Conformational Properties of Ring AB Diblock Copolymers

5 AUTHORS, INCLUDING:

Costas Vlahos
University of Ioannina

34 PUBLICATIONS **374** CITATIONS

SEE PROFILE

Hadjichristidis Nikos
King Abdullah University of Science and Techn…

301 PUBLICATIONS **8,930** CITATIONS

SEE PROFILE

Juan Freire
National Distance Education University

142 PUBLICATIONS **1,900** CITATIONS

SEE PROFILE

Conformational Properties of Ring AB Diblock Copolymers

Costas Vlahos and Nikos Hadjichristidis

*Department of Chemistry, University of Athens, Panepistimiopolis, Zografou,
15771 Athens, Greece*

Marios K. Kosmas

Department of Chemistry, University of Ioannina, Ioannina, Greece

Ana M. Rubio and Juan J. Freire*

*Departamento de Química Física, Facultad de Ciencias Químicas, Universidad
Complutense, 28040 Madrid, Spain*

ABSTRACT: Ring diblock copolymers with different lengths of the A and B blocks have been investigated using theoretical and numerical simulation methods. The theoretical calculations are based on a first-order expansion in the parameter $\epsilon = 4 - d$ and extend to chains in a common Θ solvent, in a common good solvent, and in selective solvents, though only the first case is discussed in detail. The Monte Carlo calculations are performed for a common Θ solvent case with an off-lattice model of Gaussian units which interact through a Lennard-Jones potential. Averaged dimensions for each of the blocks and for the whole chain are obtained, and the theoretical and simulation results are analyzed and discussed. From the results, we have obtained general trends for all these different properties, and the most important differences and similarities with linear or homopolymer chains have been identified.

1. Introduction

The singular characteristics of cyclic chains have stimulated numerous conformational studies of these molecules from the theoretical, numerical (computer simulation), and experimental points of view. On the other hand, block copolymers have also become objects of great interest in recent years, because of their peculiar behavior in the melt and in dilute or semidilute solution.

In diblock copolymers, the repulsive nature of interblock interactions tends to segregate the blocks, which, nevertheless, have to maintain their bond connection. For a ring diblock copolymer there are two connections between the blocks in the same chain and, therefore, it is expected that the copolymer properties should differ from those of linear chains. However, studies on ring copolymers are scarce. To the best of our knowledge, the only experimental study of solution properties of ring block copolymers has been carried out by Amis et al.[1] These authors used a cyclic block copolymer of poly-(dimethylsiloxane) (PDMS) and polystyrene (PS), prepared by Yin and Hogen-Esch,[1] and studied the dilute solution properties by static and dynamic light scattering. The synthetic approach involved capping of α,ω-dilithium polystyrene with a small amount of 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane units. This procedure is employed to decrease the reactivity of the living polymer, in order to avoid side reactions, without affecting its capability to initiate the polymerization of hexamethylcyclosiloxane. Finally, the α,ω-dilithium triblock copolymer PDMS-PS-PDMS was cyclized by addition of an equivalent amount of dichlorodimethyl-siloxane.

Conformational properties of isolated chains with different long-range interaction parameters can be predicted theoretically through different methods, some of them inspired by the renormalization group theory.

Thus, calculations in terms of three parameters representing the interactions between the same (AA, BB) or different (AB) pairs of units have been carried out for diblock linear.[2,3] and star chains whose arms are A or B blocks. (We denote these star chains as miktoarm,[4] from the Greek word μικτος meaning mixed.) The calculations are performed up to first-order perturbation in the parameter $\epsilon = 4 - d$ (d is the space dimension). These calculations have led to analytical predictions for different ratios of conformational properties of the diblocks relative to those of the homopolymer chains. The accuracy of these predictions has been assessed by comparison with Monte Carlo simulations performed on the same type of chains.[5,6]

In this work, the same theoretical approach has been used to obtain first-order analytical results for isolated ring diblock copolymer chains. The results are compared with computer simulations that use a model of Gaussian subunits perturbed by a Lennard-Jones potential (as a simple potential which includes attractive and repulsive terms) to describe long-range interactions. (The same model was employed in our previous Monte Carlo investigations of block copolymers, referenced above.) Differences between these theoretical results and simulation data and the data for linear copolymers and homopolymer rings are also discussed in order to elucidate which characteristics of the chain (architecture or composition) make the most important contributions to its properties in dilute solution.

2. Perturbation Calculations

In this section we present analytical calculations for the dimensions of the entire copolymer chain and also of the homopolymer parts. These dimensions can be expressed either as radii of gyration or as end-to-end square distances (of a block or the whole molecule) up to first order in $\epsilon = 4 - d$. We use the Gaussian model with the three excluded volume interaction parameters, u_{AA}, u_{BB}, and u_{AB}, between units of the same or different kinds. Accordingly, the probability distribution of the set of position vectors $\vec{R}_{iA}, \vec{R}_{iB}$ lying on the A and B

homopolymer parts is given by[3,4]

$$P\{\vec{R}_{iA}, \vec{R}_{iB}\}_{\vec{R}_{NA}=\vec{R}_{NB}} =$$

$$P_0\{\vec{R}_{iA}, \vec{R}_{iB}\}_{\vec{R}_{NA}=\vec{R}_{NB}}\{\exp[-u_{AA}\sum_{iA=1}^{N_A}\sum_{jA=1}^{N_A}\delta^d(\vec{R}_{iA} - \vec{R}_{jA}) -$$

$$u_{BB}\sum_{iB=1}^{N_B}\sum_{jB=1}^{N_B}\delta^d(\vec{R}_{iB} - \vec{R}_{jB}) -$$

$$2u_{AB}\sum_{iA=1}^{N_A}\sum_{jB=1}^{N_B}\delta^d(\vec{R}_{iA} - \vec{R}_{jB})]\} \quad (1)$$

$P_0\{\vec{R}_{iA}, \vec{R}_{iB}\}_{\vec{R}_{NA}=\vec{R}_{NB}}$ is the ideal distribution function expressing the connectivity of the ring chain units, and N_A and N_B are the lengths of the two different blocks A and B. The different averages of interest can be obtained from unit-to-unit mean square distances $\langle(R_l - R_k)^2\rangle$. Thus, we can calculate the mean square end-to-end square distance of the A homopolymer block $\langle R_A^2\rangle_{\text{ring AB}}$, where the terminal units are placed at the two common block junctions, and the radius of gyration of the A block, $\langle S_A^2\rangle_{\text{ring AB}}$. The latter property is obtained after a summation over all the chain unit positions belonging to the selected part of the molecule. Generally, only the following two types of averages, $\langle(R_{lA} - R_{kA})^2\rangle$ and $\langle(R_{lA} - R_{kB})^2\rangle$, need to be calculated. The remaining type, $\langle(R_{lB} - R_{kB})^2\rangle$, can be obtained from the $\langle(R_{lA} - R_{kA})^2\rangle$ with symmetric transformations between the excluded volume parameters $u_{AA} \leftrightarrow u_{BB}$ and the molecular weights $N_A \leftrightarrow N_B$. The evaluation of the unit-to-unit distances is based on the probability distribution function $P\{\vec{R}_{iA}, \vec{R}_{iB}\}_{\vec{R}_{NA}=\vec{R}_{NB}}$. The calculations correspond to the standard two-parameter model with the additional simplification of expanding additionally in the parameter $\epsilon = 4 - d$. Thus

$$\langle(R_l - R_k)^2\rangle = \int(R_l - R_k)^2 P\{\vec{R}_{iA}, \vec{R}_{iB}\}_{\vec{R}_{NA}=\vec{R}_{NB}}$$

$$\prod_{i,j}d\vec{R}_{ij} / \int P\{\vec{R}_{iA}, \vec{R}_{iB}\}_{\vec{R}_{NA}=\vec{R}_{NB}}\prod_{i,j}d\vec{R}_{ij} \quad (2)$$

Expanding the exponential[7] of $P\{\vec{R}_{iA}, \vec{R}_{iB}\}_{\vec{R}_{NA}=\vec{R}_{NB}}$ in eq 1, and after integration over all the position vectors, we finally arrive at the following diagrammatic representation for the case where both k and l belong to the same block A (bold line)

The forms of these diagrams arise from a general expression $-(EN - DC)^2/C^{d/2+1}(N - C)^{d/2+1}$, where C and D are the lengths of the segments defined by pairs of units (j,i) and (l,k), E is the length of the common part of these segments, and N is the total chain length, equal to $N_A + N_B$. Their values for $d = 4$ are obtained in a way similar to that described in previous papers.[3,4,7] Using them in eq 3 and setting $l = N_A = k = 0$, we have obtained the following expression for $\langle R_A^2\rangle_{\text{ring AB}}$.
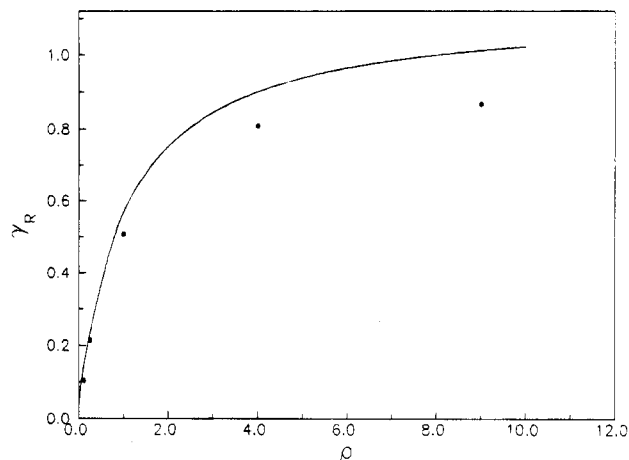

Figure 1. γ_R vs ϱ: solid line, theoretical result (eq 5); dots, extrapolated Monte Carlo data (common Θ solvent).

$$\langle R_A^2\rangle_{\text{ring AB}} = \frac{N_A\varrho}{1+\varrho}\left\{1 + 2u_{AA}\left[\frac{\varrho}{\varrho+1}\ln N_A - \frac{\varrho}{\varrho+1}\ln\left(\frac{\varrho}{1+\varrho}\right) + \frac{1-2\varrho}{2(1+\varrho)}\right] + 2u_{BB}\left[\frac{1}{\varrho+1}\ln N_A + \frac{1}{\varrho+1}\ln(\varrho(\varrho+1)) + \frac{\varrho-2}{2(1+\varrho)}\right] + 2u_{AB}\right\},$$

$$\varrho = N_B/N_A \quad (4)$$

It will be observed that the size of the A block is affected not only by the u_{AA} and u_{AB} interactions but also by the solvent conditions within the B block. In the case of a common Θ solvent, we can set $u_{AA}^* = 0$, $u_{BB}^* = 0$, and $u_{AB}^* = \epsilon/8$; therefore, the contribution of the u_{AA} and u_{BB} terms is eliminated. Consequently, the ideal term specifies a critical exponent defined by $\langle R_A^2\rangle \sim N_A^{2\nu}$, which is equal to $\nu = 0.5$ and coincides with the Θ solvent exponent of linear polymers.[7] As expected, the cross term is independent of the molecular weight and does not contribute to the critical exponent. It can be observed that if one increases the solvent quality for the A block, i.e., sets u_{AA} as a positive value, $\langle R_A^2\rangle$ increases. This corresponds to the macroscopic state for a selective solvent, for which only u_{BB} is equal to zero. In the limit of a very long A block, the term $u_{AA}\varrho/(\varrho + 1) \ln N_A$ is predominant and again $\langle R_A^2\rangle$ obeys a power law of the molecular weight N_A. The critical exponent can be obtained by introducing the fixed-point value[7] $u_{AA}^* = \epsilon/16$. In this way, we obtain $\langle R_A^2\rangle = N_A(\varrho/(\varrho + 1))\{1 + 2(\epsilon/16)(\varrho/(\varrho + 1)) \ln N_A\} = [\varrho/(\varrho + 1)]N_A^{2\nu}$, and $\nu = 1/2 + (\epsilon/16)(\varrho/(\varrho + 1))$. For $N_B \rightarrow \infty$ or $\varrho \rightarrow \infty$, the effect of the closure of the chain diminishes and the result $\nu = 1/2 + \epsilon/16$ of an open linear chain is recovered. Interestingly, these changes due to the closure of the chain are also observed in macroscopic properties such as the scattering structure factor.[8] A different exponent is also obtained for the macroscopic state of a selective solvent where the u_{BB} and u_{AB} interactions adopt values corresponding to the fixed point for excluded volume conditions,[5,6] $\epsilon/16$, $3\epsilon/32$, while $u_{AA} = 0$. In a common good solvent all the interactions are repulsive ($u_{AA}^* = u_{BB}^* = u_{AB}^* = \epsilon/16$), and the ring AB diblock copolymer is equivalent to a homopolymer ring chain. In this case $\langle R_A^2\rangle$ expresses the mean square length of the chord of a circle, with a maximum value at $\varrho = 1$, where $\langle R_A^2\rangle_{\varrho=1} = (N_A/2)\{1 + 2u(\ln N_A + \ln 2 + 1/2)\}$.

The relative expansion of the ring A block compared to that of a linear diblock copolymer with the same molecular weight N_A is expressed as

$$\gamma_R = \langle R_A^2 \rangle_{\text{ring AB}} / \langle R_A^2 \rangle_{\text{linear AB}} \tag{5}$$

(One could also define a dimensionless ratio with respect to the homopolymer precursor as is usually done to study linear diblock copolymers.[3] However, we have preferred to employ the copolymer linear chain as the reference for the ratios analyzed through this work.)

Using the analytical formula for the $\langle R_A^2 \rangle_{\text{linear AB}}$ from refs 3 and 4, we obtain the following equation for this ratio γ_R:

$$\gamma_R = \left(\frac{\varrho}{\varrho + 1}\right)\left\{1 + 2u_{AA}\left[-\frac{1}{\varrho + 1}\ln N_A - \frac{\varrho}{\varrho + 1}\ln\left(\frac{\varrho}{\varrho + 1}\right) + \frac{3}{2(\varrho + 1)}\right] + 2u_{BB}\left[\frac{1}{1 + \varrho}\ln N_A + \frac{1}{1 + \varrho}\ln(\varrho(\varrho + 1)) + \frac{\varrho - 2}{2(\varrho + 1)}\right] + 2u_{AB}\left[\frac{3\varrho + 2}{2(\varrho + 1)} + \varrho\ln\left(\frac{\varrho}{\varrho + 1}\right)\right]\right\} \tag{6}$$

Only for the macroscopic states of common Θ and common good solvents, where the contributions of the $\ln N_A$ terms cancel, can a dimensionless ratio be predicted. For the selective solvent, however, small differences in the solvent quality lead to the results depending on the molecular weight, making the experimental estimation of γ_R very uncertain.

In Figure 1 we represent these analytical results for the ratio γ_R, corresponding to the macroscopic state with a common Θ solvent, as a function of composition. We can see that γ_R increases with increasing ϱ, or the fraction of B units in the chain, $\Phi_B = N_B/(N_A + N_B)$, until a limiting value of $\gamma_R = 1.125$ is reached for high values of ϱ or $\Phi_B = 1$. In this case, the ideal term of $\langle R_A^2 \rangle_{\text{ring AB}}$ is equal to that corresponding to the linear chain, since the block is not able to distinguish if it is a part of a ring or of a linear chain (the u_{AB} term of the ring does not depend on ϱ). On the other hand, the units of the B block in the linear diblock copolymer are extended far from those of the A block and they can no longer interact with them.

The radius of gyration of the A block $\langle S_A^2 \rangle_{\text{ring AB}}$ is also obtained from the $\langle (R_{lA} - R_{kA})^2 \rangle$ distances according to the relation

$$\langle S_A^2 \rangle = \left(\frac{1}{2N_A^2}\right)\sum_{l=1}^{N_A}\sum_{k=1}^{N_A}\langle (R_{lA} - R_{kA})^2 \rangle \tag{7}$$

Replacing the double sum by integration yields the following expression for $\langle S_A^2 \rangle_{\text{ring AB}}$:

$$\langle S_A^2 \rangle_{\text{ring AB}} = \frac{N_A(1 + 2\varrho)}{12(1 + \varrho)}\left\{1 + \frac{u_{AA}}{(1 + 2\varrho)(1 + \varrho)}\left[-2\varrho^4 - 5\varrho^3 - 6\varrho^2 + 2(1 + 2\varrho + 2\varrho^2)\ln N_A - 2(-\varrho + 2\varrho^3 + 3\varrho^4 + \varrho^5)\ln\left(\frac{\varrho}{1 + \varrho}\right)\right] + \frac{u_{BB}\varrho}{(1 + \varrho)(1 + 2\varrho)}[2\ln N_A + 2\ln(\varrho(1 + \varrho)) - 2 + \varrho] + \frac{2u_{AB}}{5(1 + \varrho)(1 + 2\varrho)}[(-10\varrho + 20\varrho^3 + 20\varrho^4 + 6\varrho^5)\ln\left(\frac{\varrho}{1 + \varrho}\right) + 4\ln(1 + \varrho) + 6\varrho + 17\varrho^2 + 17\varrho^3 + 6\varrho^4]\right\} \tag{8}$$

In the limit $\varrho \to 0$, the chain becomes equivalent to a homopolymer composed of A units, and $\langle S_A^2 \rangle_{\text{ring AB}}$ takes the form $(N_A/12)\{1 + u_{AA}\ln N_A\}$. This is a well-
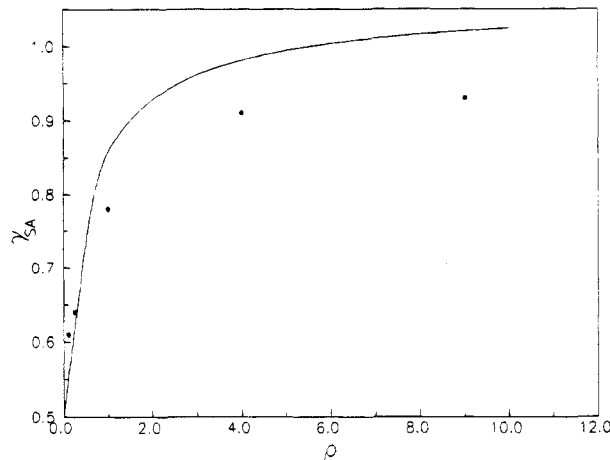

Figure 2. γ_{SA} vs ϱ: solid line, theoretical result (eq 10); dots, extrapolated Monte Carlo data (common Θ solvent).

known[9,10] result for the overall radius of gyration of a homopolymer ring (molecular weight N_A). For a longer B block, i.e., for a higher value of ϱ, the contribution of the ideal term increases (since the total molecular weight of the ring is also enhanced) until a limiting value of $N_A/6$ corresponding to the radius of gyration of the linear homopolymer is obtained when ϱ goes to infinity. Moreover, $\langle S_A^2 \rangle_{\text{ring AB}}$ increases for higher values of N_A or with an improvement of the solvent quality for the A block.

A unique property of ring AB copolymers is that the partial averages are also affected by changing the solvent conditions and the length of the other block. Thus, the excluded volume interaction within the B block expands the dimensions of this block. The expansion affects the mean distance between the ends of the blocks and, therefore, induces an expansion in the A block that is connected through these two terminal units, in this way increasing $\langle S_A^2 \rangle_{\text{ring AB}}$. The contribution of the u_{BB} term is increased by increasing ϱ until a maximum is reached. The location of this maximum depends on the molecular weight N_A. The contribution of the u_{AA} term shows opposite behavior, since the mass fraction of the A part decreases with increasing ϱ. As in the case of the block end-to-end distance, discussed above, the cross term u_{AB} is independent of the molecular weights of the blocks. However, in this case we find a strong dependence on ϱ. Starting at $\varrho = 0$, the cross interactions increase for higher values of ϱ, until we find a maximum expansion around $\Phi_B = 1/3$. Then, a limiting expansion is reached for $\varrho \to \infty$.

The behavior of the ratio γ_{SA} expressing the relative expansion of the A block to that of the respective part of the linear diblock chain, i.e.,

$$\gamma_{SA} = \langle S_A^2 \rangle_{\text{ring AB}} / \langle S_A^2 \rangle_{\text{linear AB}} \tag{9}$$

is similar to that of ratio γ_R, previously analyzed. In Figure 2 we represent this behavior according to the analytical result

$$\gamma_{SA} = \frac{1 + 2\varrho}{2(1 + \varrho)}\left\{1 + 2u_{AB}\left[\frac{4}{5(1 + 2\varrho)(1 + \varrho)}\ln(1 + \varrho) - \frac{\varrho(10 + 15\varrho + 40\varrho^2 + 55\varrho^3 + 24\varrho^4)}{5(1 + 2\varrho)(1 + \varrho)}\ln\left(\frac{\varrho}{\varrho + 1}\right) - \frac{\varrho(1 + 72\varrho + 172\varrho^2 + 96\varrho^3)}{20(1 + 2\varrho)(1 + \varrho)}\right]\right\} \tag{10}$$
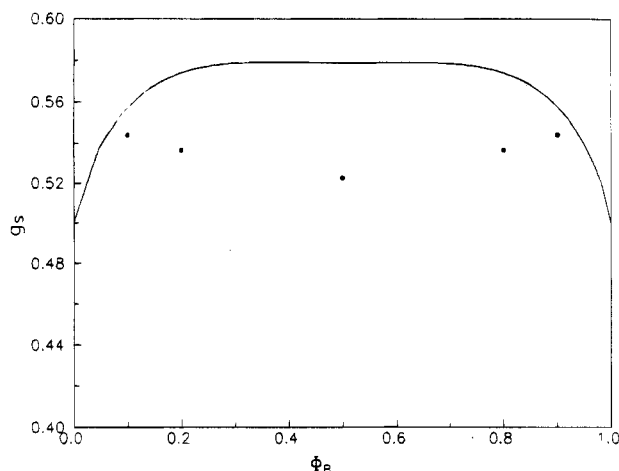
Figure 3. g_S vs Φ_B: solid line, theoretical result (eq 13); dots, extrapolated Monte Carlo data (common Θ solvent).

corresponding to the macroscopic state of common Θ solvent. γ_{SA} is higher for increasing values of ϱ, and a limiting extension of $\gamma_{SA} = 1.0625$ is obtained for very long B blocks. It should be noticed that the values of the ratios γ_R and γ_{SA} for the limit $\Phi_B = 1$ are identical to those of linear diblock copolymers with respect to homopolymer precursors for the same limit. In comparison with the results for γ_R, the values of γ_{SA} are always lower, indicating that the interior of the block is less sensitive to the cross interactions than its outer parts.

In the case of the radius of gyration of the whole molecule $\langle S^2 \rangle_{\text{ring AB}}$, the different averages $\langle (R_l - R_k)^2 \rangle$ correspond to distances between two units belonging to the same or different blocks

$$\langle S^2 \rangle_{\text{ring AB}} = \frac{1}{2(N_A + N_B)^2} [\sum_{k=1}^{N_A} \sum_{l=1}^{N_A} \langle (R_{lA} - R_{kA})^2 \rangle +$$

$$\sum_{k=1}^{N_B} \sum_{l=1}^{N_B} \langle (R_{lB} - R_{kB})^2 \rangle + \sum_{k=1}^{N_B} \sum_{l=1}^{N_A} \langle (R_{lA} - R_{kB})^2 \rangle] \quad (11)$$

The terms $\langle (R_{lA} - R_{kB})^2 \rangle$ can be obtained according to the same procedure used for the terms $\langle (R_{lA} - R_{kA})^2 \rangle$. Using the adequate expressions for the former averages in eq 11, we find the following simple relationship:

$$\langle S^2 \rangle_{\text{ring AB}} = \frac{N_A(1 + \varrho)}{12} \Big\{ 1 + \frac{2u_{AA}}{1 + \varrho} \Big[\ln N_A +$$

$$\varrho \ln\Big(\frac{\varrho}{1 + \varrho}\Big) \Big] + \frac{2u_{BB}}{1 + \varrho} [\varrho \ln N_A + \varrho \ln \varrho - \ln(1 + \varrho)] +$$

$$\frac{2u_{AB}}{1 + \varrho} [-2\varrho \ln \varrho + 2(1 + \varrho) \ln(1 + \varrho)] \Big\} \quad (12)$$

The ideal term depends only on the total molecular weight and is identical to that corresponding to homopolymer rings. Each of the other terms depend on both mass fractions Φ_A and Φ_B. For constant N_A, the u_{BB} term representing the interactions between B units is increased for higher Φ_B, because both the molecular weight and the total number of interactions are higher, while the contribution of the u_{AA} term has the opposite behavior, since the mass fraction $\Phi_A = 1 - \Phi_B$ is decreased. The cross term u_{AB} shows a typical nonmonotonous variation with Φ_B, showing a maximum at $\Phi_B = 0.5$. This maximum corresponds to blocks of equal lengths, for which the competitive contributions of the two homopolymer parts are balanced. Setting all the

interactions equal to a single value u in eq 12, the well-known expression for the radius of gyration of a homopolymer ring[9,10] (described above) is recovered. These results serve as a partial check on the correctness of our calculations. In Figure 3 we present the ratio

$$g_S = \frac{\langle S^2 \rangle_{\text{ring AB}}}{\langle S^2 \rangle_{\text{linear AB}}} = 0.5 \Big\{ 1 + 2u_{AB} \Big[-\frac{\varrho}{4(1 + \varrho)^2} -$$

$$\frac{\varrho(\varrho^2 + \varrho + 2)}{(1 + \varrho)^3} \ln \varrho + \ln(1 + \varrho) \Big] \Big\} \quad (13)$$

for the macroscopic state of a common Θ solvent plotted against Φ_B. Again, the cross interactions are more effective in the ring copolymers than in the linear diblock chains.

The mean quadratic separation between the centers of mass of the two homopolymer parts or blocks, $\langle G_{AB}^2 \rangle_{\text{ring AB}}$, can be obtained also as[3,4]

$$\langle G_{AB}^2 \rangle_{\text{ring AB}} = (1/\Phi_A \Phi_B) \langle S_{AB}^2 \rangle_{\text{ring AB}} -$$

$$(1/\Phi_B) \langle S_A^2 \rangle_{\text{ring AB}} - (1/\Phi_A) \langle S_B^2 \rangle_{\text{ring AB}} \quad (14)$$

From eqs 8, 12, and 14, we have obtained the corresponding formula

$$\langle G_{AB}^2 \rangle_{\text{ring AB}} = \frac{N_A(1 + \varrho)}{12} \Big\{ 1 + \frac{u_{AA}}{1 + \varrho} [5\varrho + 2\varrho^2 +$$

$$2 \ln N_A + (6\varrho + 6\varrho^2 + 2\varrho^3) \ln(\varrho/(\varrho + 1))] +$$

$$\frac{u_{BB}}{\varrho^2(\varrho + 1)} [2\varrho + 5\varrho^2 + 2\varrho^3 \ln(N_A \varrho) -$$

$$(2 + 6\varrho + 6\varrho^2) \ln(1 + \varrho)] - \frac{u_{AB}}{5\varrho^2(\varrho + 1)} [(12\varrho + 34\varrho^2 +$$

$$34\varrho^3 + 12\varrho^4) + (60\varrho^3 + 60\varrho^4 + 12\varrho^5) \ln(\varrho/(\varrho + 1)) +$$

$$(12 + 40\varrho + 60\varrho^2) \ln(1/(1 + \varrho))] \Big\} \quad (15)$$

From this equation, and the one previously obtained[4] for linear chains, we obtain the ratio

$$\sigma_G = \langle G_{AB}^2 \rangle_{\text{ring AB}} / \langle G_{AB}^2 \rangle_{\text{linear AB}} =$$

$$(1/4)\{1 - u_{AB}*[1/5\varrho^2(\varrho + 1)]\{12\varrho + 34\varrho^2 + 34\varrho^3 +$$

$$12\varrho^4 + (60\varrho^3 + 40\varrho^4 + 12\varrho^5) \ln[\varrho/(\varrho + 1)] + (12 +$$

$$40\varrho + 60\varrho^2) \ln[1/(\varrho + 1)]\} + 3u_{AB}*/(\varrho + 1)\{[(3 +$$

$$7\varrho + 6\varrho^2)/3\varrho^2] \ln[1/(1 + \varrho)] +$$

$$(\varrho/3)(6 + 7\varrho + 3\varrho^2) \ln[\varrho/(\varrho + 1)] +$$

$$(1/12\varrho)(12 + 22\varrho + 22\varrho^2 + 12\varrho^3)\}\} \quad (16)$$

In Figure 4, we show a plot of σ_G vs Φ_B. The aspect of this function is similar to that of g_S vs Φ_B, with a maximum at $\Phi_B = 0.5$, indicating the greatest segregation between blocks symmetric in composition.

3. Monte Carlo Simulations

The model employed for the simulations has been fully described and justified in previous work.[5,6,11,12] We consider N Gaussian units of root mean square length b (adopted as the length unit). Nonneighboring units interact through a 6-12 Lennard-Jones potential. The reduced distance at which the potential vanishes is set as $\sigma/b = 0.8$; this value is adopted according to our previous experience in the application of this model to several other types of polymer chains. The reduced energy at the bottom of the potential well, $\epsilon_{ij}/k_B T$, is the
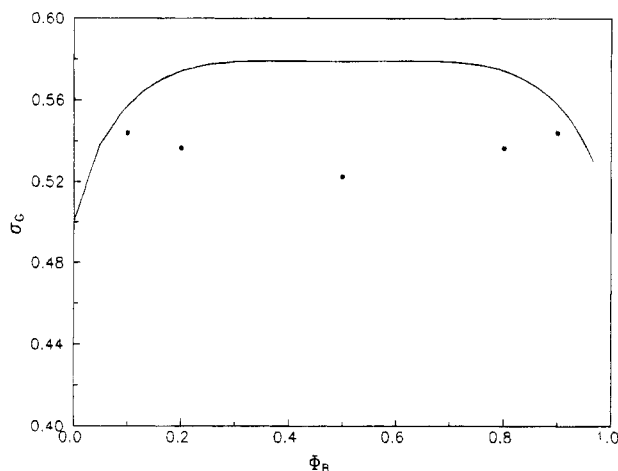
Figure 4. σ_G vs Φ_B: solid line, theoretical result (eq 16); dots extrapolated Monte Carlo data (common Θ solvent).

relevant parameter that determines the solvent conditions, depending on the nature of the interacting i and j units. In this work we want to reproduce the solvent conditions set as macroscopic states in the perturbation calculations. They correspond to $\epsilon_{AA}/k_BT = 0$, $\epsilon_{BB}/k_BT = 0$, and $\epsilon_{AB}/k_BT = 0.1$. The last value has previously served to reproduce excluded volume interactions for homopolymer molecules of different architectures[11,12] (linear chains, stars, or rings) and also to reproduce correctly the behavior of AB diblock linear copolymers and miktoarm[5,6] stars.

The Monte Carlo algorithm employed in the present work was described in detail in a previous study of homopolymer rings.[13] First, a nonoverlapping conformation is generated on a diamond lattice. New conformations are generated from this starting state by randomly choosing two chain units i and j. Then, we calculate the components of the two bond vectors that connect these units to the longest part of the cyclic chain, $\vec{v}_i$ and $\vec{v}_{j+1}$. Each of these vector components is resampled from a Gaussian distribution with mean equal to zero and mean square deviation $b^2/3$. However, the positions of the adjacent units, $i - 1$ and $j + 1$, are not changed. This is accomplished practically by keeping a constant sum for $\vec{v}_i + \vec{v}_{j+1}$ and resampling the components of vector $\vec{v}_i - \vec{v}_{j+1}$ from a Gaussian distribution with mean equal to zero and mean square deviation $2b^2/3$. This way we calculate $\vec{v}_i$, $\vec{v}_{j+1}$, and the new positions for i and j. The shorter part of the chain between i and j is then translated to connect again with the i and j units. The Metropolis criterion is used to accept or reject new conformations.

The averages are determined from eight independent runs. This allows us to estimate statistical means and uncertainties in a very simple way. From 5×10^5 to 1.5×10^6 (depending on the chain length) new conformations are attempted in each independent run. The first 25% of the conformations of each run are disregarded to allow for adequate thermalization.

The results have been obtained for six different values of N, ranging from $N = 40$ to $N = 200$. Three different composition ratios have been studied by setting $\varrho = 1$, 4, and 9. (Symmetry allows us to employ these results to characterize also the compositions corresponding to $1/\varrho$.) We have evaluated the same averages defined in the previous section, i.e., $\langle R_A^2\rangle_{\text{ring AB}}$, $\langle S_A^2\rangle_{\text{ring AB}}$ (and their symmetric counterparts), and $\langle S_{AB}^2\rangle_{\text{ring AB}}$.

The results for the averages $\langle R_A^2\rangle_{\text{ring AB}}$ and $\langle R_B^2\rangle_{\text{ring AB}}$ are identical (within their statistical uncertainties) in the case $\varrho = 1$, but the average corresponding to the
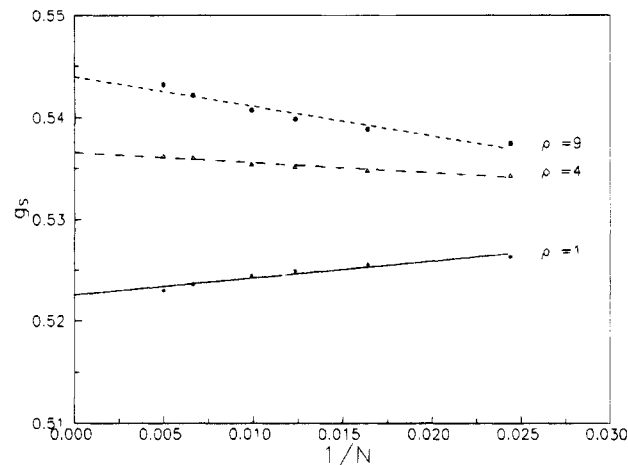

Figure 5. g_S vs $1/N$ from Monte Carlo data corresponding to different compositions (common Θ solvent): stars, $\varrho = 1$; triangles, $\varrho = 4$; dots, $\varrho = 9$. Different lines represent least-squares fits to a linear equation, employed in the extrapolations to the long-chain limit.

Table 1. Exponent ν (from Eq 17) from Monte Carlo Results for the Radius of Gyration for Rings (Present Work) and Linear (Ref 5) Diblock Copolymer Chains in a Common Θ Solvent

	ν	
ϱ	linear	rings
1	0.494	0.492
4	0.493	0.493
9	0.492	0.496

longer block is higher when $\varrho \neq 1$. Thus, the difference $\langle R_B^2\rangle_{\text{ring AB}} - \langle R_A^2\rangle_{\text{ring AB}}$ is about 2 (in b^2 units) for the smaller chains with $\varrho = 4$, and it increases to ca. 3 for chain lengths in the range $N = 100-200$. For $\varrho = 9$, we obtain a similar variation in the difference, now between the values 3 and 4. Deviations from the value $2b^2$ (corresponding to the independent contribution of the two Gaussian bonds joining the blocks) indicate strong segregation between A and B units at the junction bonds. Furthermore, we have also obtained the mean quadratic distances $\langle R_{1A,1B}^2\rangle_{\text{ring AB}}$ and $\langle R_{NA,NB}^2\rangle_{\text{ring AB}}$ between the first or last units of each one of the blocks. These two types of averages are always practically identical for a given chain, and they are intermediate between those of $\langle R_B^2\rangle_{\text{ring AB}}$ and $\langle R_A^2\rangle_{\text{ring AB}}$.

The different Monte Carlo quadratic averages can be fitted to scaling laws. Thus, the radius of gyration data are fitted by

$$\langle S^2\rangle_{\text{AB}} \sim N^{2\nu} \tag{17}$$

The results obtained this way from the present Monte Carlo data are contained in Table 1, together with the exponents calculated from the data previously obtained for linear diblock chains in a common Θ solvent.[5] All these results are in very good agreement with the exponent $\nu = 1/2$; i.e., they are consistent with the critical exponent predicted by the theory.

The previous Monte Carlo data for linear chains[5] are also employed together with the present results for rings in order to obtain the ratios of interest for each chain length in a common Θ solvent. Linear regressions vs $1/N$ yield the final numerical estimates of these ratios for the long-chain limit. Figure 5 shows these extrapolation plots for the g_S ratios.

The extrapolated Monte Carlo data have been incorporated in Figures 1-3 and, therefore, can be directly

compared with the theoretical results. Both sets of results exhibit essentially the same trends from the qualitative point of view. Quantitative agreement is very good for the block ratios corresponding to small values of ϱ and remains reasonably good (differences slightly higher than 10%) for the asymptotic limit $\varrho \rightarrow \infty$. In the case of ratio g_S, the agreement between theory and simulation is very good for the most asymmetric rings. For $\Phi_B \cong 0.5$, however, the plateau with a very slight minimum shown in the theoretical g_S vs Φ_B curve does not agree with the deeper minimum exhibited by the Monte Carlo data. (The theoretical result at $\Phi_B = 0.5$ is 0.57, while the Monte Carlo value is 0.52.)

The results obtained for g_S at $\Phi_B = 0.5$ are, on the other hand, very similar to those obtained with the same techniques for a homopolymer ring in the excluded volume region. Thus, setting $u_{AA}{}^* = u_{BB}{}^* = u_{AB}{}^* = \epsilon/16$ in the present formulas, we have obtained the value $g_S = (1/2)[1 + u^*(13/6)] \cong 0.57$, which also coincides with previous calculations.[9] The Monte Carlo results obtained for the homopolymer ring with the present model[13,14] ($\epsilon_{kl}/k_BT = 0.1$ in all cases) is close to 0.53. Some other simulation data support this finding.[15,16] Therefore, it seems that g_S is mainly determined by the chain architecture, while the effects of block segregation and global excluded volume represent similar contributions in the dimensions of ring and linear chains. A further discussion of the systematic differences between theoretical and simulation results is somehow obscured by the existence of other previous (and sometimes contradictory) data for homopolymer rings. Thus, some other theoretical schemes, mainly based on the two-parameter theory,[17-19] yield results close to 0.53. Since there is not any reason to assume that these approaches are more accurate than the first order in ϵ perturbation theory, a second-order calculation or the application of the Douglas–Freed method[20] for rings would be very useful to elucidate this point. The virtue of the latter approach is that only a first-order perturbation theory calculation is required for the properties, along with a second-order ϵ-expansion calculation for the fixed points u^* and exponents.

Moreover, we also note that some published Monte Carlo data[21,22] are closer to 0.57. Differences between Monte Carlo results may arise if the conformations generated in a given method contain permanent knots,[23] and some of the results close to 0.57 correspond to knot-free simulations.[22] It can be argued that our simulations may contain knots that contribute to decrease g_S. However, it should be considered that the model used in this work includes Gaussian bond fluctuations, which, together with the associated translations, should relax any knot contained in the initial conformation (although the same mechanism can produce new knots along the simulation). Moreover, our averages over eight runs with different starting chains should give higher uncertainties if these chains have different proportions of knots. We should also point out the similarity between the simulation results for the scaling law exponents $\nu \cong 1/2$ contained in Table 1 for different properties in the case of the linear and ring chains. This also seems to suggest that the knot effects are not important in our simulation data.

Similar differences between theory and Monte Carlo data are observed in Figure 4 for the ratio σ_G, though

the curves are simpler, showing a single maximum. Again, both sets of results are very similar for asymmetric blocks, but the Monte Carlo values are significantly (about 10%) smaller than the theoretical prediction for $\Phi_B = 0.5$; i.e., the theory predicts a stronger interblock segregation for symmetrical composition.

The only experimental data for ring diblock copolymers were obtained by Amis et al.[1] for the PS–PDMS copolymer mentioned in the Introduction. They measured the dilute-solution diffusion coefficient in cyclohexane for the ring sample and its linear triblock copolymer precursor. The ratio between these values is 0.88, which is very close to ratios preeviously obtained for homopolymer chains, both in Θ and good solvents (these experimental data are summarized in refs 14 and 24). This confirms our main conclusion that the global expansion effects due to segregation between blocks are quantitatively similar in ring and linear copolymers. The scattering properties of cyclic diblock copolymers have also been the object of recent theoretical work.[25]

References and Notes

(1) (a) Amis, E. J.; Hodgson, D. F.; Wu, W. *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 2049. (b) Yin, R.; Hogen-Esch, T. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 239.
(2) McMullen, W.; Freed, K.; Cherayil, B. *Macromolecules* **1989**, *22*, 1853.
(3) Sdranis, Y.; Kosmas, M. *Macromolecules* **1991**, *24*, 1341.
(4) Vlahos, C. H.; Horta, A.; Freire, J. J. *Macromolecules* **1992**, *25*, 5974.
(5) Vlahos, C. H.; Horta, A.; Molina, L. A.; Freire, J. J. *Macromolecules* **1994**, *27*, 2726.
(6) Vlahos, C. H.; Horta, A.; Hadjichristidis, N.; Freire, J. J. *Macromolecules* **1995**, *28*, 1500.
(7) Kosmas, M. K. *J. Phys. A: Math. Gen.* **1981**, *14*, 2779.
(8) Kosmas, M.; Benoit, H.; Hadziioannou, G. *Colloid Polym. Sci.* **1994**, *276*, 1466.
(9) Prentis, J. J. *J. Chem. Phys.* **1982**, *76*, 1574.
(10) Lipkin, M.; Oono, Y.; Freed, K. F. *Macromolecules* **1981**, *41*, 1270.
(11) Freire, J. J.; Pla, J.; Rey, A.; Prats, R. *Macromolecules* **1986**, *19*, 452.
(12) Freire, J. J.; Rey, A.; Bishop, M.; Clarke, J. H. R. *Macromolecules* **1991**, *24*, 6494.
(13) Rubio, A. M.; Freire, J. J.; Bishop, M.; Clarke, J. H. R. *Macromolecules* **1995**, *28*, 2240.
(14) García Bernal, J. M.; Tirado, M. M.; Freire, J. J.; García de la Torre, J. *Macromolecules* **1991**, *24*, 593.
(15) Bishop, M.; Saltiel, C. J. *J. Chem. Phys.* **1988**, *89*, 1159.
(16) Naghizadeh, J.; Sotobayashi, H. *J. Chem. Phys.* **1974**, *60*, 3104.
(17) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(18) Fujita, H. *Polymer Solutions*; Elsevier: Amsterdam, 1990.
(19) Casassa, E. F. *J. Polym. Sci.* **1965**, *44*, 315.
(20) Douglas, J. F.; Freed, K. F. *Macromolecules* **1984**, *17*, 1854.
(21) Bruns, W.; Naghizadeh, J. *J. Chem. Phys.* **1976**, *65*, 747.
(22) Chen, Y. *J. Chem. Phys.* **1983**, *78*, 5191.
(23) Koniaris, K.; Muthukumar, M. *J. Chem. Phys.* **1991**, *95*, 2873.
(24) Garcia Bernal, J. M.; Tirado, M. M.; Freire, J. J.; Garcia de la Torre, J. *Macromolecules* **1990**, *23*, 3357.
(25) Borsali, R.; Benmouna, M. *Macromol. Symp.* **1994**, *79*, 153.

MA9502819