Monte Carlo Calculations of A_xB_{f-x} Miktoarm Star Copolymers

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ABSTRACT: The effects of the excluded volume heterointeractions between dissimilar units on the conformational properties of miktoarm star copolymers A_xB_{f-x} in dilute solutions are studied by means of off-lattice Monte Carlo simulations. We calculate the dimensions of the two homopolymer parts and the whole molecule, the mean square distance between the two centers of masses, and other static properties for various x and f and solvent conditions. From these quantities, we calculate different expansion factors relative to homopolymer precursors. The results are analyzed considering recent renormalization group predictions for these copolymers. The differences with respect to previous results for linear diblock copolymers, due to the influence of the star core effects, are also discussed.

Introduction

Recent developments in the technique of anionic polymerization have made possible the synthesis of "miktoarm" star copolymers of the A_xB_{f-x} type.[1−6] These novel macromolecules (which combine characteristics of compact homopolymers with those of linear AB diblock copolymers) consist of f blocks (arms) of nonmixing homopolymers with different kinds of interactions between similar or dissimilar units, forced to have a common origin. Each one of the x blocks of homopolymer A is composed of N_A units, while the $f - x$ blocks of homopolymer B are constituted by N_B units. The different macroscopic behavior achieved either by changing the number of branches that specify the possibility of interactions between unlike units (heterointeractions) or by changing the solvent conditions that determine the intensity of these interactions makes such macromolecules interesting not only for theoretical reasons[7−11] but also in technical application.

In a previous paper[11] we presented a systematic theoretical study of miktoarm star copolymers based on the renormalization group method[12−14] in an effort to describe the influence of architecture and the heterointeractions on the chain conformation. Thus, calculations in terms of the three excluded volume parameters u_{AA}, u_{BB}, and u_{AB}, representing the interactions between the same and different pairs of units, have been performed, and the macroscopic properties have been obtained up to the first order in the small parameter $\epsilon = 4 - d$ (d is the space dimension of the system) for various f and x. From those analytical expressions and these corresponding to the homopolymer precursors, we have calculated the following dimensionless ratios:[11,15,16]

$$\sigma_G = = \langle G^2_{\text{miktoarm}}\rangle/[\langle G^2_{\text{A-H,star}}\rangle + \langle G^2_{\text{B-H,star}}\rangle] \quad (1)$$

$$\sigma_{R_{AB}} = \langle R^2_{\text{AB,miktoarm}}\rangle/[\langle R^2_{\text{A-arm,star}}\rangle + \langle R^2_{\text{B-arm,star}}\rangle] \quad (2)$$

$$\gamma_{R_k} = \langle R^2_{\text{k-arm,miktoarm}}\rangle/\langle R^2_{\text{k-arm,star}}\rangle \qquad (\text{k} = \text{A or B}) \quad (3)$$

$$\gamma_{S_k} = \langle S^2_{\text{k,miktoarm}}\rangle/\langle S^2_{\text{k-H,star}}\rangle \qquad (\text{k} = \text{A or B}) \quad (4)$$

$$\gamma_{G_k} = \langle G^2_{\text{k,miktoarm}}\rangle/\langle G^2_{\text{k-H,star}}\rangle \qquad (\text{k} = \text{A or B}) \quad (5)$$

where the different mean squared averages are as follows: $\langle G^2_{\text{miktoarm}}\rangle$ = distance between the centers of mass of two homopolymer parts A and B of the miktoarm star copolymer, $\langle S^2_{\text{k,miktoarm}}\rangle$ = radius of gyration of the k homopolymer part of the miktoarm star, $\langle G^2_{\text{k,miktoarm}}\rangle$ = distance between the center of mass of the homopolymer part k and the star central unit (modulus of vector $\vec{G}_k$), $\langle S^2_{\text{k-H,star}}\rangle$ = radius of gyration of the k homopolymer star precursor (i.e., of a homopolymer star chain with the same number of k branches and units as the k homopolymer part of the miktoarm star copolymer (k-H,star)), $\langle G^2_{\text{k-H,star}}\rangle$ = distance between the central unit and the center of mass of the k-H,star, $\langle R^2_{\text{AB,miktoarm}}\rangle$ = end-to-end distance of a diblock copolymer chain inside the miktoarm star copolymer (diblock copolymer span), $\langle R^2_{\text{k-arm,miktoarm}}\rangle$ = distance of the k branch end from the central unit in the miktoarm star copolymer (modulus of vector $\vec{R}_k$), and $\langle R^2_{\text{k-arm,star}}\rangle$ = distance of an arm end in the k-H,star to the central unit (k = A or B). The ratios σ_G, γ_{S_k}, and γ_{G_k} are the most important means of characterizing quantitatively the effects of heterointeractions, since their analytical formulas only depend on the chain composition and the cross excluded volume parameter u^*_{AB}. The other ratios, $\sigma_{R_{AB}}$ and γ_{R_k}, however, depend on the thermodynamic solvent conditions of the two homopolymer parts so that they can also measure quantitatively the effect

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of heterocontacts in the cases where the contributions of the A−A and B−B interactions are canceled (common Θ solvent). All these ratios adopt the value one for any ideal Gaussian chain without intramolecular interactions.

In the present work we calculate the above ratios for miktoarm star copolymers of the A_2B, A_2B_2, A_2B_4, A_3B_3, and A_6B_6 types through an off-lattice Monte Carlo model[16,17] of Gaussian units with Lennard-Jones intramolecular interactions, whose parameters have been set to mimic the different solvent conditions. For simplicity of calculations, all the arms are considered to have same molecular weight. Our arms are to check the validity of the theoretical formulas[11] for the dimensionless ratios, and then study the cases where the theory is not applicable, i.e., when the total number of branches is large and the contribution of the core effects on the chain conformation is not negligible. The results obtained with both the theoretical and simulation methods will help us gain a broader understanding of the local and global properties of miktoarm stars and, therefore, be of assistance for future experimental studies of those systems.

Model and Numerical Procedures

The model we consider here has been fully described and justified in previous studies concerning linear,[17] ring,[18] and star[17] homopolymers. The same model was also useful to investigate the conformation of the linear diblock[15] copolymer chains in different solvent conditions. We consider N Gaussian beads placed on f branches (N/f beads per branch) so that the distance between neighboring beads is not constant but follows a Gaussian distribution with mean-root-square value b. The units of the first x branches are considered as units of the A type (homopolymer A), and the rest belonging to the other $f - x$ branches are assigned to be of the B type (homopolymer B). The central unit is the common origin of the coordinates and is assigned as unit $N + 1$. Nonneighboring units interact through a 6−12 Lennard-Jones potential

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

where ϵ_{kl}/k_BT 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. Every set of values of interaction energies describes a different macroscopic state at which the miktoarm star copolymers can exist. In the limit of infinitely long chains, however, we expect that these values will be universal for all the AB copolymers, indpendently from their architecture. In a previous study of linear diblock copolymers,[15] we have performed an estimation of the sets appropriate to reproduce the most important macroscopic states. Thus, we have found that the macroscopic state with both homopolymer parts under quasi-ideal Θ conditions and excluded volume heterointeractions (common Θ solvent) corresponds to set $\epsilon_{AA}/k_BT = 0.3$, $\epsilon_{BB}/k_BT = 0.3$, $\epsilon_{AB}/k_BT = 0.1$. The same macroscopic state for the ideal (Gaussian) Θ conditions (i.e., without interactions between similar units) assumed in the analytical theories corresponds to $\epsilon_{AA}/k_BT = 0$, $\epsilon_{BB}/k_BT = 0$, $\epsilon_{AB}/k_BT = 0.1$. Both sets of interaction parameters reproduce the expected proportionality of the mean chain dimensions to $N^{1/2}$ in the range of chain lengths studied. Another macroscopic state of the selective solvent occurring frequently in real systems corresponds to a homopolymer part A−A interactions under Θ conditions (quasi-ideal or ideal), while B−B and A−B interactions are mainly repulsive (i.e., of the excluded volume type). This state can be represented by the set $\epsilon_{AA}/k_BT = 0.3$, $\epsilon_{BB}/k_BT = 0.1$, $\epsilon_{AB}/k_BT = 0.1$ or $\epsilon_{AA}/k_BT = 0$, $\epsilon_{BB}/k_BT = 0.1$, $\epsilon_{AB}/k_BT = 0.1$. Finally, the last macroscopic state considered here is a common good solvent where all kinds of interactions are of the excluded volume type $\epsilon_{kl}/k_BT = 0.1$ (k,l = A or B).

Since the above energetic parameters ϵ_{ij}/k_BT describing the main macroscopic states of a copolymer chain have been obtained by means of power laws only valid for long chains, a numerical estimation of the binary cluster integral (the basic parameter of RG theory), $u_{ij} = \int_0^\infty d\mathbf{R}_{ij}\{1 - \exp[-U(R_{ij})/k_BT]\}$, can be useful to check the microscopic connection between the two methods. A numerical integration with our specific potential gives $u_{ij} = -0.02$ for $\epsilon_{ij}/k_BT = 0.3$, which is close to the ideal fixed-point value $u^* = 0$, while we obtain the value $u_{ij} = 0.49$ for $\epsilon_{ij}/k_BT = 0.1$, which clearly corresponds to the excluded volume conditions.[20]

The Monte Carlo algorithm starts by building an initial miktoarm star chain conformation of moderate energy. New conformations are then generated by selecting a bead vector at random and resampling each of its components from a Gaussian distribution with mean zero and mean square deviation $b^2/3$. After moving the selected bead to its new location, the rest of the beads on the selected arm up to the free and are shifted to connect to the changed unit vector. For compact molecules, this sampling is more efficient than the well-known Pivot algorithm (where the selected part is also rotated), since the probability of moving a portion of an arm decreases dramatically by increasing the number of branches. A Metropolis energy criterion is used for acceptance or rejection of the new trial configuration. Eight different runs are performed (each starts with a different seed number) and each attempts from 200 000 to 500 000 configurations after appropriate thermalization. The uncertainties and means for averaged quantities are simply estimated by considering every run value as an independent result. Besides the properties enumerated in the Introduction, we also estimate the mean cosine of the angle between the arms of a diblock copolymer span chain (this mean value is zero for any ideal Gaussian chain). Averages are obtained from the following relations:

$$\langle S^2_{\mathrm{A,miktoarm}}\rangle = [1/(M_A + 1)^2] \sum_{m=1}^{M_A+1} \sum_{n\geq m}^{M_A+1} \langle(\vec{R}_m - \vec{R}_n)^2\rangle, \quad M_A = (N/f)x \quad (7)$$

$$\langle S^2_{\mathrm{B,miktoarm}}\rangle = [1/(M_B + 1)^2] \sum_{m=1}^{M_B+1} \sum_{n\geq m}^{M_B+1} \langle\vec{R}_\mathrm{m} - \vec{R}_n\rangle, \quad M_B = (N/f)(f - x) \quad (8)$$

$$\langle G^2_{\mathrm{miktoarm}}\rangle = (1/\Phi_A\Phi_B)\langle S^2_{\mathrm{miktoarm}}\rangle - (1/\Phi_B)\langle S^2_{\mathrm{A,miktoarm}}\rangle - (1/\Phi_A)\langle S^2_{\mathrm{B,miktoarm}}\rangle \quad (9)$$

$$\langle\cos(\vec{R}_A \wedge \vec{R}_B)\rangle = \langle(R^2_{\mathrm{A\text{-}arm,miktoarm}} + R^2_{\mathrm{B\text{-}arm,miktoarm}} - R^2_{\mathrm{AB,miktoarm}})/(2|\vec{R}_{\mathrm{A\text{-}arm,miktoarm}}||\vec{R}_{\mathrm{B\text{-}arm,miktoarm}}|)\rangle \quad (10)$$

$$\langle G^2_{\mathrm{k,miktoarm}}\rangle = -\langle S^2_{\mathrm{k,miktoarm}}\rangle + \langle R^2_{\mathrm{k,miktoarm}}\rangle \quad (\mathrm{k = A\ or\ B}) \quad (11)$$

Table 1. Exponent 2ν for All Miktoarm Star Cases and Θ Solvent conditions

	$\langle S^2_{\mathrm{miktoarm}}\rangle$		$\langle R^2_{\mathrm{AB,miktoarm}}\rangle$	
	ideal	quasi-ideal	ideal	quasi-ideal
A_2B	0.973 ± 0.004	0.992 ± 0.006	0.987 ± 0.008	1.014 ± 0.010
A_2B_2	0.967 ± 0.003	0.998 ± 0.004	0.987 ± 0.005	0.992 ± 0.004
A_2B_4	0.943 ± 0.005	0.992 ± 0.003	0.975 ± 0.005	1.044 ± 0.004
A_3B_3	0.943 ± 0.002	0.993 ± 0.003	0.974 ± 0.004	1.031 ± 0.006
A_6B_6	0.883 ± 0.002	0.951 ± 0.004	0.956 ± 0.003	1.033 ± 0.003

where R_m and R_n are the positions of the mth and nth units, $\langle R^2_{\mathrm{k,miktoarm}}\rangle$ is the mean square distance of the k units from the central unit,[19] $\langle S^2_{\mathrm{miktoarm}}\rangle$ is the radius of gyration of the whole molecule, and $\Phi_A = 1 - \Phi_B$ is the weight fraction of the homopolymer part A.

Results and Discussion

(a) Common Θ Solvent. First we consider the case of miktoarm stars with both homopolymer parts and B under quasi-ideal Θ conditions and excluded volume heterointeractions. Systems of the A_2B, A_2B_2, A_2B_4, A_3B_3, and A_6B_6 type with equal length branches and total number of units $N + 1 = 25$, 49, 85, 109, 145, and 205 have been generated. The simulation data for the radius of gyration of the whole chain and the end-to-end distance of a diblock copolymer chain inside the miktoarm star $\langle R^2_{\mathrm{AB,miktoarm}}\rangle$ (diblock copolymer span) have been fitted in log−log linear plots with a weighted least-squares routine to determine scaling laws with respect to the molecular weight (the $N + 1 = 25$ data point has not been used in these calculations). The results for the critical exponent 2ν are presented in Table 1. For the A_2B, the exponent values are in excellent agreement with the value $2\nu = 1$ predicted by the renormalization group theory and confirm, on one hand, that the cross interactions do not contribute to the critical exponent, and, on the other hand, that in our calculations of this particular type of star we have clearly reached the long chain asymptotic behaviors represented by these power laws. The exponents in the case of miktoarm stars of the A_2B_2 type show the same excellent agreement with the theory. The exponent of the end-to-end distance of the diblock copolymer span is more sensitive to these core effects, showing slight excluded volume behavior in these cases due to the partial cancellation of the repulsive and attractive interactions within the arms near to the core and the steric effects forcing the end of the branches far from the origin (see also Table 1). The exponents of the radius of gyration show a significant decrease only in the case of the A_6B_6, where the chain is more compact than the random walk with the majority of units near to the star center. The conformational properties of the homopolymer precursors (stars with 1, 2, 3, 4, and 6 branches), necessary for the calculation of the dimensionless ratios γ and σ, have been also computed at the same quasi-ideal Θ temperature (i.e., with the choice $\epsilon_{AA}/k_BT = \epsilon_{BB}/k_BT = 0.3$). The ratios are calculated by means of eqs 1−5 and then their extrapolated values are obtained through linear regression analysis vs N^{-1} in a way similar to that employed in previous work.[15] The resulting intercepts are listed in the second column of Tables 2−6 for the A_2B, A_2B_2, A_2B_4, A_3B_3, and A_6B_6 miktoarm stars, respectively. Although our extrapolations cannot lead to the results of infinitely long chain, where only a small fraction of each arm is affected by the central core, they can be useful to describe future experimental results for real samples of high molecular weight miktoarm copolymers.

Table 2. Dimensionless Ratios of the A_2B Type Miktoarm Star for the Macroscopic State of Common Θ Solvent[a]

	ideal	quasi-ideal	RG[a]
σ_G	1.496 ± 0.003	1.518 ± 0.013	1.498
$\sigma_{R_{AB}}$	1.205 ± 0.002	1.239 ± 0.015	1.229
γ_{R_A}	1.095 ± 0.002	1.082 ± 0.012	1.111
γ_{S_A}	1.083 ± 0.002	1.074 ± 0.015	1.127
γ_{G_A}	1.231 ± 0.004	1.224 ± 0.021	
γ_{R_B}	1.152 ± 0.002	1.192 ± 0.015	1.222
γ_{s_B}	1.038 ± 0.002	1.052 ± 0.009	1.108
γ_{G_B}	1.294 ± 0.003	1.321 ± 0.012	
$(\vec{R}_A \wedge \vec{R}_B)$	95.3 ± 0.1	96.2 ± 0.3	

[a] Reference 11.

Table 3. Dimensionless Ratios of the A_2B_2 Type Miktoarm Star for the Macroscopic State of Common Θ Solvent

	ideal	quasi-ideal	RG[a]
σ_G	1.768 ± 0.004	1.833 ± 0.024	1.648
$\sigma_{R_{AB}}$	1.237 ± 0.002	1.299 ± 0.010	1.284
γ_{R_A}	1.138 ± 0.03	1.172 ± 0.012	1.222
γ_{SA}	1.099 ± 0.003	1.103 ± 0.013	1.254
γ_{G_A}	1.390 ± 0.004	1.383 ± 0.011	
$(\vec{R}_A \wedge \vec{R}_B)$	95.96 ± 0.07	96.7 ± 0.5	

[a] Reference 11.

Table 4. Dimensionless Ratios of the A_2B_4 Type Miktoarm Star for the Macroscopic State of Common Θ Solvent

	ideal	quasi-ideal	RG[a]
σ_G	2.113 ± 0.010	2.207 ± 0.016	1.997
σ_{RAB}	1.265 ± 0.003	1.342 ± 0.007	1.395
γ_{RA}	1.192 ± 0.004	1.265 ± 0.009	1.443
γ_{S_A}	1.094 ± 0.006	1.140 ± 0.020	1.508
γ_{G_A}	1.605 ± 0.004	1.685 ± 0.017	
γ_{RB}	1.133 ± 0.003	1.139 ± 0.010	1.222
γ_{S_B}	1.109 ± 0.004	1.112 ± 0.012	1.283
γ_{G_B}	1.558 ± 0.011	1.535 ± 0.022	
$(\vec{R}_A \wedge \vec{R}_B)$	96.41 ± 0.04	97.03 ± 0.14	

[a] Reference 11.

Table 5. Dimensionless Ratios of the A_3B_3 Type Miktoarm Star for the Macroscopic State of Common Θ Solvent

	ideal	quasi-ideal	RG[a]
σ_G	2.304 ± 0.004	2.454 ± 0.022	1.971
$\sigma_{R_{AB}}$	1.277 ± 0.001	1.323 ± 0.007	1.395
γ_{R_A}	1.166 ± 0.002	1.198 ± 0.008	1.332
γ_{S_A}	1.114 ± 0.003	1.120 ± 0.009	1.413
γ_{G_A}	1.651 ± 0.004	1.659 ± 0.021	
$(\vec{R}_A \wedge \vec{R}_B)$	95.65 ± 0.08	97.2 ± 0.3	

[a] Reference 11.

Table 6. Dimensionless Ratios of the A_6B_6 Type Miktoarm Star for the Macroscopic State of Common Θ Solvent

	ideal[a]	ideal[b]	quasi-ideal	RG[c]
σ_G	4.490 ± 0.011	4.643 ± 0.009	5.021 ± 0.050	2.943
$\sigma_{R_{AB}}$	1.285 ± 0.003	1.322 ± 0.002	1.420 ± 0.008	1.727
γ_{R_A}	1.136 ± 0.004	1.159 ± 0.003	1.248 ± 0.003	1.665
γ_{S_A}	1.013 ± 0.009	1.041 ± 0.008	1.119 ± 0.013	1.872
γ_{G_A}	2.714 ± 0.012	2.809 ± 0.010	2.965 ± 0.050	
$(\vec{R}_A \wedge \vec{R}_B)$	99.1 ± 0.1	99.5 ± 0.4	99.5 ± 0.4	

[a] Extrapolations including the $N + 1 = 325$ values. [b] The $N + 1 = 325$ values are not included. [c] Reference 11.

Next we consider the same macroscopic state, but with an ideal Θ solvent for both homopolymers corresponding to a different choice of the potential parameters given by $\epsilon_{AA}/k_BT = 0$, $\epsilon_{BB}/k_BT = 0$, $\epsilon_{AB}/k_BT = 0.1$. Repeating the calculations for the same molecular weights as in the preceding case for the A_2B, A_2B_2, A_2B_4, and A_3B_3 miktoarm stars and for longer A_6B_6 chains up to $N + 1 = 325$, we have computed the critical exponent 2ν of the radius of gyration and that corresponding to the end-to-end square distance of the diblock copolymer span (Table 1). The rejection of the data concerning the short chains ($N + 1 = 49$) does not change significantly the values of the exponents. It should be pointed out that the differences between the two exponents and their deviation from the theoretical value $2\nu = 1$ increase by increasing the number of branches. This can be explained by the fact that the arms become too short to exhibit the correct scaling behavior of two properties with respect to the molecular weight. For the conformational properties of the ideal homopolymer precursors we have used the theoretical values obtained by the random walk model. Then the extrapolated values of the dimensionless ratios are also estimated and included in the Tables 2–6. The theoretical results (RG) are also contained in Tables 2–6 for comparison purposes. In Table 6, we include extrapolations performed without consideration of $N + 1 = 325$ data for the ideal case. These extrapolations do not differ by more than 3% from those obtained considering the longest chain values for this type of starting chains containing the shortest arms. A similar good convergence with increasing chain length can be expected for the quasi-ideal model. It can be observed that the general trends predicted by the first order in ϵ renormalization group theory are similar to those shown by our Monte Carlo results. For instance, in the results it can be seen that the ratios σ_G and γ_S show the largest and smallest values, respectively, at least for the cases with $x = f/2$. However, the agreement between theory and simulation varies from property to property and depends on the choice of parameters that represents the Θ state (ideal or quasi-ideal) and the total number of branches f. Analytically, for the A_2B type miktoarm stars (see Table 2), our extrapolated values of the ratios σ_G and $\sigma_{R_{AB}}$ for the case of quasi-ideal Θ solvent are in excellent agreement with the theoretical ones, while the agreement is poorer for γ_{R_A} and γ_{R_B}. For the ratios γ_{S_A} and γ_{S_B}, the RG theory predicts an expansion almost twice as large as that found in our Monte Carlo calculations. The values of the ratios we obtain for the case of an ideal Θ solvent are close to (though slightly smaller than) those calculated with the quasi-ideal model, which indicates that the core effects are not so important in the A_2B miktoarm stars. In comparison with the linear diblock copolymers,[15] however, the ratios are always greater, except in the case of the ratio γ_{R_A}, which remains unchanged. The interpretation of this behavior can be made by taking into account the AB interactions. The presence of an additional A branch (A_2B) in the vicinity of the B units increases the repulsion effects. In order to compensate the repulsions, the branches are expanded, increasing also the distance between the centers of masses. The relative expansion of the A type branch with respect to the homopolymer precursor is the same for the two copolymers in this case, since these branches feel the repulsions of only a B type branch. A further increase of the number of B branches (A_2B_2, A_2B_4) increases the cross interactions and the dimensionless ratios (Tables 2–4). Again, the agreement with the theoretical predictions is quite good for the ratios σ, while the RG theory overestimates the expansion of the various homopolymer parts expressed by the ratios γ. The angle between the center-to-end vectors $(\vec{R}_A \wedge \vec{R}_B)$ of two arms in a diblock copolymer span chain is not much affected by the core effects. Only in the A_6B_6 type miktoarm stars do the results show a clear increase of about 4° both in the ideal and in the quasi-ideal models. The core effects for this star chain are very significant, as reflected in the ratio σ_G, which takes values several times higher than the theoretical one. In order to clarify the meaning of the present results, we have also performed simulations for artificial segregated copolymer chains of the type A_2B, A_3B_3, and A_6B_6. In these simulations, ideal chains (without A–A, B–B, or A–B interactions) have the A and B parts separated by a plane passing though the star center. According to the Metropolis criterion, we accept every conformation for which the separation condition is held, considering the surface as a barrier of infinite energy. The dimensionless ratios have been calculated for various molecular weights ($N + 1 = 25, 49, 85, 109, 145$ 205 for A_2B, A_2B_2, A_2B_4, A_3B_3 and up to $N + 1 = 325$ for A_6B_6) and the extrapolated to the long-chain limit. The resulting intercepts are listed in Table 7. The comparison between the ratios of the two different models shows that the single miktoarm chains do not segregate intramolecularly (here we consider only the case of the strong segregation limit), not even in the case of A_6B_6 (where six linear diblock copolymer chains are joined). According to our simulation results, the mean conformation achieved by the miktoarm stars in the solution is characterized by a significant deformation along the arms, mainly near the star center where the possibility of interactions is high, and a change in the relative orientation of the vectors $\vec{G}_{A,\mathrm{miktoarm}}$ and $\vec{G}_{B,\mathrm{miktoarm}}$, extending the center of mass separation in order to diminish the repulsions. Our results and the adequate relationship $\langle G^2_{\mathrm{miktoarm}} \rangle = \langle G^2_{A,\mathrm{miktoarm}} \rangle + \langle G^2_{B,\mathrm{miktoarm}} \rangle - 2\langle |\vec{G}_{A,\mathrm{miktoarm}}||\vec{G}_{B,\mathrm{miktoarm}}| \cos(\vec{G}_A \wedge \vec{G}_B) \rangle$ show that both mechanisms have a similar influence in the increase of the $\langle G^2_{\mathrm{miktoarm}} \rangle$ values.

Table 7. Dimensionless Ratios for Artificial Segregated Miktoarm Star Copolymers ($\epsilon_{kl}/k_BT = 0$ (k,l = A or B))

	A_2B	A_3B_3	A_6B_6
σ_G	3.497 ± 0.004	6.053 ± 0.003	9.311 ± 0.002
$\sigma_{R_{AB}}$	2.022 ± 0.006	2.032 ± 0.002	1.929 ± 0.002
γ_{R_A}	1.457 ± 0.004	1.472 ± 0.003	1.422 ± 0.003
γ_{S_A}	1.016 ± 0.006	1.049 ± 0.004	1.008 ± 0.002
γ_{G_A}	2.868 ± 0.004	3.484 ± 0.003	5.141 ± 0.002
γ_{S_B}	1.120 ± 0.004		
γ_{G_B}	1.858 ± 0.006		
$(\vec{R}_A \wedge \vec{R}_B)$	116.1 ± 0.2	115.6 ± 0.1	113.83 ± 0.04

(b) Selective Solvent. We have also considered miktoarm stars with one homopolymer part under Θ conditions, while the other types of interactions obey the excluded volume regime. In particular, we are interested in the cases (a) $\epsilon_{AA}/k_BT = 0.1$, $\epsilon_{BB}/k_BT = 0$, $\epsilon_{AB}/k_BT = 0.1$, corresponding to ideal Θ conditions for the B arms, and (b) $\epsilon_{AA}/k_BT = 0.3$, $\epsilon_{BB}/k_BT = 0.1$, $\epsilon_{AB}/k_BT = 0.1$ (i.e., the A units under quasi-ideal conditions). This way we can obtain the information we need about the effects of heterointeractions for the A_2B and A_2B_4 type stars (where the two homopolymer parts have different molecular weights). The algorithm and the chain lengths are the same as those described in the previous sections. The extrapolated values of the dimensionless ratios are listed in Tables 8 and 9 for cases a and b, respectively.

It can be observed that the values of the ratios σ become higher as the number of arms increases, since the units suffer more cross interactions. However, when compared with the values of the macroscopic state

Table 8. Dimensionless Ratios for the Macroscopic State of Selective Solvent[a]

	A_2B	A_2B_2	A_2B_4	A_3B_3	A_6B_6
σ_G	1.379 ± 0.006 (1.374)	1.536 ± 0.006 (1.486)	1.746 ± 0.010 (1.748)	1.911 ± 0.014 (1.729)	3.364 ± 0.015 (2.457)
$\sigma_{R_{AB}}$	1.131 ± 0.005	1.172 ± 0.003 (1.241)	1.206 ± 0.004	1.193 ± 0.004 (1.352)	1.239 ± 0.003 (1.684)
γ_{R_A}	1.035 ± 0.007	1.079 ± 0.004	1.120 ± 0.005	1.096 ± 0.005	1.120 ± 0.002
γ_{S_A}	1.043 ± 0.003	1.061 ± 0.002	1.107 ± 0.005	1.081 ± 0.005	1.096 ± 0.002
γ_{G_A}	1.076 ± 0.009	1.173 ± 0.010	1.345 ± 0.014	1.314 ± 0.012	1.756 ± 0.012
γ_{R_B}	1.146 ± 0.005	1.145 ± 0.003	1.129 ± 0.003	1.178 ± 0.003	1.261 ± 0.003
γ_{S_B}	1.040 ± 0.001	1.114 ± 0.003	1.114 ± 0.004	1.141 ± 0.005	1.172 ± 0.008
γ_{G_B}	1.285 ± 0.006	1.389 ± 0.005	1.555 ± 0.007	1.620 ± 0.011	2.716 ± 0.015
$(\vec{R}_A \mid \mathrm{pt}\vec{R}_B)$	93.8 ± 0.1	94.3 ± 0.1	94.6 ± 0.1	94.5 ± 0.1	94.88 ± 0.08

[a] B−B interactions in ideal Θ regime, and A−A and A−B interactions in the excluded volume. In parentheses are the theoretical values calculated from ref 11.

Table 9. Dimensionless Ratios for the Macroscopic State of Selective Solvent[a]

	A_2B	A_2B_2	A_2B_4	A_3B_3	A_6B_6
σ_G	1.419 ± 0.005 (1.374)	1.605 ± 0.015 (1.486)	1.920 ± 0.021 (1.748)	1.980 ± 0.018 (1.729)	3.054 ± 0.038 (2.457)
$\sigma_{R_{AB}}$	1.186 ± 0.004	1.204 ± 0.012 (1.241)	1.225 ± 0.008 (1.395)	1.231 ± 0.006 (1.352)	1.276 ± 0.004 (1.648)
γ_{R_A}	1.058 ± 0.011	1.167 ± 0.011	1.253 ± 0.007	1.196 ± 0.008	1.257 ± 0.006
γ_{S_A}	1.061 ± 0.009	1.107 ± 0.018	1.173 ± 0.014	1.150 ± 0.009	1.207 ± 0.010
γ_{G_A}	1.258 ± 0.020	1.371 ± 0.014	1.584 ± 0.018	1.590 ± 0.027	2.093 ± 0.035
γ_{R_B}	1.111 ± 0.006	1.075 ± 0.007	1.068 ± 0.005	1.105 ± 0.005	1.154 ± 0.003
γ_{S_B}	1.041 ± 0.006	1.066 ± 0.005	1.057 ± 0.003	1.092 ± 0.008	1.136 ± 0.005
γ_{G_B}	1.184 ± 0.006	1.209 ± 0.006	1.227 ± 0.013	1.322 ± 0.011	1.869 ± 0.026
$(\vec{R}_A \wedge \vec{R}_B)$	95.9 ± 0.5	94.8 ± 0.3	94.4 ± 0.3	95.1 ± 0.2	94.1 ± 0.2

[a] A−A interactions in quasi-ideal Θ regime, and B−B and A−B interactions in the excluded volume. In parentheses are the theoretical values calculated from ref 11.

Table 10. Dimensionless Ratios for the Macroscopic State of Common Good Solvent

	A_2B	A_2B_2	A_2B_4	A_3B_3	A_6B_6
σ_G	1.294 ± 0.005	1.424 ± 0.009	1.562 ± 0.015	1.616 ± 0.017	2.108 ± 0.032
$\sigma_{R_{AB}}$	1.106 ± 0.006	1.142 ± 0.004	1.151 ± 0.003	1.155 ± 0.003	1.190 ± 0.003
γ_{R_A}	1.040 ± 0.005	1.083 ± 0.003	1.155 ± 0.007	1.107 ± 0.004	1.154 ± 0.002
γ_{S_A}	1.037 ± 0.004	1.068 ± 0.004	1.129 ± 0.008	1.102 ± 0.004	1.148 ± 0.003
γ_{G_A}	1.086 ± 0.007	1.171 ± 0.009	1.321 ± 0.015	1.285 ± 0.011	1.529 ± 0.006
γ_{R_B}	1.090 ± 0.007		1.059 ± 0.004		
γ_{S_B}	1.031 ± 0.003		1.062 ± 0.004		
γ_{G_B}	1.165 ± 0.005		1.192 ± 0.017		
$(\vec{R}_A \wedge \vec{R}_B)$	93.4 ± 0.2	93.6 ± 0.1	92.8 ± 0.2	92.7 ± 0.2	92.2 ± 0.1

previously described in (a) (common Θ solvent), the current values (from both theory and simulation) are significantly lower, indicating that the cross interactions are now less effective. The excluded volume repulsions within one homopolymer part tend to swell the arms in this part, thereby minimizing the interblock contacts. The values of σ_G obtained with the quasi-ideal parameters are higher than those obtained for the ideal Θ model, though both become greater than the theoretical results (the differences with theory are also greater for the chains with a higher number of arms). The opposite behavior is observed for the ratios $\sigma_{R_{AB}}$ and γ, where the theory predicts higher expansions for the various parts of the miktoarm chains. For a detailed study of the role of the heterointeractions, it is more convenient to introduce the parameter $\delta_{\sigma_G} = \sigma_G - 1$, which expresses the relative expansion of the various parts with respect to the homopolymer precursors. According to the RG theory, the ratio δ_{σ_G}(selective solvent)/δ_{σ_G}(common Θ solvent) should be equal to the ratio of the cross fixed points u^*_{AB} corresponding to each of the macroscopic states, previously defined. In first-order ϵ approximation, this ratio is equal to 0.75. Our results with the quasi-ideal model for the ratio σ_G are approximately 0.78, 0.75, 0.76, and 0.70 for the A_2B, A_2B_2, A_2B_4, and A_3B_3 type miktoarm stars, in very good agreement with the theoretical predictions. However, we observe a disagreement for the value corresponding to the A_6B_6 chain (0.53), where the core effects are very significant. Similar results are obtained with the ideal Θ model. As we can see from the values of the ratios γ in Tables 8 and 9, the expansion due to the heterointeractions is not the same for the different homopolymer parts. The branches under Θ conditions feel the heterointeractions as strongly as in the case of the common Θ solvent, while the B−B interactions swell the arms, reducing the heterointeraction effects. These trends are similar to those found in the study of linear AB diblock copolymers and corroborate our view that the fixed-point value $u^*_{AB} = 3\epsilon/32$ of the RG theory should be used to describe the conformational properties of the whole molecule or of the parts containing both kinds of monomers (like the diblock spans), while the fixed points $u^*_{AB} = 4\epsilon/32$ and $u^*_{AB} = 2\epsilon/32$ should describe the properties of the homopolymer parts for which all the intrainteractions obey the Θ and the good solvent regimes, respectively.

(c) Common Good Solvent. The last macroscopic state we study here is that of a common good solvent where all interactions between units A−A, B−B, and A−B have been set to be of the excluded volume type. In this case, the miktoarm star copolymer chain behaves as a homopolymer star with all branches equally expanded. We have calculated the dimensionless ratios for the same chain characteristics described in the previous two macroscopic states, but considering the

Table 11. Theoretical Values of Dimensionless Ratios for the Macroscopic State of Common Good Solvent Calculated from Ref 11

	A_2B	A_2B_2	A_2B_4	A_3B_3	A_6B_6
σ_G	1.249	1.324	1.498	1.486	1.971
$\sigma_{R_{AB}}$	1.142	1.197	1.308	1.197	1.641
γ_{R_A}	1.111	1.166	1.277	1.166	1.609
γ_{S_A}	1.064	1.127	1.254	1.206	1.436
γ_{R_B}	1.111		1.277		
γ_{S_B}	1.054		1.142		

parameter $\epsilon_{kl}/k_BT = 0.1$ (k,l = A or B) for all the interactions. The extrapolated values of the ratios are listed in Table 10 for all types of miktoarm stars, while their theoretical values are contained in Table 11. As expected, these values are smaller in comparison with the other two macroscopic states, since both homopolymer parts A and B are expanded, reducing the likelihood of the A−B heterocontacts. According to the RG theory, the ratio δ_{σ_G}(common good)/δ_{σ_G}(common Θ) is equal to 0.5, while the ratio δ_{σ_G}(common good)/δ_{σ_G}(selective) is equal to 0.67. Our simulation results obtained by means of the ideal model for the A_2B, A_2B_2, A_2B_4, A_3B_3, and A_6B_6, miktoarm stars respectively yield results approximately equal to $\cong$0.60, 0.55, 0.50, 0.47, and 0.32 for the common good/common Θ ratio and $\cong$0.78, 0.79, 0.75, 0.68, and 0.54 for the common good/selective ratio.

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