Macromolecules **1994,** *27,* 2726–2731

Conformational Properties of Diblock Copolymers: Monte Carlo Calculations and Comparison with the Renormalization Group Predictions

Costas H. Vlahos and Arturo Horta

Departamento de Quimica Fisica, Facultad de Ciencias, Universidad National de Education a Distancia, 28040 Madrid, Spain

Luis A. Molina and Juan J. Freire*

Departmento de Quimica Fisica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040 Madrid, Spain

Received September 27, 1993; Revised Manuscript Received February 24, 1994[⊛]

ABSTRACT: The conformational properties of an AB diblock copolymer chain with different kinds of interactions between the units are studied by off-lattice Monte Carlo simulation. Using the Pivot algorithm, we calculate the radii of gyration, the end-to-end square distances of the individual blocks and of the whole molecule, the distance between the two centers of masses, and other static properties for various molecular weights and different solvent conditions. From these results, we obtain the dimensionless ratios that describe the effects of the AB heterocontacts relative to the precursor homopolymers. These quantities are compared with previous theoretical predictions.

Introduction

The behavior of AB diblock copolymers has been the subject of an increasing number of studies[1–14] in recent years, due both to its theoretical interest and to the potential technological application of these molecules. The conformational properties of an isolated chain can be theoretically predicted with the help of methods inspired by the application of the renormalization group theory to polymers. Thus, calculations[2–7] in terms of the three excluded volume parameters representing the interactions between the same (AA, BB) and different (AB) pairs of units have been performed up to first order in the small parameter $\epsilon = 4 - d$ (d is the space dimension). These calculations lead to analytical formulas for different ratios of conformational properties of the diblock copolymer relative to those of homopolymer chains. Explicitly, one can consider the following ratios:[8]

$$\sigma_{R_{\mathrm{AB}}} = \langle R^2_{\mathrm{AB}}\rangle / [\langle R^2_{\mathrm{A\text{-}H}}\rangle + \langle R^2_{\mathrm{B\text{-}H}}\rangle] \tag{1.1}$$

$$\sigma_G = \langle G^2_{\mathrm{AB}}\rangle / [\langle G^2_{\mathrm{A\text{-}H}}\rangle + \langle G^2_{\mathrm{B\text{-}H}}\rangle] \tag{1.2}$$

$$\gamma_{R_{\mathrm{k}}} = \langle R^2_{\mathrm{k}}\rangle / \langle R^2_{\mathrm{k\text{-}H}}\rangle \qquad (\mathrm{k} = \mathrm{A\ or\ B}) \tag{1.3}$$

$$\gamma_{S_{\mathrm{k}}} = \langle S^2_{\mathrm{k}}\rangle / \langle S^2_{\mathrm{k\text{-}H}}\rangle \qquad (\mathrm{k} = \mathrm{A\ or\ B}) \tag{1.4}$$

$$\gamma_{G_{\mathrm{k}}} = \langle G^2_{\mathrm{k}}\rangle / \langle G^2_{\mathrm{k\text{-}H}}\rangle \qquad (\mathrm{k} = \mathrm{A\ or\ B}) \tag{1.5}$$

where R_{AB} = end-to-end distance of the overall diblock copolymer chain (AB), G_{AB} = distance between the centers of mass of blocks A and B, $R_{\mathrm{k\text{-}H}}$ = end-to-end distance of the homopolymer equivalent of block k (k = A or B), i.e., of a homopolymer chain with the same number of k units as the k block (k–H), $S^2_{\mathrm{k\text{-}H}}$ = quadratic radius of gyration of k–H, $G_{\mathrm{k\text{-}H}}$ = distance between the origin and the center of mass of k–H, R_{k} = distance between the end of the k block and the blocks' common origin (modulus of the k-block end-to-end vector $\vec{R}_{\mathrm{k}}$), S^2_{k} = quadratic radius of gyration of block k, and G_{k} = distance between the center of mass of block k and the blocks' common origin (modulus of the vector $\vec{G}_{\mathrm{k}}$). These ratios are a quantitative measure of the effects the AB heterocontacts have on the conformation of the copolymer chain. The theoretical formulas for these ratios depend only on the diblock composition (fraction ρ of units B to units A), the macroscopic state of the copolymer (i.e., the thermodynamic solving conditions of the homopolymer blocks), and the parameter $\epsilon = 4 - d$, related to the space dimension, d. They do not depend, however, on the chain length or molecular weight.

Due to the lack of adequate experimental data for those systems, the first-order theoretical expressions can only be checked through comparison with simulation data. However, the simulation work for conformational properties of isolated diblock chains is scarce and not very recent. Birshtein et al.[9] reported some results showing the variation of the chain mean dimensions with varying solvent quality. Tanaka et al.[8,10–14] performed a more systematic work, which, however, covered only partially the cases and properties of interest. Moreover, some of these results exhibit significant disagreements with the theoretical predictions. These discrepancies may have their origin either in the approximations involved in the first-order theory or in the finite size effects and numerical uncertainties associated with the simulations.

In the present work, we have carried out an exhaustive simulation study of conformational properties for linear diblock copolymers in different solvent conditions. The molecules are modeled as assemblies of Gaussian subunits, incorporating the interactions between them by means of added Lennard-Jones potentials with conveniently set parameters. We employ a Monte Carlo algorithm[15–17] which has been previously shown to be useful in the characterization of linear and star chains. The good numerical performance of this particular method has allowed us to obtain averages of the properties with narrow error bars. The comparison of these new simulation data with the theoretical results provides, consequently, a better clarification of the usefulness of the theoretical approach,

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[⊛] Abstract published in *Advance ACS Abstracts,* April 1, 1994.

0024-9297/94/2227-2726$04.50/0

helping us to establish a broader understanding of the global physical behavior of isolated copolymer chains.

Method

The AB diblock copolymer chain studied herein consists of $N + 1$ beads joined by N bonds with Gaussian-distributed lengths. N_{A} of these beads are considered as units of the A type (A block). They are numbered starting from the A unit which is closest to the chain center and advancing toward the corresponding chain end. The $N_{\mathrm{B}} = N - N_{\mathrm{A}}$ units belonging to the other part of the chain are assigned to be of the B type (B block). The central unit is the common origin of coordinates and is assigned as unit $N + 1$. Nonneighboring units interact through (12–6) Lennard-Jones potentials[16]

$$U(R_{\mathrm{ij}})/k_{\mathrm{B}}T = 4(\epsilon_{\mathrm{kl}}/k_{\mathrm{B}}T)[(\sigma/R_{\mathrm{ij}})^{12} - (\sigma/R_{\mathrm{ij}})^{6}], \quad \mathrm{k,l} = \mathrm{A\ or\ B} \tag{2.1}$$

where ϵ_{kl} are the interaction energies between units of the same (AA, BB) or different (AB) homopolymers, R_{ij} is the separation distance between units i and j, and σ is a steric parameter considered to be the same for all units. In general, several different macroscopic states and crossover behaviors can be achieved with the diblock copolymers because the different long-range interactions can vary independently by changing the temperature or the solvent quality. The most important macroscopic states, characterized by strong repulsions between dissimilar units, correspond to the following cases: (a) both blocks are in the Θ state (common Θ solvent); (b) one block is in the Θ state and the other is in the good solvent regime (selective type of solvent); and (c) both blocks are in the good solvent regime (common good solvent). To reproduce these different macroscopic states, we adopt previously reported sets of Lennard-Jones parameters which try to mimic the different regimes for the homopolymer blocks. Previous investigations[17] have shown that a homopolymer chain is in the good solvent regime for the value $\epsilon_{\mathrm{kl}}/k_{\mathrm{B}}T = 0.1$, whereas the choice $\epsilon_{\mathrm{kl}}/k_{\mathrm{B}}T = 0.275$ reproduces the quasi-ideal Θ state in which binary interactions cancel. (These values reproduce the expected proportionality of the mean chain dimensions and $N^{3/5}$ (good solvent) or $N^{1/2}$ (Θ solvent), respectively.) The value $\epsilon_{\mathrm{kl}}/k_{\mathrm{B}}T = 0$ corresponds to the ideal (Gaussian) Θ chain without interactions between units. The repulsive cross heterointeractions between dissimilar units are always set to correspond to $\epsilon_{\mathrm{AB}}/k_{\mathrm{B}}T = 0.1$. The value $\sigma = 0.8$ is fixed for all calculations.[16]

The properties of interest in the present study are those enumerated in the Introduction. We also estimate the radius of gyration of the diblock chain $\langle S^2_{\mathrm{AB}}\rangle$ and the mean cosine of the angle between the block end-to-end vectors $\cos(\vec{R}_{\mathrm{A}} \wedge \vec{R}_{\mathrm{B}})$. Averages are obtained from the relations[18]

$$\langle S^2_{\mathrm{AB}}\rangle = [1/(N+1)^2] \sum_{m=1}^{N+1} \sum_{n \geq m}^{N+1} \langle(\vec{R}_m - \vec{R}_n)^2\rangle \tag{2.2}$$

$$\langle S^2_{\mathrm{A}}\rangle = [1/(N_{\mathrm{A}}+1)^2] \sum_{m=1}^{N_{\mathrm{A}}+1} \sum_{n \geq m}^{N_{\mathrm{A}}+1} \langle(\vec{R}_m - \vec{R}_n)^2\rangle \tag{2.3}$$

$$\langle S^2_{\mathrm{B}}\rangle = [1/(N_{\mathrm{B}}+1)^2] \sum_{m=1}^{N_{\mathrm{B}}+1} \sum_{n \geq m}^{N_{\mathrm{B}}+1} \langle(\vec{R}_m - \vec{R}_n)^2\rangle \tag{2.4}$$

$$\langle G^2_{\mathrm{AB}}\rangle = (1/\Phi_{\mathrm{A}}\Phi_{\mathrm{B}})\langle S^2_{\mathrm{AB}}\rangle - (1/\Phi_{\mathrm{B}})\langle S^2_{\mathrm{A}}\rangle - (1/\Phi_{\mathrm{A}})\langle S^2_{\mathrm{B}}\rangle \tag{2.5}$$

$$\cos(\vec{R}_{\mathrm{A}} \wedge \vec{R}_{\mathrm{B}}) = \langle(R^2_{\mathrm{A}} + R^2_{\mathrm{B}} - R^2_{\mathrm{AB}})/(2|\vec{R}_{\mathrm{A}}||\vec{R}_{\mathrm{B}}|)\rangle \tag{2.6}$$

$$\langle G^2_{\mathrm{k}}\rangle = -\langle S^2_{\mathrm{k}}\rangle + \langle R^2_{\mathrm{k}}\rangle, \quad \mathrm{k} = \mathrm{A\ or\ B} \tag{2.7}$$

where $\vec{R}_m$ and $\vec{R}_n$ are the position vectors of the mth and nth units, and $\Phi_{\mathrm{B}} = 1 - \Phi_{\mathrm{A}}$ is the weight fraction of the B block.

Different Monte Carlo sampling methods described in earlier work[17] have been employed for the three macroscopic states. In the cases of a common good and a selective solvent, the Pivot algorithm is used. It starts by building an initial configuration of moderate energy, and then a bead is selected at random and its coordinates with respect to the preceding bead are resampled from the appropriate Gaussian distribution. The rest of the beads on the selected block up to the closest end are connected to the new bead and then rotated with respect to the moved bead according to three randomly chosen Euler angles. To explore the common Θ solvent macroscopic state, for which the chain dimensions are smaller and the units are more densely packed, we modified the Pivot algorithm,[17] to optimize the statistical efficiency of the sampling method, so that the final rotation for the chosen part of the arm is not performed. In all cases, a Metropolis energy criterion is used to test the acceptance or rejection of the new trial configurations. Eight independent runs are performed. Each run attempts from 200 000 to 400 000 configurations after appropriate thermalization. The properties are averaged first over all conformations in each run, and then the mean values and the standard deviations are determined from the eight independent runs.

Results and Discussion

(a) Common Θ Solvent. First we consider the case of the symmetric diblock copolymer with both branches under the ideal Θ conditions, similar to those established in the theoretical methods[2–7] and in the previous Monte Carlo simulations.[8–14] The conformational properties of such chains with total number of units $N + 1 = 41, 61, 81, 101, 151$, and 201 have been calculated by the modified Pivot algorithm for the values of the energetic parameters $\epsilon_{\mathrm{AA}}/k_{\mathrm{B}}T = 0$, $\epsilon_{\mathrm{BB}}/k_{\mathrm{B}}T = 0$, and $\epsilon_{\mathrm{AB}}/k_{\mathrm{B}}T = 0.1$, corresponding to ideal homopolymer blocks and excluded volume heterointeractions. The simulation data for the radius of gyration $\langle S^2_{\mathrm{AB}}\rangle$ and the end-to-end distance $\langle R^2_{\mathrm{AB}}\rangle$ have been fitted with a weighted nonlinear least-squares routine to determine the scaling law with respect to molecular weight. We found that the critical exponent 2ν for $\langle S^2_{\mathrm{AB}}\rangle$ and $\langle R^2_{\mathrm{AB}}\rangle$ has the values 0.988 ± 0.002 and 1.002 ± 0.003, respectively. These values are in excellent agreement with the value $2\nu = 1$ predicted by the renormalization group theory and confirm that the cross interactions do not contribute to the critical exponent. (Good correlations are obtained in all cases, which indicate that the studied chains have clearly reached the long-chain asymptotic behaviors represented by these power laws.) To estimate quantitatively the effects of heterointeractions, we have calculated the dimensionless ratios γ_Q and σ_Q (eqs 1.1–1.5). For the present macroscopic state we are also interested in the expansion factors $\alpha^2_Q = \langle Q^2_{\mathrm{AB}}\rangle/\langle Q^2\rangle_{\mathrm{ideal}}$, where $\langle Q^2\rangle_{\mathrm{ideal}}$ is the quadratic average which corresponds to an ideal, unperturbed chain (i.e., equivalent to AB, but without the AB heterointeractions). For $Q \equiv R$ or $Q \equiv G$, these ratios are identical to σ_G or $\sigma_{R_{\mathrm{AB}}}$,

Table 1. Dimensionless Ratios for the Macroscopic State of a Common Θ Solvent

	present work			
	ideal	quasi-ideal	previous MC[a]	RG[b]
α_s^2	1.193 ± 0.003		1.22	1.189
σ_G	1.355 ± 0.004	1.377 ± 0.004	1.43 (1.42[c])	1.324
$\sigma_{R_{AB}}$	1.185 ± 0.005	1.189 ± 0.005	1.22	1.173
γ_{R_A}	1.096 ± 0.004	1.100 ± 0.004	1.09	1.111
γ_{S_A}	1.027 ± 0.002	1.035 ± 0.002	1.02	1.054
γ_{G_A}	1.187 ± 0.002	1.188 ± 0.009		
$(\vec{R}_A \wedge \vec{R}_B)$	95.4 ± 0.1	96.38 ± 0.60		

[a] Reference 8. [b] References 4 and 6. [c] Reference 14.

respectively. For $Q \equiv S$, it is explicitly calculated. Since the theories and the previous Monte Carlo data are for infinite chains, it is necessary to obtain the extrapolated values of our ratios through linear regression analysis vs N^{-1} in a way similar to that employed in previous work.[16,17] These extrapolated results are listed in the first column of Table 1. The small uncertainties of these values are a good indication of the accuracy of this extrapolation procedure.

Next we consider the case of the quasi-ideal Θ solvent by introducing homointeractions A–A and B–B, but with the parameter values which correspond to an effective cancellation of attractive and repulsive interactions within each block. As explained in the Introduction the parameter ϵ_{kk}/k_BT is chosen to reproduce the variation of dimensions with chain length for chains in a Θ solvent.[17] This way we can compare this more realistic state with the theoretical predictions based on simpler models. As in the preceding case, the heterointeractions correspond to a net repulsion between the A and B units. Repeating the calculations for slightly shorter chains ($N + 1 = 41, 61, 81, 101$, and 151) and the energetic parameters $\epsilon_{AA}/k_BT = 0.275$, $\epsilon_{BB}/k_BT = 0.275$, and $\epsilon_{AB}/k_BT = 0.1$, we find that the critical exponent 2ν of the radius of gyration is equal to 1.058 ± 0.005. These slight excluded volume effects in the copolymer[19] at the homopolymers' Θ temperature can be explained rather simply (as in the case of cosolvent systems[20]) by considering the competitive effects between the interactions of dissimilar units and those between the solvent and the chain units. The repulsive heterointeractions, in the current case, increase the solvent power and consequently extend the chain. To study the net effects of the cross interactions, in a way similar to that used for the ideal Θ solvent, it is necessary to determine a lower temperature which is the appropriate quasi-ideal Θ for the diblock copolymer chains. After different trials, we have found that the value $\epsilon_{kl}/k_BT = 0.3$ for A–A and B–B interactions is consistent with the scaling law $\langle S_{AB}^2\rangle \sim N$. The dimensionless ratios calculated with the new parameters are independent of the molecular weight (Figure 1), in agreement with the renormalization group theory. Their extrapolated values obtained with the same procedure as before are listed in the third column in Table 1. In the same table, we also include the previous Monte Carlo and theoretical results for comparison purposes.

It can be observed that the general trends predicted by the first order in ϵ renormalization group theory are similar to those shown by the different Monte Carlo results. For instance, all the results show that the ratio σ_G has the largest value and the γ_{S_A} the smallest one. However, the values of the ratios α_S^2 and σ_Q ($Q \equiv R, G$) obtained with our methods are in much better agreement with the renormalization group predictions than with the previous Monte Carlo results. More discrepancies are observed with the ratios γ_Q, expressing the relative expansion of the blocks with respect to the homopolymer precursors, especially for γ_{S_A}, where the Monte Carlo results are in clear disagreement with the theoretical predictions. Higher order ϵ corrections, introduced to the theory by the reexponentiation[4] of the first-order ϵ results or by an alternative method,[21] yield values that are even closer to our findings in several cases ($\sigma_G = 1.36$ or 1.38, $\gamma_{S_A} = 1.03$,). The ideal and quasi-ideal models give almost identical values, which indicates the lack of regions with high internal densities, therefore suggesting negligible third-order interaction effects.

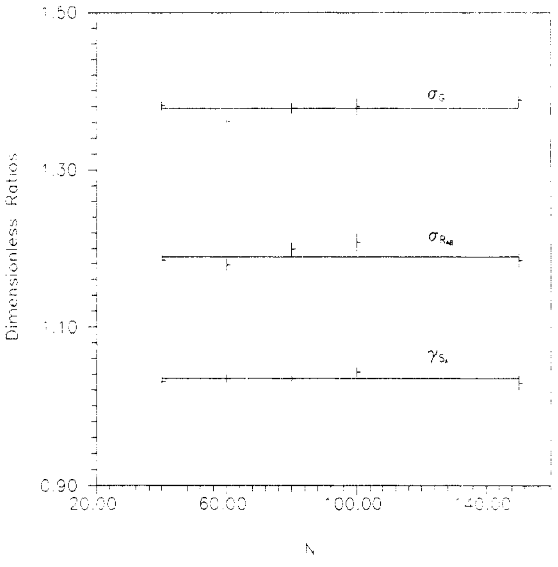

Figure 1. Plots of various dimensionless ratios vs chain size N for symmetrical diblock copolymers (quasi-ideal Θ conditions for the blocks).

The calculation of the mean square distances between each block center of mass and the blocks' common junction ($\langle G_A^2\rangle$ and $\langle G_B^2\rangle$) can help us understand the mechanism responsible for the large value of σ_G. The increase of $\langle G_{AB}^2\rangle$ due to A–B interactions can be obtained from the equation

$$\langle G_{AB}^2\rangle = \langle G_A^2\rangle + \langle G_B^2\rangle - 2\langle|\vec{G}_A||\vec{G}_B|\cos(\vec{G}_A \wedge \vec{G}_B)\rangle$$

as

$$\delta\langle G_{AB}^2\rangle = \delta\langle G_A^2\rangle + \delta\langle G_B^2\rangle - 2\langle|\vec{G}_A||\vec{G}_B|\cos(\vec{G}_A \wedge \vec{G}_B)\rangle$$

where $(\vec{G}_A \wedge \vec{G}_B)$ is the angle between the vectors $\vec{G}_A$ and $\vec{G}_B$ and $\delta\langle G_x^2\rangle = \langle G_x^2\rangle - \langle G_x^2\rangle_{\text{ideal}}$ (x = a or B or AB). According to our simulation results, the contribution of the term $\delta\langle G_A^2\rangle + \delta\langle G_B^2\rangle$ is equal to or slightly higher than the contribution from the cross term. This means that the copolymer chain, in order to reduce the effects of heterointeractions, achieves a new configurations, characterized by a significant deformation along the blocks (mainly near the A–B junction, where the possibility of heterointeractions is high), which causes a change in the relative orientation of the two blocks. $\langle S_A^2\rangle$ remains almost constant, indicating that the bead density increases toward the center of each block to compensate for the increase of the end-to-end distance.

With the aim of clarifying the meaning of some of the present results, we have also performed simulations for artificial[8] segregated diblock copolymer chains. In these simulations, the blocks in a copolymer chain without A–A, B–B, or A–B interactions are separated by a noninteracting plane passing through the blocks' common origin. According to the Metropolis criterion, we accept every

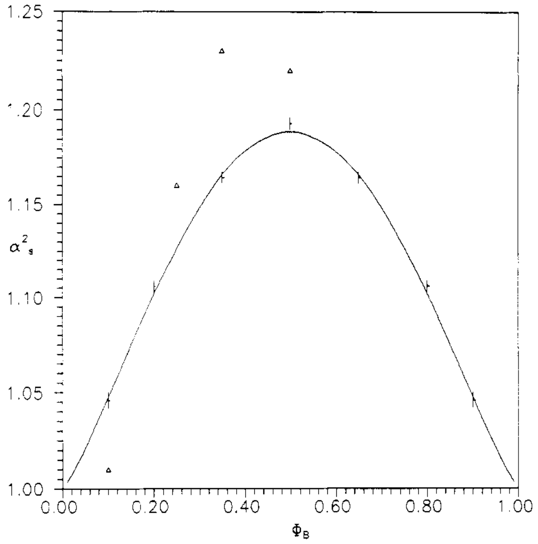

Figure 2. Expansion factor, α_S^2, as a function of the length fraction of B block, $\Phi_B = N_B/(N_A + N_B)$, for chains under ideal Θ conditions and excluded volume heterointeractions. Solid line, theoretical results; (Δ) previous Monte Carlo results; (|-) results of the current work.

conformation for which the separation condition is held; i.e., the surface is considered as a barrier with infinite energy. We use the chain lengths previously specified. In this way, we obtain the following extrapolated results for the dimensionless ratios: $\alpha_S^2 = 1.987 \pm 0.002$, $\sigma_G = 2.855 \pm 0.004$, $\sigma_{R_{AB}} = 2.012 \pm 0.005$, $\gamma_{R_A} = 1.449 \pm 0.004$, $\gamma_{S_A} = 1.129 \pm 0.003$, $\gamma_{G_A} = 1.875 \pm 0.004$, and $(\vec{R}_A \wedge \vec{R}_B) = 116.21 \pm 0.14$. These values are much greater than those of the previous Monte Carlo calculation[8] and reinforce the conclusion that the single chain does not segregate intramolecularly.

We have also studied the conformation of the non-equimolar copolymer chain for the case of the ideal Θ solvent and excluded volume cross interactions. Calculations were performed for chains with total length $N + 1$ = 41, 61, 81, 101, 151, and 201 and a wide range of compositions (Φ_B = 0.1, 0.2, 0.35, 0.65, 0.8, and 0.9). The different properties depend on N according to the same power laws established for the symmetric case. The corresponding extrapolated expansion ratios allow us to obtain new expansion ratios which describe more generally the behavior of diblock chains for the considered macroscopic states. Both theory and simulations show that the variation of the radius of gyration expansion factor α_S^2 and the ratios σ_Q vary with increasing mass fraction Φ_B (i.e., for longer B block) in a nonmonotonous way (Figures 2–4). From Figures 3 and 4, we observe that our values for $\sigma_{R_{AB}}$ and σ_G are always slightly above the theoretical curve for the entire range of Φ_B. The previous Monte Carlo result,[8] corresponding to a fixed molecular weight (N = 200), showed a stronger variation with Φ_B. Figures 5–7 show the Φ_B dependence of the ratios γ_{S_A}, γ_{R_A}, and γ_{G_A}. The values of γ_{S_A} are nearly the same as the values for the equimolar case, unless the chain architecture becomes too asymmetrical, while the other ratios are more sensitive to the change of Φ_B. In the limit $\Phi_B = 1$, γ_{R_A} and γ_{G_A} take the highest values, 1.109 (γ_{R_A}(theoretical) = 1.125) and 1.218, respectively. The variation of the angle between vectors $\vec{R}_A$ and $\vec{R}_B$ is only a few degrees in the whole range of values for Φ_B, as we can see in Figure 8. The branches tend to be apart to compensate for the increase of the cross interactions, until a maximum value is reached, corresponding to the equimolar chain.

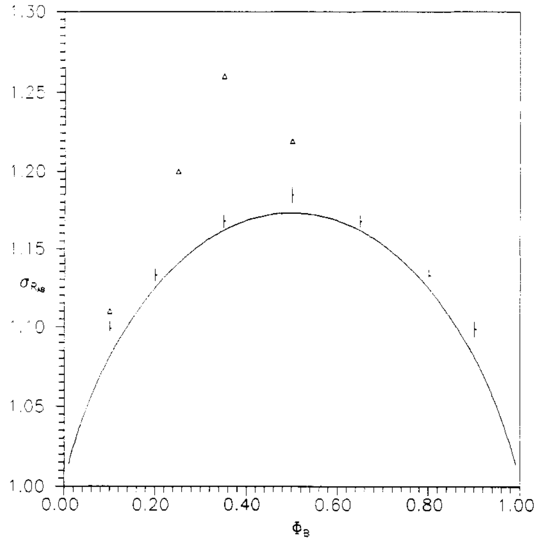

Figure 3. Ratio $\sigma_{R_{AB}}$ as a function of Φ_B. Notation and solvent conditions as in Figure 2.

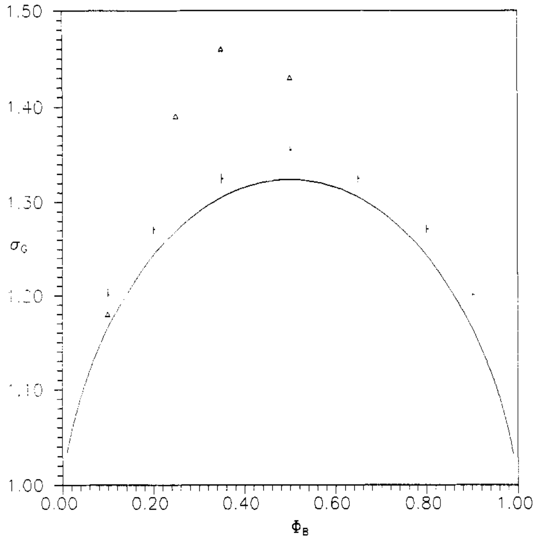

Figure 4. Ratio σ_G as a function of Φ_B. Notation and solvent conditions as in Figure 2.

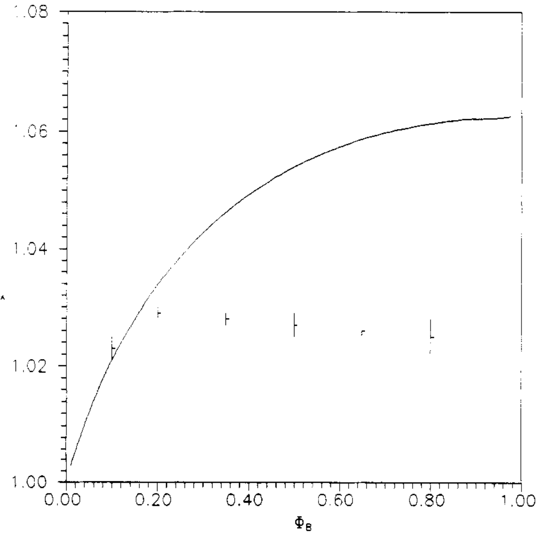

Figure 5. Ratio γ_{S_A} vs Φ_B for chains under ideal Θ conditions and excluded volume heterointeractions. Solid line, theoretical results; (|-) results of the current work.

(b) Selective Solvent. We have also considered a symmetric diblock copolymer chain with the A block under Θ conditions, while the B–B and A–B interactions obey

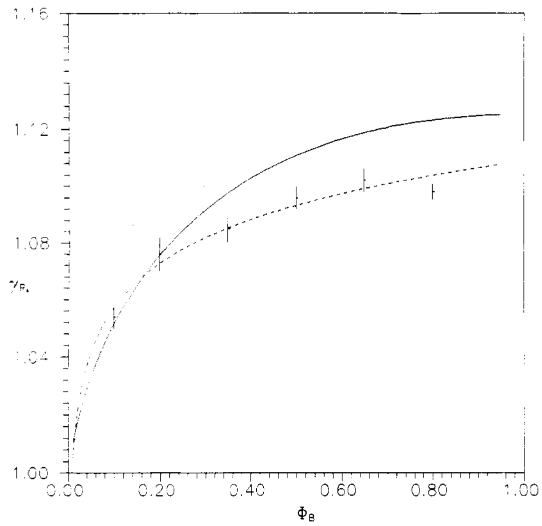

Figure 6. Ratio γ_{R_A} vs Φ_B. Notation and solvent conditions as in Figure 5. The dashed curve is a guide for the eye.

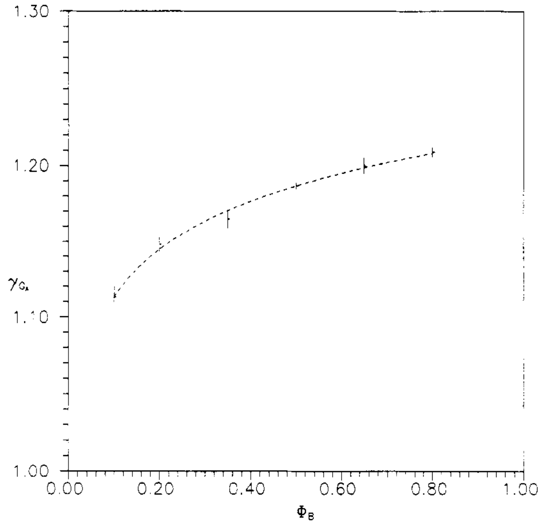

Figure 7. Ratio γ_{G_A} vs Φ_B for chains under ideal Θ conditions and excluded volume heterointeractions. The dashed curve is a guide for the eye.

the excluded volume regime. By means of the Pivot algorithm, the dimensionless ratios σ_Q and γ_Q have been calculated for the interaction parameters $\epsilon_{AA}/k_BT = 0$, $\epsilon_{BB}/k_BT = 0.1$, and $\epsilon_{AB}/k_BT = 0.1$ and $\epsilon_{AA}/k_BT = 0.3$, $\epsilon_{BB}/k_BT = 0.1$, and $\epsilon_{AB}/k_BT = 0.1$, corresponding to ideal and quasi-ideal Θ solvent for block A, as described in the previous section. The chain lengths are the same as described in the common Θ solvent case (up to $N + 1 = 201$ for the ideal block model and up to 151 for the quasi-ideal one). The extrapolated values of the dimensionless ratios, together with the theoretical and the previous Monte Carlo results, are listed in Table 2.

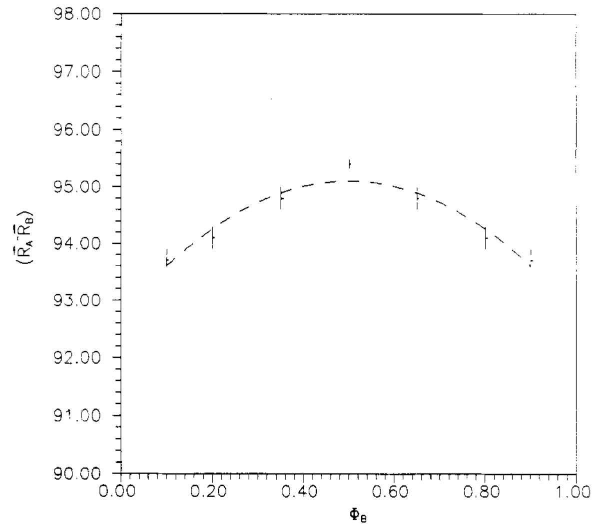

Figure 8. Variation of the angle between the block end-to-end vectors, $\vec{R}_A$ and $\vec{R}_B$, with Φ_B. The dashed curve is a guide for the eye.

Table 2. Dimensionless Ratios for the Macroscopic State of a Selective Solvent

	present work			
	ideal	quasi-ideal	previous MC[a]	RG[b]
σ_G	1.253 ± 0.003	1.290 ± 0.009		1.243
$\sigma_{R_{AB}}$	1.135 ± 0.003	1.163 ± 0.010		1.130
γ_{R_A}	1.097 ± 0.003	1.088 ± 0.005		
γ_{S_A}	1.029 ± 0.001	1.029 ± 0.002	~1	
γ_{G_A}	1.187 ± 0.003	1.159 ± 0.008		
γ_{R_B}	1.053 ± 0.001	1.066 ± 0.006		
γ_{S_B}	1.015 ± 0.001	1.019 ± 0.002	~1	
γ_{G_B}	1.091 ± 0.003	1.102 ± 0.005		
$(\vec{R}_A \wedge \vec{R}_B)$	94.41 ± 0.09	95.47 ± 0.20		
σ_T	1.258 ± 0.003		<1.42	

[a] Reference 14. [b] Values calculated from the equations of refs 6 and 7. For the definition of σ_T, see text.

It can be observed that our extrapolated values for the ratios σ_G and $\sigma_{R_{AB}}$ obtained with the ideal block model are in excellent agreement with the theoretical predictions corresponding to the same solvent conditions, while the values obtained with the quasi-ideal model are significantly higher. In comparison with the respective results of the common Θ solvent, however, the present values (both from theory and simulation) are significantly smaller, indicating that the cross interactions in the current case are less effective than in the previously described macroscopic state. For a detailed study of the relative role of the heterointeractions in different macroscopic states, it is more convenient to introduce at this point the parameters $\delta_{\sigma_Q} = \sigma_Q - 1$ and $\delta_{\gamma_Q} = \gamma_Q - 1$, expressing the relative expansion of the diblock copolymer chain or of the homopolymer blocks with respect to the homopolymer precursors. According to the renormalization group theory, the ratio δ_{σ_Q}(selective solvent)/δ_{σ_Q}(common Θ solvent) should be independent of the type of configurational average ($\langle G_{AB}^2\rangle$ or $\langle R_{AB}^2\rangle$) used for the calculation of σ_Q. It should be also equal to the ratio of the cross fixed points u_{AB}* corresponding to each of the macroscopic states[4-7] defined above. In first-order ϵ approximation, this ratio is equal to 0.75 (see Tables 1 and 2). Our results with the ideal model for the ratios σ_G and $\sigma_{R_{AB}}$ yield 0.71 and 0.73, while we obtain 0.77 and ~0.86 with the quasi-ideal model. As we can see from the ratios γ_Q in Table 2, the expansion due to the heterointeractions is not the same for the two blocks. For the A block the heterointeractions are as effective as for the common Θ solvent macroscopic state, while the repulsive B–B interactions tend to swell the B block, thereby minimizing the interblock contacts and their influence on this block. These trends are similar to those found for the configuration of a polymer interacting with a surface where the polymer–surface interactions play the role of the heterocontacts.[22] In terms of the parameters δ_{γ_Q}, the relative expansion of the two blocks in the two macroscopic states, δ_{γ_Q}(selective solvent)/δ_{γ_Q}(common Θ solvent), for the ideal block model is ~1 for the A block and between 0.49 and 0.56 for the B block. This may indicate that, though the overall dimensions behave as predicted by the chain macroscopic state defined by the whole set of interactions A–A, B–B, and A–B, the

Table 3. Dimensionless Ratios for the Macroscopic State of a Common Good Solvent

	present work	previous MC[a]	RG[b]
σ_G	1.219 ± 0.003		1.162
$\sigma_{R_{AB}}$	1.123 ± 0.005		1.087
γ_{R_A}	1.054 ± 0.002		1.055
γ_{S_A}	1.018 ± 0.001	≤1.02	1.027
γ_{G_A}	1.092 ± 0.001		
$(\vec{R}_A \wedge \vec{R}_B)$	94.3 ± 0.1		
σ_T	1.227 ± 0.003	1.25	

[a] References 8 and 14. [b] Values calculated from the equations of refs 6 and 7. For the definition of σ_T, see text.

properties of individual blocks are governed by a macroscopic state consistent with the prevailing solvent conditions (Θ or good) within the block (A–A or B–B) and by the heterocontacts. Consequently, the solvent conditions within the opposite block (B or A) are not influencing those partial properties.

So far, we have considered the ratio σ_G to be defined through eq 1.2 as $\sigma_G = \langle G^2_{AB}\rangle/[\langle G^2_{A-H}\rangle + \langle G^2_{B-H}\rangle]$. However, in their previous Monte Carlo simulations, Tanaka et al.[8] calculate the ratio σ_G for every macroscopic state as $\sigma_T = \langle G^2_{AB}\rangle/[\langle S^2_{A-H}\rangle + \langle S^2_{B-H}\rangle]$ using the relation $\langle G^2_{A-H}\rangle = 2\langle S^2_{A-H}\rangle$ valid for the Θ solvents. To estimate the relative error introduced when we consider A–A or B–B interactions, we have also calculated the latter ratio. From Table 2 we can see that the difference between the extrapolated values of σ_G and σ_T is within the statistical deviation.

(c) Common Good Solvent. The last case considered in this work is a copolymer chain where all three types of interactions are in the excluded volume regime (equivalent to a homopolymer chain). Using the Pivot algorithm, we have calculated the dimensionless ratios considering the interaction parameter $\epsilon_{kl}/k_BT = 0.1$ equal for all interactions and for the same characteristics described in the previous macroscopic state. The extrapolated values of these ratios are included in Table 3. As expected, these values are the smallest ones in comparison with the other two macroscopic states, since the intrablock A–A and B–B interactions swell the blocks, reducing the likelihood of A–B heterocontacts. According to the renormalization group theory, the ratio δ_{σ_Q}(common good solvent)/δ_{σ_Q}(common Θ solvent) is equal to 0.5, while the ratio δ_{σ_Q}(common good solvent)/δ_{σ_Q}(selective solvent) is equal to 0.67. Our simulation results for the ideal A block case (similar to that considered by the theory) yield ~0.6 and ~0.87 for the same ratios. In terms of the angle between the center-to-end vectors $(\vec{R}_A \wedge \vec{R}_B)$ the difference between the macroscopic states of common Θ solvent and common good solvent is only one degree.

Acknowledgment. C.V. expresses his sincere thanks to Ana Rubio for helpful discussions. He also acknowledges in Spanish Ministry of Education for financial support in the form of the program "Estancias Temporales de Cientificos y Tecnólogos Extranjeros en España". This research has been supported in part by Grant PB92-0227 from the DGICYT (Spain).

References and Notes

(1) Noshay, A.; McGrath, J. *Block Copolymer Overview and Critical Survey*; Academic Press: New York, 1977.
(2) Joanny, J. F.; Leibler, L.; Ball, R. *J. Chem. Phys.* **1984**, *81*, 4640.
(3) Sdranis, Y.; Kosmas, M. K. *J. Chem. Soc., Faraday Trans. 2* **1987**, *83*, 819.
(4) Douglas, J. F.; Freed, K. F. *J. Chem. Phys.* **1987**, *86*, 4280.
(5) McMullen, W. E.; Freed, K. F.; Cherayil, B. J. *Macromolecules* **1989**, *22*, 1853.
(6) Sdranis, Y.; Kosmas, M. K. *Macromolecules* **1991**, *24*, 1341.
(7) Vlahos, C. H.; Horta, A.; Freire, J. J. *Macromolecules* **1992**, *25*, 5974.
(8) Tanaka, T.; Kotaka, T.; Inagaki, H. *Macromolecules* **1976**, *9*, 561.
(9) Birshtein, T.; Skvortsov, A. M.; Sariban, A. A. *Macromolecules* **1976**, *9*, 888.
(10) Tanaka, T.; Kotaka, T.; Ban, K.; Hattori, M.; Inagaki, H. *Macromolecules* **1977**, *10*, 960.
(11) Tanaka, T.; Omoto, M.; Inagaki, H. *Macromolecules* **1979**, *12*, 146.
(12) Tanaka, T.; Inagaki, H. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1979**, *20*, 9.
(13) Fukuda, T.; Inagaki, H. *Pure Appl. Chem.* **1983**, *55*, 1541.
(14) Tanaka, T.; Omoto, M.; Inagaki, H. *J. Macromol. Sci., Phys.* **1980**, *B17* (2), 229.
(15) Freire, J. J.; Horta, A. *J. Chem. Phys.* **1976**, *65*, 4049.
(16) Freire, J. J.; Pla, J.; Rey, A.; Prats, R. *Macromolecules* **1986**, *19*, 453.
(17) Freire, J. J.; Rey, A.; Bishop, M.; Clarke, J. *Macromolecules* **1991**, *24*, 6494.
(18) Miyake, A.; Freed, K. *Macromolecules* **1984**, *17*, 678.
(19) Molina, L. A.; Lopez Rodriguez, A.; Freire, J. J. *Macromolecules* **1994**, *27*, 1160.
(20) Horta, A.; Fernandez-Pierola, I. *Polymer* **1981**, *22*, 783.
(21) Tanaka, T.; Kotaka, T. *Bull. Inst. Chem. Res.* **1972**, *50*, 107.
(22) Douglas, J. F.; Nemirovsky, A. M.; Freed, K. F. *Macromolecules* **1986**, *19*, 2041.