2, 0.06 to 0.09 for $\alpha_A{}^2$ and $\alpha_{GA}{}^2$, 0.02 to 0.03 for $\alpha_B{}^2$ and $\alpha_{GB}{}^2$, and 0.04 for $\alpha_G{}^2$.

such points is no assurance that the molecule is close to its true theta state.

(V) Discussion

Under all conditions examined in this paper, the general conclusions formulated by TKI[22] on the basis of their own and others' results have been confirmed, in particular: (1) For $z_{AB} > 0$, the parameters γ_I exceed one but remain close to unity within several percent. (2) The parameter σ is also close to one for $z_{AB} = 0$, and it does not exceed 1.5 in the examined cases. At the same value of z_{AB}, σ becomes smaller with growing expansion of the blocks.

From the present work, these conclusions can now be complemented and also formulated for the negative region of z_{AB}. As previously seen, for $z_{AB} < 0$, γ_I has to be smaller than one. The extent γ_I deviates from one, however, depends strongly on the type of the solvent. In a good solvent for both blocks, γ_I again stays within a few percent of 1 since the intensity of perturbation is low and the distance from the transition region is large. In a preferential solvent, both blocks show very similar γ_I, only slightly lower than in the previous case, since at least one of the above factors is always present. It is only in theta solvent that negative z_{AB} can strongly affect the block dimensions, eventually causing not only orientational collapse but also a condensation of each block. The higher sensitivity of blocks in the theta state to AB interactions is also apparent for $z_{AB} > 0$.

As expected, the angular average $\langle\cos\theta\rangle$ also shows simple behavior; it is zero for $z_{AB} = 0$, positive for $z_{AB} < 0$, and negative for $z_{AB} > 0$. Although one can notice a definite pattern even in the region of positive z_{AB} indicating that at the same value of z_{AB} the angular perturbation diminishes with increasing size of the blocks, the differences are here minor (e.g., at $z_{AB} = 3$, $\langle\theta\rangle \simeq 106°$ if both blocks are in their theta solvent, compared to $\langle\theta\rangle \simeq 101°$ if both blocks are in a good solvent at $z_{II} = 3$). The effect becomes more dramatic in the negative region where, e.g., in the extreme case of $z_{AB} = -1$ we find $\langle\theta\rangle \simeq 75°$ for the case of good solvent for both blocks, while $\langle\theta\rangle \simeq 13°$ in the homopolymer where both blocks are most shrunken.

Other parameters listed in the tables do not always assume trivial values for $z_{AB} = 0$. For instance, both $\alpha_I{}^2$ and $\alpha_{GI}{}^2$ reflect the degree of swelling of each block and become unity only if $z_{II} = 0$ also. The parameter $\alpha_G{}^2$ equals one at $z_{AB} = 0$ if both blocks are in the theta state, or if it is held at one artificially in a preferential solvent by balancing a negative z_{II} against a positive z_{JJ}, where $z_{JJ} > |z_{II}|$. In example D (Table V) the solvent is not poor enough for the B block ($z_{BB} = 0$) and $(\alpha_G{}^2)_{z_{AB}=0}$ is thus greater than one. In another unreported calculation for (3,−0.5,0), z_{BB} was again too negative, yielding $\alpha_G{}^2$ too small, $(\alpha_G{}^2)_{z_{AB}=0} \simeq 0.77$. It is apparent, however, that for $z_{AA} = 3$ the balancing value of z_{BB} lies in the interval $-0.5 \leq z_{BB} \leq 0$. Analogous comments hold for the overall expansion coefficient α^2 which is closely associated with $\alpha_G{}^2$ (eq 12d).

While all expansion coefficients may differ appreciably from unity at $z_{AB} = 0$, the parameter σ is usually very close (although not necessarily identical) to one. From eq 13b and 14, σ reduces for $z_{AB} = 0$ to

$$\sigma = \frac{\alpha_{GA}{}^2(z_{AA},z_{BB},0) + \alpha_{GB}{}^2(z_{AA},z_{BB},0)}{\alpha_A{}^2(z_{AA},z_{BB},0) + \alpha_B{}^2(z_{AA},z_{BB},0)} \qquad (17)$$

That is, $\sigma = 1$ at the true theta state, and any deviations from unity for $z_{AA} \neq 0$, $z_{BB} \neq 0$ result solely from the nonuniform expansion of the isolated blocks. Recalling the above mentioned results of Wall and Hioe,[40] σ should be confined to the region $1 \leq \sigma(z_{AA},z_{BB},0) \leq 1.02$ provided none of the z_{II}'s is negative. In fact, it may be argued that σ will not be too far from one even when one of the z_{II}'s is negative (i.e., generally in preferential solvents with $z_{AB} = 0$): if the solvent is very poor for the B block but good for A, then $\alpha_{GB}{}^2 \ll \alpha_{GA}{}^2$ and $\alpha_B{}^2 \ll \alpha_A{}^2$, and the effect of the B expansion coefficients on the ratio is small. Before examining our data in the light of these considerations we note that σ is the only parameter which is a property of a pair of blocks and is defined as the ratio of two different quantities, $\langle G^2\rangle$ and $\langle S_{HI}{}^2\rangle$. It is apparent that any deficiencies of our ensemble to correctly match the true structural parameters of the coil would appear here as deviations of σ from expected values. At the theta state, σ differs from one by $\simeq$½% (Table I). The larger negative deviation of σ at (3,0,0) (Table V) is caused by the lack of adequate expansion $\alpha_{GI}{}^2$ of the end segment employed for the construction of the diblock. It is apparent that the deviation would be smaller if both ends of the chains in the file (or a bigger ensemble) were used for averaging. On the other hand, the excellent agreement observed for σ at (3,3,0) has to be credited to favorably biased sampling since in view of eq 17, the complete sample (of the limited ensemble employed) should yield σ even lower than the value computed for (3,0,0). In fact, reasonable behavior has been observed for the entire series (z,z,0) (not tabulated in this paper) where $\sigma = 1$ in the wide range $-0.25 \leq z \leq 1$, slowly rising to 1.03 for $z = 6$, and rapidly increasing in the collapsed region to 1.25 for $z = -1$. It thus appears that the preferential solvent (Table V) is the only case where the σ values are suspected of having somewhat larger errors, being underestimated by probably 5–6%.

Experimentally, the most easily accessible of the listed quantities is the overall radius of gyration $\langle S^2\rangle$ or its expansion coefficient α^2, closely related to the $\alpha_I{}^2$'s and $\alpha_G{}^2$. A frequent point of discussion has been under what conditions (besides the trivial theta state) would the general eq 15 and 12d reduce to the simple additive form

$$\langle S^2\rangle = w_A(1 + 2w_B)\langle S_A^2\rangle + w_B(1 + 2w_A)\langle S_B^2\rangle \quad (18)$$

or its equivalent for our special case of $N_A = N_B$, $\sigma_A = \sigma_B$

$$\alpha^2 = \tfrac{1}{2}(\alpha_A^2 + \alpha_B^2) \quad (19)$$

Let us first examine how well this additivity rule is satisfied in the simplest case of $z_{AB} = 0$. Here, irrespective of z_{AA} and z_{BB}, one finds from eq 14

$$\alpha_G^2 = x_A\alpha_{GA}^2 + x_B\alpha_{GB}^2 \quad (20)$$

Substituted into eq 12d, α_G^2 of eq 20 then gives for our special case

$$\alpha^2 = \tfrac{1}{4}(\alpha_A^2 + \alpha_B^2 + \alpha_{GA}^2 + \alpha_{GB}^2) \quad (21)$$

Since for nonnegative z_{II}'s, α_{GI}^2 is very close to α_I^2,[40] the additivity rule is expected to hold in this region (i.e., in principle for copolymers in both good and preferential solvents) within a few percent whenever $z_{AB} = 0$, slightly underestimating α^2. (For additivity to be rigorously obeyed, z_{AB} should be slightly negative if $z_{II} > 0$ and $z_{JJ} \geq 0$.) This expectation is supported by our data in Tables IV and V where for $z_{AB} = 0$ the deviations from additivity amount to only ca. −2%. The opposite sense of the deviations found by us has to be again attributed to the lack of expansion in α_{GI}^2. For $z_{AB} > 0$, the monotonic trends displayed by our data support the intuitive expectation that deviations from the additivity rule should rise with increasing z_{AB}. The relative deviations are strongest in the case of theta solvent for both blocks. For instance, for $z_{AB} = 5$, $(\Delta\alpha^2)_{rel} \simeq 25\%$, rising to more than 30% if the slight expansion of the two blocks is disregarded in calculation. For all other examined cases, at $z_{AB} = 6$, the deviations are smaller: $\simeq$16% for a copolymer in a preferential solvent, $\simeq$14% in a good solvent, and $\simeq$11% for a homopolymer. In general the order of the three cases will depend on the actual values of z_{IJ}'s used for comparison, but this example shows the magnitude of the effect one can expect. The present results clearly indicate that the additivity rule does not survive the process of segregation in a copolymer molecule at high z_{AB}, as has been sometimes implied.[3a] Besides the numerical evidence, this is obvious from the model itself (Figure 1). Even if the internal conformation of each block were not affected by $z_{AB} \gg 0$, $\langle S^2\rangle$ would still increase beyond the sum $\langle S_A^2\rangle + \langle S_B^2\rangle$ because of negative $\langle\cos\theta\rangle$ (cf. eq 14 and 15). The relative orientation of the two blocks becomes more open to reduce unfavorable AB contacts. Moreover, we have seen that both blocks swell slightly above their isolated dimensions ($\gamma_I > 1$), and more importantly, the end segments are pulled out of the two blocks, both of which factors contribute to a further increase in $\langle S^2\rangle$. The relatively low sensitivity of the additivity criterion to z_{AB} for other than theta solvents explains why the experimentally observed deviations from it have often been small.[2a,3a,15] On the other hand, it is obvious that it is difficult if not impossible to make any valid conclusions about the conformation or the precise magnitude of z_{AB} from the approximate compliance of the experimental data with the additivity rule. Certainly such agreement does not prove that the conformation is segregated (i.e., more segregated than a Gaussian conformation).[3a]

The last sentence brings to mind the ambiguity associated with the term "segregation". What molecular parameter, if any, can be used to compare the segregation in different solvents, say at $z_{AB} = 3$? If one chose the relative deviation of α^2 from additivity, or σ, or perhaps $\langle\cos\theta\rangle$ indicating the angular separation of the blocks, the highest segregation would be achieved in a theta solvent. On the other hand, if one measured the segregation in terms of the expansion of the distance between the centers of mass of the two blocks α_G^2, or the number of AB contacts N_{AB}, the winner would be the copolymer in a good solvent and, somewhat surprisingly, the homopolymer (which takes over exclusively this category for $z_{AB} > 3$). Hence, although a rise in z_{AB} at constant z_{AA} and z_{BB} could always be interpreted in terms of increasing segregation (whatever measure is adopted), such an unequivocal correspondence does not exist in general. We believe that, whenever possible, this term should be replaced by physically well-defined molecular quantities. Also, it appears that the phenomenon of segregation is in no way limited to block copolymers. Whatever measure is chosen for its description, the segregation of the two halves of the molecule always occurs in homopolymers too.

The geometrical picture of polymer molecules in dilute solutions represented by the present model is new. So far, the block copolymer molecules have often been discussed in terms of two fundamentally different conformations: Gaussian (usually in a spherically symmetrical form) and the segregated dumbbell conformation (implying a uniaxial symmetry).[3a,21,42] The latter model originated intuitively, because of the clear need to separate the two blocks for $z_{AB} \gg 0$, but it has also been supported by some sophisticated arguments.[21] BEM, on the other hand, presents a somewhat different and hopefully more realistic picture of the overall shape. Because of the undeniably highly asymmetric shape of the two halves (blocks) of the molecule, and a strong correlation of the end-segment vectors $\mathbf{G}_I$ with the longest principal axes of the blocks, the average conformation of the molecule in BEM is best described as "bent" or "arrowhead-like" (Figure 1). There is too little energetical incentive for the molecule to assume the geometrically unique linear conformations)either completely overlapped, or dumbbell). The two blocks prefer rather to pivot about their common joint-segment, with the average position depending on z_{IJ}'s. The above mentioned theoretical support[21] for the segregated dumbbell conformation of block copolymers should not be taken literally. It has been obtained by solving a diffusion equation which, by following simultaneously an infinite number of paths originating from a source, preaverages the chain conformations. Hence, the result is not expected to describe accurately the conformation of an isolated block copolymer molecule. For the very same reason, the analogous diffusion-equation approach for a homopolymer yields a spherically symmetrical segment density distribution, although its true shape is far from spherical.

Another model suggested for a "segregated" copolymer molecule is the core-in-shell (or monomolecular micelle) model.[8,42,43] It assumes a compact core of the block B surrounded by a shell of the expanded block A, with both blocks roughly having spherical symmetry and being concentric. Although it has been originally proposed for a solvent which is good for A block but poor for B block, the model was recently invoked also for a case where the solvent is good for both blocks.[44] In our opinion, it is improbable that such a model would be generally valid. Let us first examine the case where the unperturbed dimensions of both blocks are of comparable magnitude, and neither of the two blocks is collapsed due to the solvent action itself ($z_{AA} \geq 0$, $z_{BB} \geq 0$). It is apparent that a shelllike conformation of the A block with a void size the same order of magnitude as the mean square radius is extremely unlikely, and could be realized only if the entropy loss were compensated by a large energetical gain. But what source of energy is available in the present case? The increased number of AB contacts in the core-in-shell conformation, as compared to other "segregated" conformations, is a disadvantage energetically since the two kinds of segments dislike each other (otherwise segregation would not have occurred). Similarly, the "shielding" of the B core from the solvent by shell A could not produce the desired effect since both blocks still contain a high amount of the solvent even if

B is in a theta solvent. The picture becomes somewhat different for the other extreme situation when one block, say B, is substantially smaller than the other, either as the result of a great discrepancy in their unperturbed dimensions ($x_B \ll x_A$), or because B is collapsed into a dense particle ($z_{BB} \ll 0$), while A is expanded. In this case, the B block cannot avoid being almost entirely surrounded by solvent containing some A segments, but the position of the B block core is very different from that usually associated with the core-in-shell model. The collapsed B block is far from the center of A, in the less dense tip-region around the end segment of A. The graphical representation of this special case now depends on how far one draws the "region" of the A block (Figure 3). If attention is focused on the high-density region, and the A boundary is identified with the ellipsoid L_{Ak}^2, then the end segment of A (and hence the B block) lies outside the block A. As emphasized above, the ratio $\langle G_A^2\rangle/\langle S_A^2\rangle \simeq 2$ in the isolated A block and grows even larger for $z_{AB} > 0$. On the other hand, if the A-block boundary is extended to include a greater portion of A segments, the B block becomes either partially or entirely enveloped by it, in the latter case resembling in a way an asymmetrical core-in-shell model. Hence, it appears that only when there is a large difference between block sizes and a particular boundary representation is chosen the core-in-shell description is justified, though even here in a modified sense. If the B block should start growing (either through more positive z_{BB} or relaxation of the condition $x_B \ll x_A$, while keeping $z_{AB} \gg 0$), it will grow away from the A block, making the arrowhead-like structure more pronounced, and not inwards, creating a nearly concentric structure of two segregated bodies.

It should be pointed out that for the homopolymer the BEM yields an overall molecular shape surprisingly consistent with the average shape of the random-flight chains in the ensemble. For instance, for BEM at the theta state the overall principal components ratio $\langle L_3^2\rangle:\langle L_2^2\rangle:\langle L_1^2\rangle \simeq 12.1:2.69:1$, practically identical with the ratio for our ensemble, 12.1:2.71:1. BEM also correctly predicts an increase in asymmetry with growing z for a homopolymer:[24,45] $\langle L_3^2\rangle:\langle L_2^2\rangle:\langle L_1^2\rangle \simeq 14.3:2.98:1$ for $z = 3$; 15.8:3.20:1 for $z = 6$; and 9.2:2.4:1 for $z = -0.25$.

(VI) Conclusion

The biellipsoidal model (BEM) for polymer molecules offers several advantages as compared to other models. (i) The model represents a higher level description of conformations of homopolymer molecules than the previously reported single ellipsoid model (SEM).[24] By mentally dividing the molecule into two parts, one-half of the molecule is allowed to expand differently than the other, and the orientations of the principal axes of the two halves are not forced to coincide. In spite of this increase in the number of degrees of freedom for a molecule, the average overall size and shape (as measured by the square principal components of the radius, L_k^2) at the theta point are well reproduced. (ii) Even before quantitative evaluations, the model yields qualitatively correct answers to some problems which posed difficulty in the past. For instance, by merely employing the concept of the joint segment and the angle θ, it is immediately seen that in block copolymers, the heterocontact interactions z_{AB} must affect the overall radius even if z_{AA} and z_{BB} are kept constant. (iii) The model is simple enough to permit the calculation of block copolymer conformations under general conditions. In the special cases which have been approached by other more rigorous methods, the model shows good agreement. (iv) The model offers a unified view of both homopolymers and block copolymers, with one category continuously changing into the other. It becomes apparent that the terms which have often been associated exclusively with block copolymers (e.g., the extent of segregation of the two parts of the molecule) have their counterpart in homopolymers as well. (v) Without introducing any new concepts, the present model can be easily generalized to triblock copolymer molecules, as well as employed in the calculation of the second virial coefficient for block copolymer solutions.

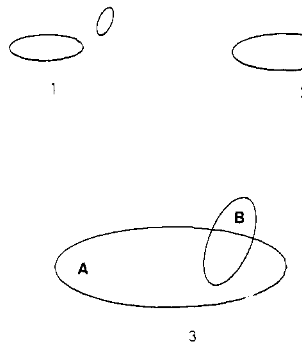

Figure 3. Three possible representations of an AB block copolymer molecule for the triplet (3,−0.5,3) (good solvent for A, nonsolvent for B, A and B incompatible). The semiaxes of each of the ellipses are related to the corresponding block dimensions by $l_I = n^{1/2}\cdot\text{constant}(\langle L_1^2\rangle + \langle L_2^2\rangle)^{1/2}$, $l_{II} = n^{1/2}\text{constant}\langle L_3^2\rangle^{1/2}$, while the center-of-mass distance $g = \text{constant}\langle G^2\rangle^{1/2}$. Different values of n chosen for the three cases affect the boundary used to represent each block as well as the portion of segments p contained within that boundary: (1) $n = 1, p \simeq 60\%$; (2) $n \simeq 2, p = 87\%$; (3) $n = 10, p \simeq 100\%$. The two ellipses only start touching each other when they contain almost 90% of segments, and B is not entirely engulfed by A even in the most extreme case (3).

A disadvantage inherent to the BEM is the inferior random sampling of pairs of chains from the ensemble, as compared to the sampling of single chains for SEM. Although the introduced bias can be partly reduced by suitable definitions of expansion coefficients, the best recipe seems to be to employ some form of nonrandom sampling. Another factor very important for the intrinsic consistency of the computed data is the adequate behavior of the end segment coordinates of chains in the ensemble. In hindsight, it appears that we should have employed both ends of each selected chain for constructing the copolymer molecule, rather than only one randomly selected end; this would have improved the performance of the model with only little cost in computer time. We feel that by taking into consideration these two points, the reliability of the model would be extended beyond the present limit of $z_{IJ} \approx 3$.

Similarly to other smooth-density models, the BEM is capable of reproducing an intramolecular transition. The more detailed description of the molecule employed in this model makes it possible to distinguish several different types of transitions. The transition may result from a volume collapse of one or both blocks (if z_{II} grows negative); it may be due to orientational collapse followed by a volume collapse of both blocks (for instance, if z_{AB} becomes strongly negative and z_{AA} and z_{BB} are zero); and it may also be caused by a simultaneous orientational and volume collapse (as occurs in the most common case, the homopolymer, if $z_{AA} \equiv z_{BB} \equiv z_{AB}$ grow negative). In these cases the transition should experimentally appear as a more or less sudden drop (depending on the molecular weight) in the respective dimension of the molecule, not unsimilar to the behavior observed for the helix–coil transition. Preliminary investigation shows that even more complex types of dependences may arise under suitable conditions. We do not believe that segregation per se could provoke a transition between the Gaussian and "segregated" conformation, due only to z_{AB} increasing from zero to positive values. This conclusion is not necessarily contradicted by transitions experimentally observed (as pointed out to us by one reviewer) in the region where all z's are purportedly positive. While the parameters z_{AA} and z_{BB} are usually known with reasonable confidence from dilute solution studies on homopolymers, reliable methods for estimating z_{AB} are not available. It is yet possible that the parameter z_{AB} behaves differently in the transition region than assumed in such experimental studies.

In the positive region, the magnitude of the heterocontact interactions z_{AB} has very little effect on the size of each block which remains within several percent the same as if the blocks were disconnected. More sensitive are the angle θ describing the relative orientation of the blocks and the distance of the joint segment from the centers of mass of each block G_I, both of which grow steadily with increasing z_{AB}. The strongest effect is then seen in the distance between the centers of mass of the blocks G where both of the above contributions are combined. The extent of the effect depends on the solvent in which the block copolymer is immersed. In a theta solvent for both blocks, the segment densities are high and the blocks themselves close to their transition region, hence the z_{AB} effect is strongest. The effect becomes weaker in a preferential solvent, and is smallest in a good solvent for both blocks.

The shape of a polymer molecule can best be characterized as "arrowhead-like", with the angle and sizes of the two arms of the arrowhead depending on the solvent and temperature. It is doubtful that a block copolymer molecule would ever assume either a dumbbell conformation or a concentric spherically symmetrical core-in-shell conformation.

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