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Conformation of A_2B and A_3B Miktoarm Star Copolymers in Dilute Solutions

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ABSTRACT: The dimensionless ratio σ_G, expressing quantitatively the effects of heterointeractions between unlike units on the conformational properties of copolymers, has been determined experimentally by intrinsic viscosity analysis for the A_2B and A_3B miktoarm stars in various solvent conditions. In the case of symmetric samples (where the lengths of A and B arms are the same) in a common good solvent, the values of the required Flory parameter Φ for homopolymer stars with three and four arms were used. For the other cases and solvent conditions, Φ was determined by extended Monte Carlo calculations which provide a lower bound of this quantity. The experimental values of σ_G are compared with the results obtained by Monte Carlo simulations and recent renormalization group predictions.

1. Introduction

Recently, the synthesis[1−4] and the study[2,5−12] of A_xB_y miktoarm (from the Greek word *μικτος*, meaning mixed) star copolymers consisting of A and B arms of different homopolymers has received much attention because of their peculiar behavior in the melt[5−10] and in dilute solution.[11,12] The latter arises from the compact structure of these copolymers which yields an increasing possibility of heterointeractions between dissimilar units. This possibility is controlled by several variables, namely, the total number of branches $f = x + y$, their relative number $L = y/x$, and the branch length ratio $\rho = N_B/N_A$ (N_i being the number of A or B units per arm).

In preceding papers,[11,12] we presented a systematic theoretical study on A_xB_y miktoarm star polymers in an effort to describe the effects of the excluded volume heterointeractions on the mean conformation of an isolated chain in various macroscopic states. The following dimensionless ratios were obtained:

$$\sigma_G = \langle G^2_{A_xB_y}\rangle/[\langle G^2_{A_x}\rangle + \langle G^2_{B_y}\rangle] \qquad (1)$$

$$\sigma_{R_{AB}} = \langle R^2_{AB,A_xB_y}\rangle/[\langle R^2_A\rangle + \langle R^2_B\rangle] \qquad (2)$$

$$\gamma_{G_k} = \langle R^2_{k,A_xB_y}\rangle/\langle R^2_k\rangle \qquad (k = A \text{ or } B) \qquad (3)$$

$$\gamma_{S_k} = \langle S^2_{k,A_xB_y}\rangle/\langle S^2_k\rangle \qquad (k = A_x \text{ or } B_x) \qquad (4)$$

$$\gamma_{G_k} = \langle G^2_{k,A_xB_y}\rangle/\langle G^2_k\rangle \qquad (k = A_x \text{ or } B_x) \qquad (5)$$

where the different mean-squared averages are defined as follows: $\langle G^2_{A_xB_y}\rangle$ = the distance between the centers of mass of the two homopolymer parts A and B of the miktoarm star copolymer; $\langle G^2_k\rangle$ = the distance between the unit connected to the branch point (central unit) and the center of mass 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; $\langle R^2_{AB,A_xB_y}\rangle$ = the end-to-end distance of a diblock copolymer chain inside the miktoarm star copolymer (diblock copolymer span); $\langle R^2_k\rangle$ = the distance of an arm end in the k homopolymer star precursor to the unit connected to the branch point (k = A or B); $\langle R^2_{k,A_xB_y}\rangle$ = the distance of the k branch end from the central unit in the miktoarm star copolymer (modulus of vector $\vec{R}_k$); $\langle S^2_{k,A_xB_y}\rangle$ = the radius of gyration of the k homopolymer part of the miktoarm star; $\langle S^2_k\rangle$ = the radius of gyration of the k homopolymer star precursor; and $\langle G^2_{k,A_xB_y}\rangle$ = the distance between the center of mass of the homopolymer part k and the star central unit (modulus of vector $\vec{G}_k$).

These averages express the expansion of various parts and the whole miktoarm chain relative to homopolymer precursors and have been calculated with both renormalization group analysis[11] and Monte Carlo simulations.[12] It was established that the ratios σ_G, γ_{S_k}, and γ_{G_k} can be used to estimate quantitatively the effects of heterointeractions under any solvent condition, while the remaining ratios $\sigma_{R_{AB}}$ and γ_{R_k}, which depend on the thermodynamic type of solvent condition of the two homopolymer parts, can be used only in a common Θ solvent, where the contributions of the A−A and B−B interactions are canceled. For random flight chains, all ratios are equal to one for any number of arms x,y. The validity of the theoretical approach and the MC calculations can be checked only by adequate experimental determination of these ratios. As far as we know, the only previous experimental study on dilute solutions of miktoarm stars has been carried out by Iatrou et al.[2] for A_2B and A_2B_2 chains in a common good solvent and

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a selective solvent. These authors, however, follow the Bywater–Prud'homme scheme[13] which considers the property of a copolymer as a weighted average of the two homopolymer parts with the same total molecular weight M ($M = xN_A + yN_B$). It is purely intuitive and ascribes any observed positive deviation from the weighted average as due to heterocontact interactions, without determining averages like $\langle S^2\rangle$ or $\langle G^2\rangle$ necessary for the calculation of the dimensionless ratios. Long ago, Tanaka et al.[14] studied linear AB diblock copolymers in common good and selective solvents and suggested two promising methods for the calculation of the ratio σ_G. The first one is based on intrinsic viscosity measurements of the whole chain and the homopolymer precursors. The conformational averages then are obtained from the well-known Flory equation $[\eta]_\kappa = \Phi_\kappa\langle S^2\rangle^{3/2}/M_\kappa$ relating these quantities with the intrinsic viscosity assuming that the Flory parameter Φ_κ has the same value for all the copolymer and homopolymer species independently of the type of solvent. The values of σ_G obtained this way were close to the theoretical values for a common good solvent. However, the method failed for the selective solvent case due to a lack of universality of the Flory parameter, at least in the particular solvents used in that study. The second method consists in determining the ratio σ_G by means of light scattering experiments in a solvent having large refractive index increments for both blocks. Then, according to the Benoit relation for a heterogeneous copolymer,[15] the ratio σ_G is expressed in terms of the apparent radius of gyration of the copolymer, the radii of gyration of the homopolymer precursors, and some coefficients depending on the weight fractions and the refractive index increments. Both methods can be extended for the case of miktoarm stars if some additional requirements are met. However, the light scattering method is limited in the case of copolymers with long branches, while the application of the viscosity method is restricted to small values of γ_{S_k} and some appropriate values of Φ are needed (see next section).

In the present paper, we perform a combined experimental and Monte Carlo study in order to calculate the dimensionless ratio σ_G for miktoarm stars of the A_2B and A_3B type. Due to the molecular weights of our copolymers, we are limited to the application of the intrinsic viscosity method. Thus, the intrinsic viscosities of $(PI)_3PS$ samples with different branch length ratio $\rho = N_B/N_A$ were measured in toluene at 35 °C (common good solvent), while the viscosities of $(PI)_2PS$ samples in toluene at 35 °C and dioxane at 34 °C (Θ for PI) were obtained from ref 2. Using appropriate values of Φ which take into account the branching asymmetry and the effect of the selective solvent, we calculate the ratio σ_G according to the Tanaka scheme. The results are compared with recent renormalization group predictions and Monte Carlo values also obtained in this work.

2. Intrinsic Viscosity Analysis

First we consider the case of A_2B miktoarm stars where both precursor homopolymers A and B are linear chains with molecular weights $2N_A$ and N_B, respectively. Writing eq 3.8 from ref 11 for the A_2B stars, we get

$$\langle S^2_{A_2B}\rangle = x_A\langle S^2_{A_2,A_2B}\rangle + x_B\langle S^2_{B,A_2B}\rangle + x_Ax_B\langle G^2_{A_2B}\rangle \quad (6)$$

where x_A and x_B are the weight fractions[16] of the A and B components, equal to $x_A = 2N_A/(2N_A + N_B)$ and $x_B = N_B/(2N_A + N_B)$. In general, we wish to express the total radius of gyration $\langle S^2_{A_2B}\rangle$ in terms of the radii of gyration $\langle S^2_{A_2}\rangle$ and $\langle S^2_B\rangle$ of the homopolymer precursors and the ratio σ_G, with the aim of introducing the intrinsic viscosities through the Flory relation. As a first step, we substitute in eq 6 the averages $\langle G^2_{A_2B}\rangle$, $\langle S^2_{A_2,A_2B}\rangle$, and $\langle S^2_{B,A_2B}\rangle$ in terms of the ratios and averages included in eqs 1 and 4

$$\langle S^2_{A_2B}\rangle = x_A\gamma_{S_A}\langle S^2_{A_2}\rangle + x_B\gamma_{S_B}\langle S^2_B\rangle + x_Ax_B\sigma_G[\langle G^2_{A_2}\rangle + \langle G^2_B\rangle] \quad (7)$$

Then we look for a relation connecting the averages $\langle G^2_k\rangle$ and $\langle S^2_k\rangle$ (k = A_2, B) ($\langle G^2_{A_2}\rangle = N_A/(3x)$ and $\langle G^2_B\rangle = N_B/(3y)$ for ideal star[17] chains). Following Tanaka's approach,[14] we set $\langle G^2_{A_2}\rangle \cong \langle S^2_{A_2}\rangle$ and $\langle G^2_B\rangle \cong 2\langle S^2_B\rangle$. These expressions are exact for a linear homopolymer in a Θ solvent, while $\langle G^2_k\rangle$ should be slightly larger than $\langle S^2_{A_2}\rangle$ or $2\langle S^2_B\rangle$ for perturbed chains. The deviation should be similar to those corresponding to the approximation $\langle R^2\rangle \cong 6\langle S^2\rangle$ for a linear chain, just a few percent.[14] However, we performed computer simulations[18] for two different ratios $\sigma_G = \langle G^2_{AB,linear}\rangle/(\langle G^2_A\rangle + \langle G^2_B\rangle$ and $\sigma_T = \langle G^2_{AB,linear}\rangle/2(\langle S^2_A\rangle + \langle S^2_B\rangle)$ for the case of linear AB diblock copolymers, obtaining $\sigma_G = 1.219 \pm 0.003$ and $\sigma_T = 1.227 \pm 0.003$ in a common good solvent and $\sigma_G = 1.253 \pm 0.003$ and $\sigma_T = 1.258 \pm 0.003$ in a selective solvent. This indicates that the approximation is practically exact when extrapolated values are considered. Therefore we set

$$\langle S^2_{A_2B}\rangle = x_A\gamma_{S_A}\langle S^2_{A_2}\rangle + x_B\gamma_{S_B}\langle S^2_B\rangle + x_Ax_B\sigma_G[\langle S^2_{A_2}\rangle + 2\langle S^2_B\rangle] \quad (8)$$

At this point, eq 8 can be expressed in terms of intrinsic viscosities. Introducing $[\eta]_\kappa = \Phi_\kappa\langle S^2\rangle^{3/2}/M_\kappa$, we finally obtain after straightforward calculations

$$[\eta]^{2/3}_{A_2B} = x_A^{5/3}(\gamma_{S_A} + x_B\sigma_G)[\eta]^{2/3}_{A_2}\left(\frac{\Phi_{A_2B}}{\Phi_{A_2}}\right)^{2/3} + x_B^{5/3}(\gamma_{S_B} + x_A2\sigma_G)[\eta]^{2/3}_B\left(\frac{\Phi_{A_2B}}{\Phi_B}\right)^{2/3} \quad (9)$$

Equation 9 and a similar equation for A_3B stars, obtained with the same method, can be further simplified by considering the ratios γ_{S_A} and γ_{S_B} to be equal to one in the case of the miktoarms studied here. Thus, computer simulation results, which for the case of AB linear diblock copolymers have been confirmed experimentally,[14] show that the expansion of the radii of gyration of the two homopolymer parts due to the heterocontacts (see section 4) is not greater than 6% for A_2B and A_3B stars. Therefore the error introduced by this approximation does not exceed the accuracy of the viscosity method. Consequently, we arrive at the final equations

$$[\eta]^{2/3}_{A_2B} = x_A^{5/3}(1 + x_B\sigma_G)[\eta]^{2/3}_{A_2}\left(\frac{\Phi_{A_2B}}{\Phi_{A_2}}\right)^{2/3} + x_B^{5/3}(1 + x_A2\sigma_G)[\eta]^{2/3}_B\left(\frac{\Phi_{A_2B}}{\Phi_B}\right)^{2/3} \quad (10)$$

Table 1. Molecular Characterization and Intrinsic Viscosities of A_2B and A_3B Miktoarm Stars

					wt % PS				
sample	$(M_n)_{PS} \times 10^3$	$M_n \times 10^3$	$M_w \times 10^3$	$\rho = N_B/N_A$	UV	NMR	M_n	$[\eta]$,[a] mL/g	$[\eta]$,[b] mL/g
$(PI)_2PS3$	21.7	50.3	53.4	1.0	40	38	41	38.9	26.7
$(PI)_2PS8$	79.1	145.7	147.1	1.7		57	54	72.9	
$(PI)_3PS55$	35.2	73.0	78.4	2.0	50.1	50.6	48	40.4	
$(PI)_3PS40$	59.3	104.2	108.3	2.8	58.1	59.8	57.0	49.3	
$(PI)_3PS35$	59.3	92.3	97.3	3.9	63.8	65.2	64.2	45.2	

[a] In toluene at 35 °C. [b] In dioxane at 34 °C.

$$[\eta]^{2/3}_{A_3B} = x_A^{5/3}\left(1 + \frac{2}{7}x_B\sigma_G\right)[\eta]^{2/3}_{A_3}\left(\frac{\Phi_{A_3B}}{\Phi_{A_3}}\right)^{2/3} + x_B^{5/3}(1 + x_A 2\sigma_G)[\eta]^{2/3}_B\left(\frac{\Phi_{A_3B}}{\Phi_B}\right)^{2/3} \quad (11)$$

for A_2B and A_3B miktoarm stars, respectively.

For other miktoarm stars (with higher number of branches) the contribution of γ_{S_A} and γ_{S_B} is not negligible and the values of these ratios must also be determined. The suitable method to measure γ_{S_k} depends on the MW of the homopolymer part. Neutron scattering experiments for deuterium-labeled samples are needed when short arms are present. For longer branches, the ratios γ_{S_A} and γ_{S_B} can be obtained by means of light scattering experiments similar to those described in the Introduction. The ratios σ_G for the A_2B and A_3B stars can be obtained from eqs 10 and 11 so that the right-hand side yields the experimental value of the intrinsic viscosity of the miktoarm star. Before eqs 10 and 11 can be used, the proper values of the $\Phi_{A_xB_y}$ have to be established. The general idea is to consider symmetric ($\rho = 1$) miktoarm samples in a common good solvent to be equivalent to the perturbed homopolymer stars with the same number of branches. Thus, the experimental values of the Flory parameter Φ corresponding to star homopolymers with three and four arms in a good solvent can be used. For asymmetric ($\rho \neq 1$) miktoarm stars at the same solvent conditions, a correction to the experimental values of Φ has been calculated for each sample separately in terms of the ratio $(\Phi_\rho/\Phi_{\rho=1})$. These ratios were evaluated by means of Monte Carlo simulations which yield a lower bound[19] for Φ. This lower bound procedure has been previously shown to reproduce adequately the ratios g' obtained as viscosities of star chains to those of homologous linear chains.[20] Consequently, we believe that it should also give accurate predictions of the present ratios. Despite that the value of Φ depends on the type of bound method, we believe that their ratio will be closer to the experimental value. With the same method, the selective solvent correction $(\Phi_{\text{selective}}/\Phi_{\text{good}})$ to the experimental value of Φ for the A_2B star has been obtained. The procedure is described in section 4 in detail.

3. Experimental Section

The synthesis of all the miktoarm star copolymers was carried out using anionic polymerization under vacuum conditions. Chlorosilane compounds were used as linking agents. Manipulations under vacuum were made using apparatuses equipped with breakseals and heat-sealable constrictions. In short, the synthesis involves the linking of the reactive macroanion of the first precursor with a large excess of the appropriate linking agent ($SiCH_3Cl_3$ or $SiCl_4$), in order to substitute only one of the available chlorine atoms on the silicon atom with the precursor chain. After quantitative removal of the excess linking agent, the macromolecular linking agent formed is allowed to react with a small excess of the macroanion of the second precursor. The second arm excess is finally removed by fractionation. The details of the experimental procedures followed for the preparation of the A_2B and A_3B miktoarm stars are given elsewhere.[2,3]

All miktoarm star copolymers were characterized in terms of their molecular weight, molecular weight distribution, and composition by size exclusion chromatography (SEC), membrane osmometry (MO), low-angle laser light scattering (LALLS), and UV and ^{1}H NMR spectroscopy. The molecular characterization proved the high degree of structural and compositional homogeneity of the miktoarm stars prepared. Details on the instrumentation and the experimental conditions of the measurements are given in refs 2 and 3.

Intrinsic viscosities were measured in toluene at 35 °C (common good solvent) and in dioxane at 34 °C (Θ conditions for PI arms) using Cannon-Ubbelohde viscometers (dilution series) and a Scott-Gerate automatic timer. The solvent flow time was about 200 s in all cases. The intrinsic viscosity values were obtained by extrapolation of the η_{sp}/c and ln η_r/c against c plots to zero concentration and are listed together with the molecular characteristics of our samples in Table 1. The branch length ratio ρ was obtained from the corresponding ratios of the squared radii of gyration of the two different arms under Θ conditions calculated from experimental relations obtained by the Baumman method.[21]

4. Results and Discussion

As we mentioned in previous section, the ratio σ_G for the symmetric A_2B miktoarm star (sample $(PI)_2PS3$) in a common good solvent (toluene at 35 °C) can be directly calculated from eq 10 using for the ratio (Φ_{A_2B}/Φ_{A_2}) the values of Φ for the perturbed homopolymer stars with three branches and the one for linear homopolymers. Applying the Flory equation for stars and linear chains, this ratio can be expressed in terms of g' and g_s (ratio of the mean square radius of gyration of the star to that of the homopologous linear chain) as $g' = (\Phi_{\text{star}}/\Phi_{\text{linear}})g^{3/2}$. Using the values $g' = 0.833$ and $g_s = 0.79$ from ref 22 for symmetric stars with $f = 3$, we obtain the value 1.19 for the ratio $(\Phi_{A_2B}/\Phi_{\text{linear}})$. The following experimental relations for linear chains have been used for the calculation of intrinsic viscosities of the linear precursors $[\eta_{A_2}]$ and $[\eta_B]$:

$$\text{PS:} \quad [\eta] = 9.27 \times 10^{-3} M_w^{\ 0.734} \qquad (\text{toluene, } 35\ ^\circ\text{C}^{16}) \qquad (12)$$

$$\text{PI:} \quad [\eta] = 1.72 \times 10^{-2} M_w^{\ 0.74} \qquad (\text{toluene, } 35\ ^\circ\text{C}^{16}) \qquad (13)$$

Substituting the values of intrinsic viscosities and $(\Phi_{A_2B}/\Phi_{\text{linear}})$ in eq 10, we finally obtain for the ratio σ_G the value $\sigma_G = 1.236$. This is in excellent agreement with the RG prediction[11] of $\sigma_G = 1.249$ corresponding to the same solvent conditions ($u^*_A = {}^1/_{16}$, $u^*_B = {}^1/_{16}$, $u^*_{AB} = {}^1/_{16}$) and asymmetry ratio $\rho = 1$, while the result obtained from the Monte Carlo simulation[12] is sligtly higher, $\sigma_G = 1.294 \pm 0.005$. Compared to the experimental ratios $\sigma_G = 1.1-1.20$ corresponding to the symmetric linear AB diblock copolymers,[14,23] our result is clearly higher,

Table 2. Results for Viscosity and Parameter Φ Obtained by Monte Carlo Simulations for A_2B Miktoarm Stars in a Common Good Solvent and a Selective Solvent with the Lower Bound Method

		common good solvent		selective solvent	
$\rho = N_B/N_A$	$N+1$	$[\eta]^*$	$\Phi \times 10^{-23}$	$[\eta]^*$	$\Phi \times 10^{-23}$
1	49	222.6 ± 1.4	2.116 ± 0.023	213.2 ± 1.2	2.242 ± 0.020
	85	584.9 ± 3.8	2.201 ± 0.022	545.4 ± 2.5	2.250 ± 0.017
	109	909.5 ± 1.7	2.210 ± 0.010	837.7 ± 4.1	2.265 ± 0.020
	145	1499 ± 12	2.212 ± 0.030	1346.2 ± 5.2	2.251 ± 0.017
	199	2599 ± 17	2.208 ± 0.025	2324 ± 8.0	2.266 ± 0.016
1.7	38	143.71 ± 0.76	2.146 ± 0.015		
	75	478.8 ± 2.9	2.164 ± 0.024		
	112	967.1 ± 4.3	2.145 ± 0.016		
	149	1600.2 ± 9.9	2.151 ± 0.021		
	186	2377 ± 11	2.156 ± 0.015		

indicating that the presence of another A arm in the vicinity of the B block increases the cross interactions and consequently expands more the A_2B chain.

Table 3. Results for Viscosity and Parameter Φ Obtained by Monte Carlo Simulations for A_3B Miktoarm Stars in a Common Good Solvent with the Lower Bound Method

$\rho = N_B/N_A$	$N+1$	$[\eta]^*$	$\Phi \times 10^{-23}$
1	49	191.65 ± 0.87	2.626 ± 0.016
	85	498.2 ± 2.4	2.611 ± 0.019
	109	775.2 ± 3.5	2.622 ± 0.018
	145	1285.6 ± 9.8	2.640 ± 0.025
	201	2280 ± 14	2.639 ± 0.028
2	51	210.2 ± 1.5	2.426 ± 0.023
	101	704.1 ± 3.9	2.453 ± 0.024
	151	1439.8 ± 6.4	2.471 ± 0.019
	201	2.372 ± 14	2.450 ± 0.027
2.8	59	283.8 ± 2.0	2.272 ± 0.027
	117	957.4 ± 6.3	2.299 ± 0.031
	175	1940.8 ± 8.1	2.284 ± 0.024
3.9	70	405.1 ± 3.1	2.122 ± 0.033
	139	1343 ± 14	2.126 ± 0.037
	208	2736 ± 20	2.078 ± 0.028

Next, we study the influence of asymmetry ratio ρ on σ_G. From several samples of synthesized miktoarms described in ref 2, we have chosen for the present purposes $(PI)_2PS8$, which is one of the most asymmetric samples, with $\rho = 1.7$ (we note that our ρ corresponds to $1/L$ of ref 2). The values of σ_G of the other samples with $\rho \leq 1.7$ lie between those of the two samples reported here. The asymmetry correction $(\Phi_{\rho=1.7}/\Phi_{\rho=1})$ to Φ_{A_2B} has been calculated by means of Monte Carlo simulations with the lower bound method.[19] The method derives the lower bounds for the intrinsic viscosity from a variational theory. Monte Carlo calculations over a sample of rigid equilibrium conformations are performed in order to obtain averages required for the final formulas given by the variational procedure. In this respect, similar to the calculation of equilibrium averages of the intrinsic viscosities of individual chains considered as rigid bodies[24] (which provides upper bounds), it has the great computational advantage of not requiring the inversion of the diffusion matrix at every simulation step. The model has been described and justified in previous work.[12,20] We consider N Gaussian beads placed on f branches so that the distance between neighboring beads is not constant but follows a Gaussian distribution of mean root square value b. The first x branches consist of N_A beads (each one) which are considered as units of the A type (A homopolymer), and the remaining $y = f - x$ branches with N_B units are assigned to be of the B type. The central unit is the common origin of the coordinates and is assigned as the unit $N + 1$. Neighboring units interact through a 6−12 Lennard-Jones potential

$$U(R_{ij})/k_BT = 4(\epsilon_{kl}/k_BT)[(\sigma/R_{ij})^{12} - (\sigma/R_{ij})^{6}] \qquad (k,l = A \text{ or } B) \quad (14)$$

The reduced distance at which the potential vanishes is set as $\sigma/b = 0.8$ according to our previous experience in the application of this model in several copolymer chains. The reduced energy at the bottom of the potential well, ϵ_{kl}/k_BT is the relevant parameter that determines the solvent conditions, depending on the type of interacting units of the same (AA, BB) or different (AB) homopolymers. The macroscopic state of the common good and the selective solvent (Θ for the A units) corresponds to $\epsilon_{AA}/k_BT = 0.1$, $\epsilon_{BB}/k_BT = 0.1$, $\epsilon_{AB}/k_BT = 0.1$ and $\epsilon_{AA}/k_BT = 0.3$, $\epsilon_{BB}/k_BT = 0.1$, $\epsilon_{AB}/k_BT = 0.1$, respectively. The algorithm starts by building an initial chain with moderate energy. New conformations are 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 $b^2/3$. Then the rest of the beads on the selected arm up to the free end are shifted to connect to the changed unit vector. We only use a small fraction of the total number of generated conformations (1/100) to perform the hydrodynamic calculations, since these calculations require a large computational effort, considerably higher than that needed for the sampling process. We employ a total number of steps ranging from 200 000 to 400 000. Configurational-dependent hydrodynamic interactions are introduced through a diffusion tensor D, depending on the relative positions between pairs of beads, R_{ij}. The strength of these interactions is gauged by the parameter $h^* = (3/\pi)^{1/2}(\sigma/b)$, where σ is the Stokes friction radius of the units. We use a Rotne−Prager−Yamakawa tensor, which takes into account the finite size of the units and the possibility of overlap between them. According to our experience,[19,20] we have set $h^* = 0.25$. In Tables 2 and 3 we report in detail our results for the intrinsic viscosities and Φ (calculated from the Flory equation $[\eta] = \Phi\langle S^2\rangle^{3/2}/M$) corresponding to different chain lengths $N + 1$. It can be seen that Φ remains almost constant in the range of $N + 1$ we use here. Thus, taking their mean value, we calculate the asymmetry correction coefficient $(\Phi_{\rho=1.7}/\Phi_{\rho=1}) = 0.973$. The final ratio $(\Phi_{A_2B}/\Phi_{\text{linear}})$ is equal to $1.19 \times 0.973 = 1.158$, a value which is not very different from that of the symmetric star, in agreement with the experimental results of Khasat et al.[25] However, even these small changes in the Φ ratio affect the final value of σ_G (we observed that a 1% difference in the ratio of Φ values results in approximately 2% change in the final value of σ_G). Using in eq 10 the intrinsic viscosity of the $(PI)_2$-PS8 miktoarm star from Table 1 and the ones calculated with eqs 12 and 13 for the precursor homopolymers, we obtain $\sigma_G = 1.241$. For the same miktoarm star ($\rho =$

Table 4. Dimensionless Ratios of the A$_2$B and A$_3$B Miktoarm Stars for the Macroscopic State of a Common Good Solvent

	A$_3$B, $\rho = 2$ (sample (PI)$_3$PS55)		A$_3$B, $\rho = 2.8$ (sample (PI)$_3$PS40)		A$_3$B, $\rho = 3.9$ (sample (PI)$_3$PS35)		A$_2$B, $\rho = 1.7$ (sample (PI)$_2$PS8)	
	MC	RG^a	MC	RG^a	MC	RG^a	MC	RG^a
σ_G	1.342 ± 0.010 (1.402)	1.316	1.340 ± 0.013 (1.350)	1.291	1.241 ± 0.017 (1.402)	1.262	1.289 ± 0.006 (1.241)	1.238
$\sigma_{R_{\mathrm{AB}}}$	1.154 ± 0.008	1.180	1.192 ± 0.012	1.165	1.150 ± 0.014	1.147	1.119 ± 0.010	1.134
$\gamma_{R_{\mathrm{A}}}$	1.056 ± 0.007	1.170	1.034 ± 0.007	1.172	1.025 ± 0.005	1.172	1.043 ± 0.007	1.114
$\gamma_{S_{\mathrm{A}}}$	1.030 ± 0.001	1.073	1.030 ± 0.006	1.074	1.032 ± 0.005	1.075	1.030 ± 0.004	1.067
$\gamma_{G_{\mathrm{A}}}$	1.173 ± 0.017		1.115 ± 0.023		1.075 ± 0.016		1.114 ± 0.017	
$\gamma_{R_{\mathrm{B}}}$	1.137 ± 0.002	1.143	1.184 ± 0.014	1.129	1.137 ± 0.020	1.115	1.086 ± 0.009	1.100
$\gamma_{S_{\mathrm{B}}}$	1.052 ± 0.008	1.068	1.063 ± 0.006	1.060	1.041 ± 0.001	1.051	1.030 ± 0.002	1.048
$\gamma_{G_{\mathrm{B}}}$	1.246 ± 0.011		1.303 ± 0.025		1.165 ± 0.015		1.160 ± 0.003	
$(\vec{R}_{\mathrm{A}} \wedge \vec{R}_{\mathrm{B}})$	93.29 ± 0.28		92.80 ± 0.36		93.74 ± 0.31		93.42 ± 0.46	

[a] RG results from ref 11 ($u^*_{\mathrm{A}} = u^*_{\mathrm{B}} = u^*_{\mathrm{AB}} = {}^1/_{16}$). The results obtained from experimental data (eqs 10 and 11) are included in parentheses together with the Monte Carlo results.

1.7) in a common good solvent ($u^*_{\mathrm{A}} = {}^1/_{16}$, $u^*_{\mathrm{B}} = {}^1/_{16}$, $u^*_{\mathrm{AB}} = {}^1/_{16}$), RG predicts[11] $\sigma_G = 1.238$, which is again in excellent agreement with the experimental value. Monte Carlo data concerning asymmetric miktoarm stars were not obtained in our previous work. For comparison with the current results, we extend the numerical Monte Carlo calculations[12] to all samples listed in Table 1. Using the algorithm described above, we generate miktoarm chains as follows: A$_2$B with $N_{\mathrm{A}} = 10$, 20, 30, 40, 60 and total units $N + 1 = 38$, 75, 112, 149, 223 for $\rho = 1.7$; A$_3$B with $N_{\mathrm{A}} = 10$, 20, 30, 40, 60 and $N + 1 =$ 51, 101, 151, 201, 301 for $\rho = 2$; A$_3$B with $N_{\mathrm{A}} = 10$, 20, 30, 50 and $N + 1 = 59$, 117, 175, 292 for $\rho = 2.8$; A$_3$B with $N_{\mathrm{A}} = 10$, 20, 30, 47 and $N + 1 = 70$, 139, 208, 326 for $\rho = 3.9$. The extrapolated values of the ratios in the limit of long chains have been obtained by linear regression analysis and are listed in Table 4. It can be seen that the MC value of $\sigma_G = 1.289 \pm 0.006$ is again higher than the experimental one. All these methods, however, indicate that we are in a plateau region since the σ_G values are almost identical to the values for the symmetric miktoarm star.

Furthermore, we calculate here the ratio σ_G for the macroscopic state of the selective solvent. In this case, the PI or the PS part is under Θ solvent conditions while the interactions in the other part obey the excluded volume regime. In order to underline the influence of the solvent on σ_G, we are considering the case in which the majority of the units are in Θ conditions. This experimentally corresponds to the choice of dioxane at 34 °C. Morover, in order to avoid the multiple corrections to the ratio of values of Φ which lead possibly to a large error in the final value of σ_G, we are considering in the current study only the case of the symmetric miktoarm star (sample(PI)$_2$PS3). The selective solvent correction coefficient ($\Phi_{\mathrm{good}}/\Phi_{\mathrm{selective}}$) is calculated from Table 2 with the method previously described and is equal to 0.98. Then the ratio $\Phi_{\mathrm{A_2B}}$(selective)/Φ_{B}(good) in eq 10 is evaluated as $\Phi_{\mathrm{A_2B}}$(good)/(0.98Φ_{B}(good)) = 1.19/0.98 = 1.214. Similarly, using the relation[20,26] $\Phi_{\mathrm{A_2}}$(good) = 0.78$\Phi_{\mathrm{A_2}}(\Theta)$, we obtain for the ratio $\Phi_{\mathrm{A_2B}}$(selective)/$\Phi_{\mathrm{A2}}(\Theta)$ = $\Phi_{\mathrm{A_2B}}$(good)/(0.98$\Phi_{\mathrm{A_2}}(\Theta)$) = (0.78$\Phi_{\mathrm{A_2B}}$(good))/(0.98$\Phi_{\mathrm{A_2}}$(good)) = 0.78 × 1.19/0.98 = 0.947. For the intrinsic viscosities of the homopolymer precursors in dioxane, we use the following experimental relations:

$$\text{PI:}\quad [\eta] = 1.11 \times 10^{-1} M_{\mathrm{w}}^{0.513} \qquad \text{(dioxane, 34 °C)} \tag{15}$$

$$\text{PS:}\quad [\eta] = 1.45 \times 10^{-2} M_{\mathrm{w}}^{0.695} \qquad \text{(dioxane, 34 °C)} \tag{16}$$

The final value for σ_G from eq 10 is equal to 1.331. This value is 9% greater than the corresponding value in a common good solvent, in good agreement with the theoretical RG[11] and Monte Carlo values, which show an increase of 12 and 13%, respectively ($\sigma_G{}^{\mathrm{RG}} = 1.374$ for $u^*_{\mathrm{A}} = 0$, $u^*_{\mathrm{B}} = {}^1/_{16}$, $u^*_{\mathrm{AB}} = {}^3/_{32}$, $\rho = 1$ and $\sigma_G{}^{\mathrm{MC}} = 1.419 \pm 0.005$).[12] The (PI)$_3$PS miktoarm stars in a common good solvent are treated similarly. The ratio σ_G is now calculated from eq 11, which takes into account the adequate expressions between the averages of the homopolymer precursors, $\langle G^2_{\mathrm{A_3}}\rangle \cong (2/7)\langle S^2_{\mathrm{A_3}}\rangle$ and $\langle G^2_{\mathrm{B}}\rangle \cong 2\langle S^2_{\mathrm{B}}\rangle$, while the values of $\Phi_{\mathrm{A_3B}}/\Phi_{\mathrm{B}}$ and $\Phi_{\mathrm{A_3B}}/\Phi_{\mathrm{A_3}}$ have been obtained from experimental data for star homopolymers with four and three branches. Roovers et al.[27] studied symmetric polystyrene stars in Θ solvent and found the ratio $\Phi_{f=4}/\Phi_{\mathrm{linear}}$ to be equal to 1.48. For good solvent, $\Phi_{f=4}/\Phi_{\mathrm{linear}}$ can be calculated to be 1.46. In the literature[22] are reported g' and g_{s} values for polystyrene and polybutadiene stars in good solvents which lead to $\Phi_{f=4}/\Phi_{\mathrm{linear}} = 1.50$. (From the simulation values in Table 3 and the Φ_{linear} previously obtained for linear chains,[20] we obtain $\Phi_{f=4}/\Phi_{\mathrm{linear}} = 1.49$.) The asymmetry correction coefficients to the ratios for the samples (PI)$_3$PS55, (PI)$_3$PS40, and (PI)$_3$PS35 are obtained as the mean values from Table 3 and are equal to 0.934, 0.870, and 0.802, respectively. Using the intrinsic viscosities of miktoarm stars from Table 1 and the ones calculated from eqs 12 and 13 for the homopolymer precursors, we obtain the following values of σ_G: 1.402 for $\rho = 2$, 1.350 for $\rho = 2.8$, and 1.402 for $\rho = 3.9$. For the same miktoarms, RG ($u^*_{\mathrm{A}} = {}^1/_{16}$, $u^*_{\mathrm{B}} = {}^1/_{16}$, $u^*_{\mathrm{AB}} = {}^1/_{16}$) predicts 1.316, 1.291, and 1.262, while the Monte Carlo simulations yield the values 1.342 ± 0.010, 1.340 ± 0.013, and 1.241 ± 0.017, respectively. It can be seen that RG predicts a continuous decrease of σ_G by increasing the length of the B branch since the B units are now placed far from the A ones while the MC shows a more gradual decrease of σ_G for values of $\rho > 2$. The experimental results show a decrease of 5% when ρ goes from 2 to 2.8, while the value of σ_G for the case of $\rho = 3.9$ can be explained by the uncertainties in the asymmetry correction coefficient, due to the important finite size effects associated with this case. All the σ_G values however are higher than those corresponding to A$_2$B miktoarm stars since the density of A units in the neighborhood of B ones is much higher. The other dimensionless ratios in Table 4 (expressing the relative expansions of the various parts of the miktoarm copolymers) are also of great importance in understanding the chain configuration though they cannot be directly evaluated from the present viscosity experimental data.

5. Conclusions

We have used intrinsic viscosity data to probe the conformation of A_2B and A_3B miktoarm star copolymers. The results depend on the assumption that $\gamma_{S_k} = \langle S^2_{k,A_xB_y}\rangle / \langle S^2_k \rangle \cong 1$ (k = A_x or B_y) and that estimates of Φ_{A_2B} and Φ_{A_3B}, made on the basis of lower bound Monte Carlo calculations, can be applied in order to convert hydrodynamic properties to static conformational properties. It is observed that the compact star architecture of these miktoarm copolymers leads to a more pronounced separation of the different types of arms. This is quantified by σ_G, which is equal to 1.24 for the A_2B and 1.35−1.40 for the A_3B copolymers. This compares to $\sigma_G = 1.1-1.2$ for typical diblock copolymers. The increase in σ_G for the miktoarm stars is supported by Monte Carlo and RG calculations.

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References and Notes

(1) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 2479.
(2) Iatrou, H.; Siakali-kioulafa, E.; Hadjichristidis, N.; Roovers, J.; Mays, J. *J. Polym. Sci., Polym. Phys.* **1995**, *33*, 1925.
(3) Tselikas, Y.; Hadjichristidis, N.; Iatrou, H.; Liang, K.; Mohanty, K.; Lohse, D. *J. Chem. Phys.*, submitted.
(4) Tsitsilianis, C.; Ghaumont, Ph.; Rempp, P. *Macromol. Chem.* **1990**, *191*, 2319.
(5) Milner, S.; Witten, T. *Macromolecules* **1992**, *25*, 5495.
(6) Tsitsilianis, C. *Macromolecules* **1993**, *26*, 2977.
(7) Olvera de la Cruz, M.; Sanchez, I. *Macromolecules* **1986**, *19*, 2501.
(8) Milner, S. *Macromolecules* **1994**, *27*, 2333.
(9) Floudas, G.; Hadjichristidis, N.; Iatrou, H.; Pakoula, T.; Fischer, E. *Macromolecules* **1994**, *27*, 7735.
(10) Hadjichristidis, N.; Iatrou, H.; Behal, S.; Chludzinski, J.; Disko, M.; Garner, R.; Liang, K.; Lohse, D.; Milner, S. *Macromolecules* **1993**, *26*, 5812.
(11) Vlahos, C.; Horta, A.; Freire, J. *Macromolecules* **1992**, *25*, 5974.
(12) Vlahos, C.; Horta, A.; Hadjichristidis, N.; Freire, J. *Macromolecules* **1995**, *28*, 1500.
(13) Prud'homme, J.; Roovers, J.; Bywater, S. *Eur. Polym. J.* **1972**, *8*, 901.
(14) Tanaka, T.; Omoto, M.; Inagaki, H. *J. Macromol. Sci., Phys.* **1980**, *B17* (2), 229.
(15) Benoit, H.; Froelich, D. *Light Scattering from Polymer Solutions*; Academic Press: New York, 1972.
(16) Hadjichristidis, N.; Roovers, J. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 851.
(17) Miyake, A.; Freed, K. *Macromolecules* **1984**, *17*, 678.
(18) Vlahos, C.; Horta, A.; Molina, L.; Freire, J. *Macromolecules* **1994**, *27*, 2726.
(19) Freire, J.; Rey, A. *Comput. Phys. Commun.* **1990**, *61*, 297. Fixman, M. *J. Chem. Phys.* **1983**, *78*, 1588.
(20) Freire, J.; Rey, A.; Bishop, M.; Clarke, J. *Macromolecules* **1991**, *24*, 6494.
(21) Fetters, L.; Hadjichristidis, N.; Lindner, J.; Mays, J. *J. Phys. Chem. Ref. Data* **1994**, *23*,619.
(22) Douglas, J.; Roovers, J.; Freed, K. *Macromolecules* **1990**, *23*, 4168.
(23) Tanaka, T.; Omoto, M.; Inagaki, H. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1979**, *20*, 9.
(24) Zimm, B. H. *Macromolecules* **1980**, *13*, 592.
(25) Khasat, R.; Pennisi, R.; Hadjichristidis, N.; Fetters, L. *Macromolecules* **1988**, *12*, 1100.
(26) Freed, K.; Wang, S. Q.; Roovers, J.; Douglas, J. *Macromolecules* **1988**, *21*, 2219.
(27) Roovers, J.; Bywater, S. *Macromolecules* **1972**, *5*, 384.

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