Effect of Architecture on the Micellization Properties of Block Copolymers: A_2B Miktoarm Stars vs AB Diblocks

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ABSTRACT: Light-scattering and viscometric results are presented from micellar solutions of $(PI)_2PS$ (I_2S) and $(PS)_2PI$ (S_2I) three-miktoarm stars and a PSPI (SI) diblock copolymer in *n*-decane. The influence of architecture on the micellization properties of simple graft copolymers is investigated by keeping the overall molecular weights and compositions of the samples constant. All samples formed spherical micelles in *n*-decane, a selective solvent for polyisoprene. Aggregation numbers were found to increase in the order $I_2S < S_2I <$ SI. Hydrodynamic radii of the micelles increased in the same order. The thickness of the corona is determined by the length of the soluble blocks, which they were found to be stretched to almost the same extent in all cases. The area of the core−corona interface per copolymer chain, A_c, depends on the architecture of the molecule, and it is larger in the case of I_2S micelles. In the case of S_2I, larger A_c values were found compared to the SI reference sample, indicating that the PS arms are arranged in different ways in the two kinds of micelles. The presence of only one grafted chain per molecule can change considerably the micellar characteristics of complex block copolymers. A simple scaling theory is developed taking into account the free energy contributions from the core, the corona, and the interfacial region of the micelle in the different cases. Theoretical predictions agree qualitatively with the experimental results.

Introduction

Block copolymers can self-assemble into micelles if they are dissolved in a selective solvent, i.e., a thermodynamically good solvent for one of the blocks and a precipitant for the other. The micellization of block copolymers obeys the model of closed association characterized by an equilibrium between molecular dissolved unimers (free chains) and well-defined micelles.[1] The stability, the narrow size distribution, and, especially, the core−shell microstructure of the micelles make them important materials in the fields of colloid stabilization, drug delivery, coating, and microreactors applications.

The structural parameters of the micelles (overall size, core and shell dimensions, and microstructure) and their fundamental properties such as aggregation number are influenced by many factors such as chemical nature and molecular weight of the blocks, solvent−block interactions, concentration, temperature, and architecture of the copolymer. The last factor is the least studied so far since most experimental studies involve linear block copolymers.[1−8] Due to advances in polymer synthesis, well-defined copolymers with complex architectures were prepared and their micellization properties have been investigated in several cases.[9−16] However much experimental work is still needed in order to elucidate the influence of architecture on the fundamental parameters of the micelles and on the micellization process in general. Such studies will help in the understanding of the fundamental principles governing the organization of block copolymers into micelles, which in turn will provide guidelines for designing polymer molecules for specific applications.

In this paper, we report results on the micellization properties of two carefully synthesized simple graft copolymers of the types $(PI)_2PS$ (I_2S) and $(PS)_2PI$ (S_2I). These results are compared with data on a linear PSPI (SI) diblock copolymer. All samples have the same composition and overall molecular weights. The PI arm of I_2S has approximately half the molecular weight of the PI block in the diblock, whereas an analogous relation holds for the molecular weights of the PS arm of S_2I and the PS block of SI. In this way, conclusions about the influence of architecture on the micellizing properties are more straightforward, and some understanding of the fundamental laws that govern micelle formation can be gained. Differences in fundamental properties of the micelles formed in *n*-decane, a selective solvent for the PI part of the molecules, are discussed. Finally a simple scaling theory is developed in order to explain the differences in micelle formation between A_2B, AB_2 and AB copolymers.

Experimental Section

Polymer Synthesis: All samples were synthesized by anionic polymerization high vacuum techniques. The diblock sample was synthesized by sequential polymerization of the two monomers. Styrene was first polymerized by *sec*-BuLi followed by the addition of isoprene and deactivation with degassed methanol. The A_2B miktoarm stars were prepared by reaction of the single arm with an excess of CH_3SiCl_3 to produce the difunctional chlorosilane end-capped macromolecular agent. After removal of the CH_3SiCl_3 excess on the vacuum line, a stoichiometric excess of the second arms was added. When the coupling reaction was completed, the excess double arm was deactivated with methanol. The desired A_2B three-arm star was isolated from the reaction mixture by solvent/nonsolvent fractionation. The fractionated final products (pure miktoarm stars) were rigorously characterized by size exclusion chromatography with RI and UV detection, membrane osmometry, LALLS, and ^1H NMR in order to provide the molecular characteristics of the materials. These measurements confirmed the high degree of compositional,

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Table 1. Molecular Characteristics of Block Copolymers

sample	$M_{w,cop}$[a] $\times 10^{-4}$	$M_{n,cop}$[b] $\times 10^{-4}$	M_w/M_n[c]	A_2[a] $\times 10^4$	$M_{n,PS}$[b] $\times 10^{-4}$	$M_{n,PI}$[b] $\times 10^{-4}$	wt % PS[d]
I_2S	9.20	8.25	1.05	7.6	4.44	2.13	49
S_2I	9.30	8.61	1.06	8.4	2.24	4.77	48
SI	9.87	9.49	1.05	7.1	4.71	4.78	50

[a] By LALLS in THF at 25 °C. [b] By membrane osmometry in toluene at 35 °C. [c] By SEC in THF at 40 °C. [d] By ^{1}H NMR in $CDCl_3$.

molecular weight and architectural homogeneity of the copolymers. Details on the synthesis and the molecular characterization of the miktoarm stars were given elsewhere.[17-19] The molecular characteristics of the samples under study are given in Table 1. All samples have approximately the same overall molecular weight and composition, the differences being within the reproducibility of the polymerization technique. Sample SI is a linear diblock copolymer where sample S_2I has two PS arms with half the molecular weight of the PS block of SI and a PI arm with molecular weight similar to that of the PI block of SI. On the other hand, sample I_2S has two PI arms with almost half the molecular weight of the PI block in SI and one PS arm with molecular weight close to that of the PS block of sample SI.

Solvent Purification and Solution Preparation. Analytical grade *n*-decane was dried over CaH_2 by reflux for 24 h and was fractionally distilled just before use. Stock solutions were prepared by dissolving a weighed amount of sample in the appropriate volume of dried solvent with occasional stirring. All the samples were dissolved in *n*-decane after 24 h. The stock solutions were heated at 60 °C for 2 h before the measurements to ensure complete dissolution of the samples and removal of possible memory effects. Stock solutions had the characteristic bluish tint related to the presence of micelles. No polymer precipitation was observed from these solutions after standing at room temperature for several weeks. Solutions of lower concentration were obtained by subsequent dilution of the stock solutions. Before light scattering measurements the solutions were filtered through 0.45 μm nylon filters where for viscosity measurements 1.2 μm nylon filters were used.

Methods. Initial light scattering measurements were performed at 25 °C with a Chromatix KMX-6 low-angle laser-light-scattering photometer, equipped with a 2 mW He–Ne laser operating at $\lambda = 633$ nm. Apparent weight-average molecular weights, M_w, and second virial coefficients, A_2, were obtained from the concentration dependence of the reduced scattering intensity, at high concentrations. Multiangle light scattering measurements were conducted with a Series 4700 Malvern system composed of a PCS5101 goniometer with a PCS7 stepper motor controller, a Cyonics variable power Ar^+ laser, operating at 488 nm and with 10 mW power, a PCS8 temperature control unit, and a RR98 pump/filtering unit. Apparent mean square radii of gyration, R_g, were determined by the initial slope of the angular dependence of the reduced scattering intensity measured at angles between 30 and 135°. Toluene, dried over CaH_2 and fractionally distilled, was used as a calibration standard. The general equation for light scattering was used in this case

$$Kc/\Delta R_\theta = 1/M_w\{1+[(16\pi^2 n_o^2)/(3\lambda_o^2)]\langle R_g^2\rangle \sin^2(\theta/2)\} + 2A_2c + ... \quad (1)$$

where $K = (2\pi n_o)^2(dn/dc)^2(N_A\lambda_o^4)^{-1}$, c is the polymer concentration, ΔR_θ is the excess Rayleigh ratio, θ is the scattering angle, n_o is the solvent refractive index, λ_o is the wavelength of light in a vacuum, dn/dc is the specific refractive index increment, and N_A is the Avogadro number.

Dynamic light scattering experiments were carried out, at 25 °C, on the same Malvern system operating in the dynamic mode. A 192 channel correlator was used for accumulation of the data. Correlation functions were analyzed by the cumulant method and the Contin software provided by the manufacturer.

Table 2. Static Light Scattering Results from *n*-Decane Solutions at 25 °C

sample	$M_{w,mic} \times 10^{-6}$	$A_2 \times 10^6$	N_w	R_g (nm)
I_2S	6.11	6.2	66	21.5
S_2I	12.1	3.2	130	20.9
SI	24.0	2.1	243	24.2

Estimated errors: M_w about 10%; R_g about 15%.

The correlation function was collected at angles between 45 and 135°. There was no indication of the presence of unimers from Contin analysis at the concentration range studied for each sample. In this region the equilibrium is shifted in favor of the micelles and the properties measured correspond to those of the micelles. Static light scattering plots are linear in the same concentration range. The ratio μ_2/Γ^2, where μ_2 is the second cumulant and Γ the decay rate of the correlation function, derived from cumulant analysis was <0.1 for all angles and concentrations indicating the low polydispersity of the micelles. Apparent diffusion coefficients at zero concentration, $D_{o,app}$, were obtained after extrapolation to zero angle by the use of eq 2, where D_{app} is the diffusion coefficient

$$D_{app} = D_{o,\,app}(1 + k_Dc) \quad (2)$$

measured at each concentration and k_D the coefficient at the concentration dependence of D_{app}. Apparent hydrodynamic radii, R_h, were determined by eq 3, where k_B is the Boltzmann

$$R_h = k_BT/6\pi\eta_oD_{o,app} \quad (3)$$

constant, T the absolute temperature, and η_o the viscosity of the solvent.

For the viscosity measurements, Cannon–Ubbelohde dilution viscometers were used in a temperature controlled bath ($\Theta = 25 \pm 0.02$ °C). Flow times for the solvent and the micellar solutions were measured with a Scott-Gerate AVS 410 automatic flow timer. Data were analyzed by means of the Huggins (eq 4) and Kraemer (eq 5) equations, where $[\eta]$ is the intrinsic

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2c + ... \quad (4)$$

$$\ln \eta_r/c = [\eta] + k_K[\eta]^2c + ... \quad (5)$$

viscosity and k_H and k_K the Huggins and Kraemer coefficients, respectively. Viscometric equivalent sphere radii, R_v, were calculated from eq 6, where $M_{w,app}$ is the weight-average

$$R_v = (3/10\pi N_A)^{1/3}([\eta]M_{w,app})^{1/3} \quad (6)$$

molecular weight determined by light scattering by extrapolation at zero concentration.

Results and Discussion

Experiment. The results from the static light scattering measurements are given in Table 2. A representative plot for the concentration dependence of reduced scattering intensity of sample I_2S in *n*-decane is shown in Figure 1. All light-scattering plots have the same U-like shape, characteristic of micellizing systems that follow the model of closed association.[1] There is no evidence for the existence of a critical micelle concentration in the concentration range (10^{-6}–10^{-3} g mL^{-1}) used in the experiments. As has been observed for similar systems, cmc must be very low and must be outside the accessible concentration window. The region of micelles–unimers coexistence is seen at the lowest concentration region studied. Apparent weight-average molecular weights of the micelles, which must be close to the true ones due to the high degree of molecular uniformity of the samples and the high dn/dc values, were determined from the linear parts of the plots at

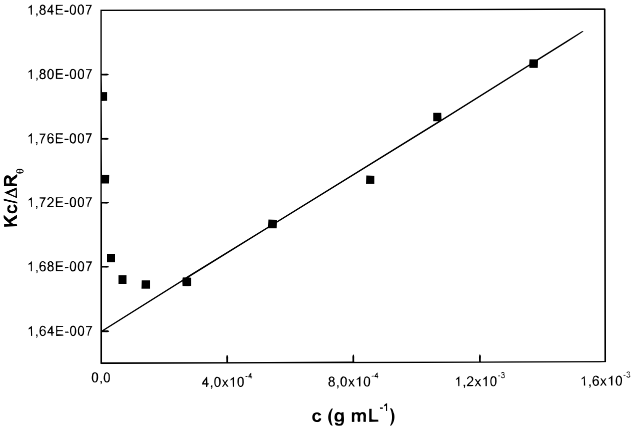

Figure 1. $Kc/\Delta R_\theta$ vs concentration for sample I_2S in *n*-decane at 25 °C.

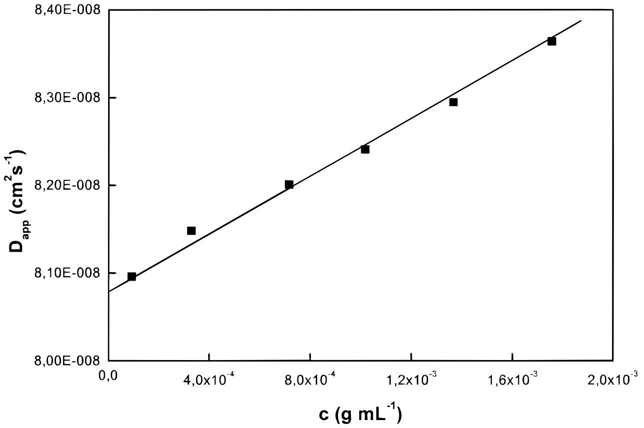

Figure 2. Concentration dependence of apparent diffusion coefficient for sample I_2S in *n*-decane at 25 °C.

Table 3. Dynamic Light Scattering Results from *n*-Decane Solutions at 25 °C

sample	D (cm^2/s) × 10^8	k_D	R_h (nm)
I_2S	8.09	19	31.3
S_2I	5.87	29	43.1
SI	5.54	~0	45.7

the highest concentrations. Obviously all the samples form micelles of high molecular weight. The values for the second virial coefficient are much smaller than the ones determined for the unimers in a good solvent (Table 1) due to the worsening of the thermodynamic quality of the micellizing solvent and also the high molecular weight and the branched nature of the micelles. A_2 values in *n*-decane decrease as the molecular weight of the micelles increases as expected. The weight-average aggregation number, N_w, decreases in the order SI > S_2I > I_2S. The micelles of the two miktoarm stars have approximately equal apparent radii of gyration, despite their differences in aggregation number, whereas R_g for the diblock is slightly larger. R_g is sensitive to the density profile of the micelle, because it also depends on the absolute value of the density in the micellar core and corona.

The results from dynamic light scattering are given in Table 3 and a representative plot of the concentration dependence of the diffusion coefficient is shown in Figure 2. $D_{o,app}$ values are very low as expected for high molecular weight slowly diffusing species. The corresponding values of the hydrodynamic radii are similar for samples S_2I and SI. R_h for I_2S micelles is considerably lower. The values for k_D are rather low and show no definite trend with molecular weight of the micelles. The interplay between thermodynamic and hydrodynamic factors, which both influence k_D, in these systems seems to be rather complex and difficult to interpret.

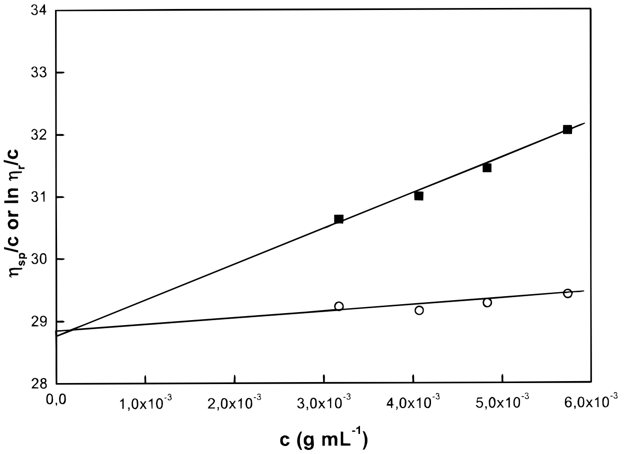

Figure 3. η_{sp}/c (■) and ln η_r/c (○) vs concentration plots for sample S_2I in *n*-decane at 25 °C.

Table 4. Viscometric Results from *n*-Decane Solutions at 25 °C

sample	[η] (mL/g)	k_H	R_v (nm)
I_2S	22.0	0.62	27.7
S_2I	28.8	0.67	38.1
SI	27.1	1.2	46.9

Dilute solution viscometric results for the micelles of the samples under study are presented in Table 4 and the corresponding plots for sample S_2I are given in Figure 3. [η] values are low compared to the high molecular weight of the micelles. This illustrates the compact structure of the micelles formed in each case. Again [η] values for SI and S_2I are close where the value for I_2S is smaller. This correlates well with the smaller hydrodynamic radius obtained from dynamic light scattering for this sample. However the k_H values for the miktoarm samples are close whereas for the diblock k_H is very high and higher than the one expected for hard spheres ($k_H \cong 0.99$). Presumably hydrodynamic interactions are larger in the case of diblock micellar solutions. This result can also be seen as evidence of greater compactness for the SI micelles. This interaction is mediated through the PI corona blocks and it must be related to the way corona blocks are grafted on the micellar core and also to their length. The calculated viscometric radii increase in the order I_2S < S_2I < SI which agrees with the trend in R_h values.

The experimental evidence clearly show that both A_2B miktoarm stars and diblock copolymer form multimolecular micelles in *n*-decane a selective solvent for the PI part of the molecules. The micelles of the diblock incorporate the greatest number of unimers whereas the micelles of the miktoarm star with two soluble arms have the lowest association number. The micelles of the sample with two insoluble arms have an intermediate aggregation number. Interestingly there seems to be a relation between N_w for the samples under investigation: $N_{w,SI} \cong 2N_{w,S_2I} \cong 4N_{w,I_2S}$. Generally the dependence of aggregation number on the length of the insoluble block is stronger than the dependence on the length of the soluble block.[1,20] However an interpretation based on the effects of molecular weights of the soluble and

Table 5. Experimentally Determined Ratios of the Different Radii for the Micelles of Block Copolymers in *n*-Decane

sample	R_g/R_h	R_v/R_h
I_2S	0.69	1.12
S_2I	0.49	0.88
SI	0.53	1.03

Table 6. Geometrical Characteristics of the Micelles of Block Copolymers Formed in *n*-Decane

sample	R_{core} (nm)	W_{corona} (nm)	A_c (nm^2)	A_c/n (nm^2)	$\langle r^2\rangle_o^{1/2}$ PI arm[a] (nm)	$R_{corona}/\langle r^2\rangle_o^{1/2}$
I_2S	10.4	20.9	20.6	10.3	11.2	1.9
S_2I	12.8	30.3	15.8	15.8	16.6	1.8
SI	16.5	29.2	14.1	14.1	16.9	1.7

[a] Calculated from data of ref 25.

insoluble parts is not directly applicable in our case, due to the complexity of the architecture. From this rather naive point of view, one might have expected that the I_2S micelles would contain more copolymer chains than those of S_2I. Clearly this is not the case. Some other factors influencing the micelle formation must also be active.

To get some information on the shape of the micelles of these copolymers the ratios R_g/R_h and R_v/R_h have been calculated (Table 5). The ratio R_g/R_h is sensitive to the density profile of the dissolved species across the radius of the particle. It acquires a value of 0.775 for hard spheres.[21] Its experimental values for flexible polymers have been found in the range 1.1−1.3,[21,22] whereas smaller values ($R_g/R_h \geq 0.55$) have been reported for spherical gels.[23,24] The ratios R_g/R_h for all the samples are characteristic for spherical structures, with that of I_2S being closer to the theoretical value for hard spheres. A more complex decreasing density profile across the micelles' radii must be assumed in order to better represent the calculated results for samples S_2I and SI.[23] The ratios R_v/R_h are close to unity (within experimental error) for the three samples studied, a value calculated for hard spheres,[21] but values around unity have also been observed for linear coils.[21,22] The examination of the radii data allows us to conclude safely that the micelles formed by the copolymers have a more or less spherical shape.

Hydrodynamic radii are closer to the actual radius of a spherical object in solution. R_h and R_v values for micelles of S_2I and SI are close but larger than those of I_2S micelles. From the data on hydrodynamic and viscometric radii, it is apparent that the overall dimensions of the micelles are controlled primarily by the length of the soluble block. The radius of the PS core in spherical micelles can be calculated by eq 7, where

$$R_c = (3M_{w,mic}\mathrm{wt}_{PS}/4\pi N_A d_{PS}\phi_{PS})^{1/3} \qquad (7)$$

$M_{w,mic}$ is the apparent weight-average molecular weight of the micelles determined by light scattering, wt_{PS} is the weight fraction of PS in the copolymer, N_A the Avogadro number, d_{PS} the density of PS, and ϕ_{PS} the volume fraction of PS in the core of the micelle, which in the case of PS in *n*-decane can be assumed to be equal to 1 (the case of a dry PS core).

The difference $W_{corona} = R_h - R_c$ is a measure of the PI corona thickness in the micelles. Additionally the core area per copolymer chain (or per junction point) can be calculated by

$$A_c = 4\pi R_c^{\,2}/N_w \qquad (8)$$

The calculated geometrical characteristics for the micelles of miktoarm star and diblock copolymers are given in Table 6. Also in this table are given the values of the area per copolymer chain divided by the number, n, of soluble PI blocks per junction point and the unperturbed end-to-end distance for linear PI chains of the same molecular weight as the corresponding blocks of the copolymers, in dioxane (a Θ solvent for PI).[25] It can be seen that the core radius increases in the order $I_2S < S_2I <$ SI in parallel to the increase of the aggregation number. The corona thickness depends on the length of the PI block, and it is lower for I_2S. The corona thicknesses for S_2I and SI are similar as a result of the similar molecular weights of the PI blocks in these samples. The area per copolymer chain is larger in the case of I_2S and lower for SI. This may be attributed to the presence of two PI chains per junction point in I_2S. The difference for this parameter between S_2I and SI is not so large. However, it exists, and this implies that the position of the PI block plays some role in the way that the PS arms of the S_2I miktoarm organize themselves in the micellar core. Apparently, due to crowding around the junction point a somewhat larger area on the core−corona interface is required to accommodate the two PS arms of S_2I, in a relaxed conformation, in contrast to the single PS block in SI micelles. The differences in area per junction may be related to the lower k_H values obtained for the miktoarm star micelles (smaller hydrodynamic interactions in the corona blocks). Since both A_2B copolymer micelles exhibit a larger area per junction point this results in a less dense corona than in the SI copolymer micelles, i.e., softer spheres.

If A_c is divided by the number of soluble arms per junction point the area per soluble block, obtained in this way, increases in the order $I_2S <$ SI $< S_2I$, which is reasonable if one takes into account the lower molecular weight of the PI arms in I_2S. In an analogous way the two PI arms of I_2S need more space on the core−corona interface to relax some of the stretching coming from their confinement in the coronal zone. In other words the presence of two soluble arms on the junction point favors the bending of the core−corona interface toward the core and stabilizes in this way a smaller micelle.

The ratio of the corona thickness to the unperturbed end-to-end distance is a measure of the stretching of the PI chains due to their confinement in the corona. From the values of the ratio $R_{corona}/\langle r_o^2\rangle^{1/2}$ in Table 6, it can be seen that in all cases the PI blocks are stretched and they acquire dimensions almost twice of that of their unperturbed ones. The PI arms of I_2S seems to be a bit more stretched whereas the PI blocks of SI are the less perturbed chains, but differences are not significant.

Scaling Theory. In this section we present simple scaling estimations to explain the decrease of aggregation number of miktoarm star micelles with respect to the aggregation number of diblock copolymer ones. In the present paper we use equilibrium scaling theory to describe the spherical micelle formation in the solution of miktoarm block copolymers. We assume that the system under consideration attains its equilibrium state and quenching effect (leading to the decrease of aggregation number of the micelles) is small in comparison to the case of block copolymers in the melt reported by

Hashimoto et al.[26a] According to Flory's mean field theory,[26b] the free energy of the micelles in a selective solvent can be written as a sum of three terms

$$F = F_{\text{int}} + F_{\text{core}} + F_{\text{corona}} \tag{9}$$

where F_{int} is the surface energy of core–corona interface, F_{core} is the elastic energy of the stretching of insoluble blocks forming the core of the micelle, and F_{corona} is the energy of the soluble blocks in the corona region of the micelle. Let us consider first the case of diblock copolymer micelles. Apart from the numerical factor the surface energy in eq 9 has the form

$$F_{\text{int}} \cong \gamma R^2 \tag{10}$$

where we denote as γ the tension coefficient of the interface and R is the radius of the core of the micelle. We assume that for PS in *n*-decane, the volume fraction of PS monomer units in the core is close to unity and dense packing condition

$$R^3 \cong v_1 M_1 N \tag{11}$$

gives the dependence of R on aggregation number N of the micelle and degree of polymerization M_1 of PS block. Here v_1 is the excluded volume of PS monomer units. The elastic energy of the blocks in the core can be estimated as[26]

$$F_{\text{core}} \cong k_B T N \frac{R^2}{a_1 l_1 M_1} \tag{12}$$

where a_1 and l_1 are the linear size of monomer units and the persistence length of PS blocks, respectively, T is the absolute temperature, and k_B is the Boltzmann constant. The stretching of the soluble PI blocks in the corona is caused by excluded volume interactions of monomer units of PI blocks in good solvent and the free energy of the corona in mean-field approximation can be written as a sum of elastic and osmotic terms:

$$\frac{F_{\text{corona}}}{k_{\text{B}} T} \cong N\left(\frac{L^2}{a_2 l_2 M_2} + B M_2 \phi\right) \tag{13}$$

Here L is the end-to-end distance of PI blocks; B is the dimensionless second virial coefficient, $0 < B < 1$, and the volume fraction of PI monomer units is written as

$$\phi = \frac{v_2 M_2 N}{(L + R)^3 - R^3} \tag{14}$$

Index 2 in eqs 13 and 14 denotes corresponding magnitudes for PI blocks. The resulting free energy F_{corona} as a function of N can be obtained by minimization of eq 13 with respect to L:

$$\frac{F_{\text{corona}}}{k_{\text{B}} T} = N^{7/5} B^{2/5} M_2^{\ 1/5} \xi_2^{\ 1/5}, \ \xi_2 = \frac{v_2^{\ 2}}{a_2^{\ 3} l_2^{\ 3}} \tag{15}$$

where we take into account condition $L > R$. The soluble blocks are much more stretched than insoluble ones, and the above unequality is equivalent to $M_2 > M_1^{5/9} N^{2/9}$ which is always valid for the equation considered in this paper case: $M_2 > M_1$.

So, to calculate the aggregation number N of the micelle formed by diblock copolymer chains we have to minimize free energy (eq 9), which is done by eqs 10–12 and 15, per one chain, F/N, with respect to N.

In parallel with the free energy of linear copolymer micelles, the free energy of S_2I and I_2S miktoarm micelles can be easily calculated introducing the following renormalizations for the parameters N, M_1, and M_2. If insoluble PS blocks have $f = 2$ arms and the number of monomer units per each arm is M_1/f, we have to perform the substitutions $N \rightarrow fN$ and $M_1 \rightarrow M_1/f$ in eq 12. In the case of I_2S miktoarm micelles, the renormalization $N \rightarrow fN$ and $M_2 \rightarrow M_2/f$ should be done as in eq 15. Finally, free energies of the micelles of different copolymers have the form

$$\text{SI:}\ \ \frac{F}{N k_{\text{B}} T} = B\left(\frac{\xi_1}{\xi_2} M_1 M_2\right)^{1/2}\left(n^{2/3} + n^{2/5} + \frac{\alpha}{n^{1/3}}\right)$$

$$\text{S}_2\text{I:}\ \ \frac{F}{N k_{\text{B}} T} = B\left(\frac{\xi_1}{\xi_2} M_1 M_2\right)^{1/2}\left(f^2 n^{2/3} + n^{2/5} + \frac{\alpha}{n^{1/3}}\right)$$

$$\text{SI}_2\text{:}\ \ \frac{F}{N k_{\text{B}} T} = B\left(\frac{\xi_1}{\xi_2} M_1 M_2\right)^{1/2}\left(n^{2/3} + f^{6/5} n^{2/5} + \frac{\alpha}{n^{1/3}}\right) \tag{16}$$

$$\alpha = \frac{\gamma \nu_2^{\ 2/3}}{k_{\text{B}} T B^{3/2}} \frac{1}{(M_1^{\ 3} M_2)^{1/4}} \left(\frac{\xi_2^{\ 11/3}}{\xi_1^{\ 3}}\right)^{1/4},$$

$$N = n B^{3/2} M_1^{\ 3/4} M_2^{\ 5/4} \frac{\xi_1^{\ 3/4}}{\xi_2^{\ 5/4}}$$

Here we introduce the dimensionless parameter α, which is proportional to the tension coefficient, γ, and normalized aggregation number, n. In our case $\gamma v_2^{2/3} \sim k_{\text{B}} T$; B, ξ_1, $\xi_2 \sim 1$; $M_1 \sim M_2$, and parameter $\alpha \sim 1/M_1$ is much smaller than unity. As a consequence of performed renormalizations for aggregation number and degrees of polymerization of the blocks, the difference between free energies, eq 16, of various copolymers appears to be only due to the parameter f. Since the ratios of aggregation numbers of the micelles of different copolymers, $N_{\text{SI}}/N_{\text{I}_2\text{S}}$ and $N_{\text{SI}}/N_{\text{S}_2\text{I}}$, are equal to the corresponding ratios of normalized numbers n, we can plot them as a universal function of parameter α. One can see in Figure 4 that the aggregation number of the micelles formed by linear copolymer is always larger than the aggregation number of S_2I miktoarm micelles (lower curve) and I_2S miktoarm micelles (upper curve): the values of the ratios of aggregation numbers are larger than unity. The upper curve never crosses the lower one which means that $N_{\text{I}_2\text{S}} < N_{\text{S}_2\text{I}} < N_{\text{IS}}$. The physical reason for this relation between aggregation numbers of different copolymers is the following. With the increase of the number of arms of both soluble and insoluble blocks, their elastic energy per molecule is increased. In this case, it becomes rather unfavorable for the micelle to have the same aggregation number as for the linear case and if a fixed gain in aggregation energy has to be compensated, the aggregation number of the micelle should be decreased. Comparing elastic contributions, eqs 12 and 15, in the free energy of the micelle, eq 9, we can see that the energy of the soluble blocks, F_{corona}, exceeds the energy of the insoluble blocks, F_{core}, due to a stronger stretching of the soluble blocks. Therefore, the increase of the elastic energy of the corona's blocks in I_2S micelles is larger than the one for the core's blocks

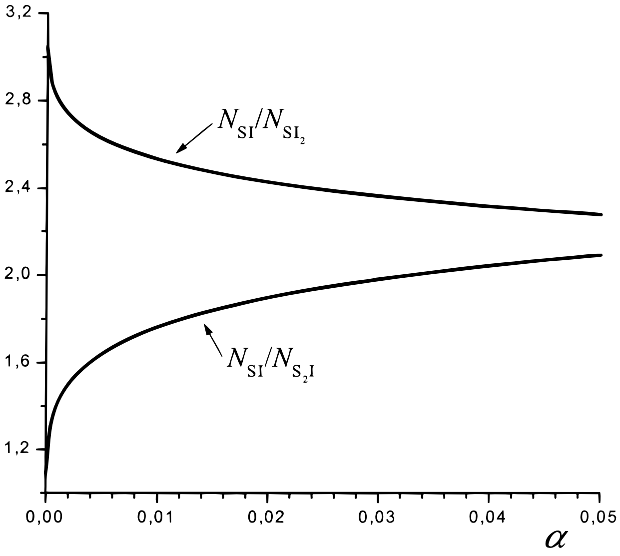

Figure 4. Dependence of the ratios of aggregation numbers of the micelles formed by linear SI (N_{SI}), S$_2$I miktoarm (N_{S_2I}), and I$_2$S miktoarm (N_{I_2S}) copolymers on parameter *a*.

in S$_2$I micelles. As a result, the aggregation number of I$_2$S micelles becomes smaller than aggregation number of S$_2$I micelles.

Conclusions

The two miktoarm stars, I$_2$S and S$_2$I, were found to have different micellization properties than the linear SI diblock copolymer of the same molecular weight and composition in many aspects. The aggregation number increased in the order I$_2$S < S$_2$I < SI. Hydrodynamic radii of the micelles determined by dynamic light scattering and viscometry follow the trend in aggregation number. The values for the ratios R_g/R_h and R_v/R_h indicate that the micelles formed in *n*-decane are spherical. The area per copolymer chain, calculated for the case of a dry PS core, is larger in the case of I$_2$S, as a consequence of the existence of two PI arms per junction point and it is the lowest for the SI case. Presumably in the case of S$_2$I and SI micelles, although the PS arms form the core, there may be some difference in the structure of the interfacial core−corona regions, originating from the different topology around the junction point. The micellar corona dimensions correspond, in all cases, to chain dimensions almost twice as large as the unperturbed end-to-end distance. The experimental findings lead to the conclusion that coronal chain stretching and chain topology around the junction point are important factors that determine micellar size. In a reverse way of thinking, micellar size can be regulated through macromolecular architecture.

The developed simple scaling theory describes qualitatively correctly the experimentally obtained relation between aggregation numbers of micelles formed by different miktoarm copolymers and linear diblock.

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