

ORIGINAL ARTICLE

Micellization behavior of model asymmetric miktoarm star copolymers of the AA'B type, where A is polyisoprene and B is polystyrene

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Model asymmetric miktoarm star copolymers of the type AA'B, where A and A' are polyisoprenes (PIs) and B is deuterated polystyrene (PS), were synthesized by anionic polymerization high-vacuum techniques. Their micellization behavior was studied in *n*-decane, a selective solvent for the PI blocks, and *N,N*-dimethylacetamide (DMA), selective for the PS blocks. Utilizing static and dynamic light-scattering techniques along with dilute solution viscometry, parameters such as the aggregation number, N_w , the hydrodynamic and viscometric radii were determined. Based on these results, structural parameters of the micelles, that is, core and corona radii, as well as core-corona interfacial area, were calculated. The thermal stability of the micelles was also examined in both selective solvents. The macromolecular architecture was found to have a considerable effect on the micellization behavior of the block copolymers.

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INTRODUCTION

One of the most intriguing features of block copolymers is their ability to self-assemble either in bulk or in selective solvents.^{1,2} In bulk, the immiscibility of the constituent blocks leads to microphase separation with the formation of long-range ordered structures, such as cubic arrays, cylinders, bicontinuous phases and lamellae, with sizes comparable to the chain dimensions.^{3,4} In a selective solvent, that is, a thermodynamically good solvent for the one block and precipitant for the other, block copolymers associate and form micellar aggregates, which resemble the micelles obtained from low-molecular-weight surfactants.^{5–8} From a morphological point of view, block copolymer micelles consist of a more or less swollen core of the insoluble blocks surrounded by a corona formed by the soluble blocks. Because of their stability, variety of sizes and core-shell structure, micelles can be used in diverse practical applications, such as colloidal stabilization,^{9,10} latex technology,¹¹ compatibilization in polymer blends,¹² controlled drug delivery,^{13–16} water purification,^{17,18} viscosity and surface modification^{19–22} and so on.

Many studies, both experimental^{23–27} and theoretical,^{28–34} have been devoted to the study of micellar and associating structural parameters (critical micelle concentration, aggregation number, overall micellar size and core and shell dimensions), as well as the kinetics and thermodynamics of micellization. A combination of several experimental techniques is required to explore these parameters.^{35–43} The most important techniques include scattering techniques (static and dynamic light scattering (DLS), neutron

scattering and small-angle X-ray scattering), but other methods such as membrane osmometry, dilute solution viscometry, electron microscopy, nuclear magnetic resonance spectroscopy, sedimentation velocity, fluorescence techniques and size exclusion chromatography have also been used. Micellization is a dynamic procedure and thus can be influenced by many factors, for example, chemical nature, composition and molecular weight of the blocks, solvent quality, pH, concentration, temperature^{44,45} and so on.

An enormous number of studies has been conducted using di- and triblock copolymers.^{46,47} However, recent advances in synthetic polymer chemistry^{48–68} have enabled the preparation of various well-defined complex macromolecular topologies, stimulating efforts to link polymer architecture and supramolecular assembly of copolymers in selective solvents. From these reports, the macromolecular architecture has been emerged as a very important parameter for the manipulation of micellar properties, thereby providing a new tool for tuning of micellization behavior and designing materials with specific applications. As a result, tapered copolymers,⁶⁹ star-block,⁷⁰ linear-dendritic,⁷¹ cyclic⁷² and miktoarm stars of the type A_nB_m ,^{73–78} A_2B ,⁷⁹ A_3B ,⁸⁰ graft,^{81–85} H-, super H-, π -shaped^{86–89} and more complex brush-like copolymers have been studied in selective solvents, confirming the tremendous impact of macromolecular architecture on micellization properties.

In the present work, the micellization behavior in *n*-decane (selective solvent for polyisoprene (PI)) and *N,N*-dimethylacetamide (DMA; selective solvent for polystyrene (PS)) was studied for

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asymmetric miktoarm star copolymers consisting of a deuterated PS arm and two PI arms having different molecular weights (Scheme 1). The synthesis of these materials was previously published using the chlorosilane methodology and anionic polymerization high-vacuum techniques.^{90–92} The ultimate goal of this study was to compare the experimental results with those reported for PS-*b*-PI diblock copolymers and PS(PI)₂ symmetric miktoarm stars.

EXPERIMENTAL PROCEDURE

Polymer synthesis

All the samples were synthesized by anionic polymerization high-vacuum techniques^{93,94} using the chlorosilane methodology. The detailed procedure has been described in a previous publication.⁹⁵

Preparation of the micellar solutions

n-Decane (analytical grade; Aldrich, Steinheim, Germany), the selective solvent for the PI blocks, was dried in CaH₂ by refluxing for at least 24 h and was fractionally distilled just before use. For each sample, a stock solution was prepared by dissolving a weighed amount of polymer in the desired amount of selective solvent. To facilitate the dissolution and destroy the thermal history of the samples, the solutions were heated at 60 °C for 4–8 h. No precipitation or other visible change was observed after leaving the solutions at room temperature for several weeks. Solutions of lower concentrations were obtained by dilution of the stock solution. Before conducting the measurements, the solutions were filtered through 0.45 µm nylon filters.

DMA, the selective solvent for the PS block, was also dried over CaH₂ and distilled before its use. A stock solution was prepared by dissolving a weighed amount of polymer in the desired amount of DMA. After dissolution, the solutions were heated at 60 °C for 4–8 h to achieve equilibrium structures. The characteristic blue tint, indicating micelle formation, gradually developed. The solutions were stable and no polymer precipitation was observed.

Size exclusion chromatography analysis in both selective solvents revealed that no degradation or cross-linking took place after the thermal treatment for all samples.

Methods of micellar characterization

Static light-scattering measurements were performed with a Chromatix (Riviera Beach, FL, USA) KMX-6 low-angle laser light scattering (LALLS) photometer at 25 °C equipped with a 2-mW He–Ne laser operating at λ = 633 nm. The Equation (1) describing the concentration dependence of the reduced intensity is as follows:

$$\frac{Kc}{\Delta R_0} = \frac{1}{M_w} + 2A_2c + \dots \quad (1)$$

where *K* is a combination of optical and physical constants, including the refractive index increment, *dn/dc*, and the excess Rayleigh ratio of the solution over that of the solvent, Δ*R*₀.

Refractive index increments, *dn/dc*, at 25 °C were measured with a Chromatix KMX-16 refractometer operating at 633 nm and calibrated with aqueous NaCl solutions.

DLS measurements were conducted with a Series 4700 Malvern Instruments (Spring Lane South, Malvern, UK) composed of a PCS5101 goniometer with a PCS stepper motor controller, a Cyonics variable power Ar⁺ laser, operating at 488 nm, a PCS8 temperature control unit, a RR98 pump/filtering unit and a 192 channel correlator for accumulation of the data (Malvern Instruments). The correlation functions were analyzed by the cumulant method and the CONTIN software (Malvern Instruments). Measurements were carried out at 45, 90 and 135°. The angular dependence of the ratio Γ/*q*², where Γ is the decay rate of the correlation function and *q* is the scattering vector, was negligible for the micellar solutions. Therefore, the measurements conducted at 90° were used. Measurements were conducted starting from 25° and heating gradually with increments of 5° up to 55 °C. After each heating step, the solution was allowed to equilibrate for 15 min. The apparent translational diffusion coefficients at zero concentration *D*_{0,app} were measured using the Equation (2):

$$D_{app} = D_{0,app}(1 + k_D c) \quad (2)$$

where *k*_D is the coefficient of the concentration dependence of the diffusion coefficient. Apparent hydrodynamic radii at infinite dilutions, *R*_h, were calculated with the aid of the Stokes–Einstein (Equation (3)):

$$R_h = kT / 6\pi\eta_s D_{0,app} \quad (3)$$

where *k* is the Boltzmann's constant, *T* is the absolute temperature and η_s is the viscosity of the solvent.

Viscometric data were analyzed according to the Huggins equation:

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

as well as the Kraemer equation:

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

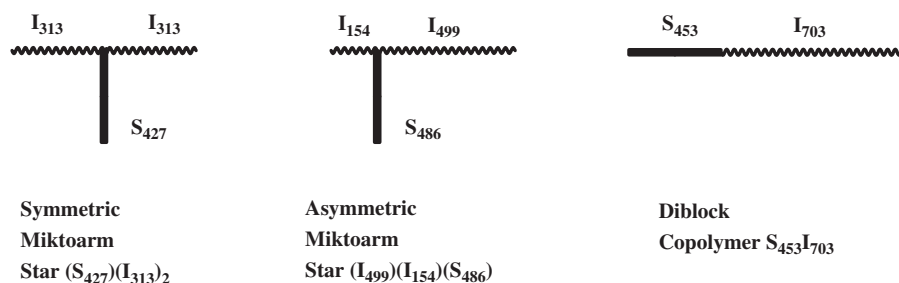
where η_r, η_{sp} and [η] are the relative, specific and intrinsic viscosities, respectively, and *k*_H and *k*_K are the Huggins and Kraemer constants, respectively. All the measurements were carried out at 25 °C using Cannon–Ubbelohde dilution viscometers with a Schott–Geräte (Hofheim, Germany) AVS 410 automatic flow timer. Viscometric radii, *R*_v, were calculated from the equation:

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

where *M*_{w,app} is the weight average molecular weight determined by light-scattering measurements.

RESULTS AND DISCUSSION

The chlorosilane approach was employed for the synthesis of the asymmetric miktoarm star copolymers composed from a deuterated PS arm and two PI arms of different molecular weights.⁹⁵ The longer PI arm has about three times the molecular weight of the shorter PI arm. These polymers can be also considered as asymmetrically single-grafted copolymers bearing one PS chain grafted along a PI chain. The grafting point is located at the 1/4-point of the PI chain. The molecular characteristics of the samples are given in Table 1. The samples are denoted by two numbers indicating the wt% content in PS and PI. Therefore, sample 10/90 is a (PI)(PI')(PS) asymmetric miktoarm star having 10% wt PS and 90% wt PI.



Scheme 1 Schematic representation of the diblock, SI, the symmetric, I₂S, and the asymmetric, 50/50, miktoarm star copolymers with similar compositions (~50% wt PS, Table 1).

Micellization behavior in *n*-decane

n-Decane is a selective solvent for the PI chains. Therefore, the micellar structures consist of a PS core surrounded by a PI corona. The sample with the highest PS content (sample 88/12) was not soluble in *n*-decane, because of the very low PI content. PS is a glassy polymer, and because it is located at the core, care should be taken to achieve equilibrium micellar structures. It is known that when block copolymers are dissolved into the selective solvent from the solid state, metastable micelles are formed having micellar cores preserved as formed from fracture of the morphology in the solid state.⁹⁶ These non-equilibrium micelles have much larger degrees of association than those obtained after first heating the solution, followed by cooling. During this process, the micelles equilibrate with the unimer at high temperature and are then trapped into a new frozen state when the solution is cooled at room temperature. Therefore, in order to achieve equilibrium structures, the stock solutions were heated at 60 °C for a few hours before they were used for subsequent measurements. Size exclusion chromatography analysis showed that this procedure does not cause any change (degradation or cross-linking) in the polymer structure. Following the heating procedure, the solutions were cooled gradually to room temperature and were left for at least 2 days before being used for the measurements. Under these conditions, equilibrium structures can be achieved as was evidenced by the reproducibility of the measurements using stock solutions of different initial concentrations.

The LALLS data of the other copolymers in *n*-decane are reported in Table 2, and characteristic plots are given in Figure 1. It is clear that multimolecular micelles exist in solution. The $Kc/\Delta R_\theta$ vs c plots were linear for all samples for concentrations higher than

$1.0 \times 10^{-4} \text{ g ml}^{-1}$ (stable micelles), showing that the critical micelle concentration is much lower than this value and is outside the experimentally accessible concentration range of light-scattering measurements. The second virial coefficients were low, even negative in one case, due to the higher apparent molecular weight of the micelles and the lack of interactions between the selective solvent and the PS block, the core-forming component.

The aggregation numbers, N_w , defined as the ratio of the molecular weight of the sample in the selective solvent over that measured in the common good solvent, depend on the composition of the copolymers. The higher the PS content, the higher the aggregation number, as expected from the theoretical predictions.^{97–99} A comparison of the aggregation numbers between the samples 50/50, a linear diblock copolymer of styrene and isoprene,¹⁰⁰ and a symmetric miktoarm star PS(PI)₂ having similar composition and molecular weights (shown in Table 1) in the same selective solvent, *n*-decane, reveals that the asymmetric miktoarm stars possess N_w values lower than those of the diblock copolymers but higher than the symmetric miktoarm stars (Table 2). This result can be attributed to the differences in topology, whose influence can be explained through the increase of steric hindrance of both the soluble and insoluble components upon increasing the complexity of the architecture, and through the solubilization effect of the multiple soluble blocks surrounding the micellar cores. Therefore, the more complicated the structure regarding the steric hindrance of the copolymer components and the higher the number of soluble blocks, the less favored the formation of large micellar structures. In terms of architectural complexity, the asym-

Table 1 Molecular characteristics of the miktoarm stars

Sample	(M_n) _{PIa} $\times 10^{3a}$	(M_n) _{PIb} $\times 10^{3a}$	(M_n) _{PS} $\times 10^{3a}$	(M_n) _{star} $\times 10^{3a}$	(M_w) _{star} $\times 10^{3b}$	$I = M_w/M_n$ M_n^c	% wt PS ^d
10/90 ^e	96.9	31.0	15.2	135.0	139.0	1.03	10.1
33/67 ^e	54.5	13.9	27.9	92.3	96.7	1.05	29.1
50/50 ^e	33.9	10.5	50.5	93.4	99.6	1.07	51.5
67/33 ^e	23.7	6.1	56.7	84.4	93.8	1.11	67.4
88/12 ^e	12.7	3.6	90.6	117.0	118.0	1.03	80.1
PS(PI) ₂ ^f	21.3	—	44.4	82.5	92.0	1.05	49.0
PSPI ^f	47.8	—	47.1	94.9	98.7	1.05	50.0

Abbreviations: PI, polyisoprene; PS, polystyrene.

^aBy membrane osmometry in toluene.

^bBy LALLS.

^cBy size exclusion chromatography.

^dBy ultraviolet size exclusion chromatography.

^eFrom Lee *et al.*⁹⁵

^fFrom Pispas *et al.*¹⁰⁰

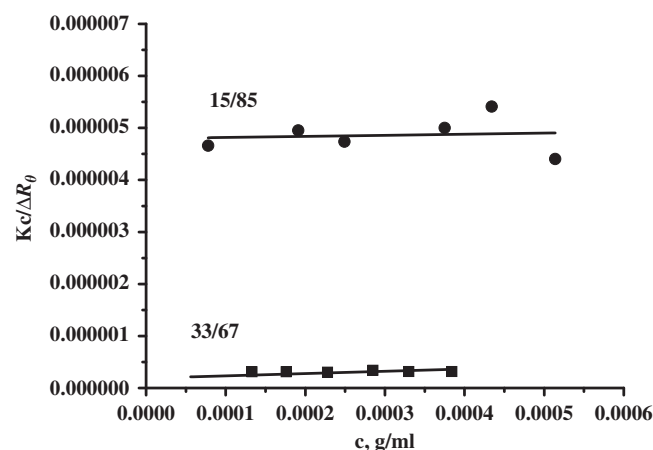


Figure 1 $Kc/\Delta R_\theta$ vs concentration plots for samples 15/85 (●) and 33/67 (■) in *n*-decane at 25 °C.

Table 2 Micellization properties in *n*-decane of the miktoarm stars

Sample	% wt PS	$M_w \times 10^{4a}$	A_2^a	N_w	k_d^b	R_h, nm^b	k_H^c	$[\eta] \text{ ml g}^{-1}^c$	R_w, nm^c	R_w/R_h
10/90	10.1	29.11	8.0×10^{-4}	2.1	15	18.8	0.31	78.0	15.3	0.81
33/67	29.1	370.9	-0.8×10^{-8}	38.4	20	30.7	0.77	20.0	22.7	0.74
50/50	51.5	1854	2.0×10^{-4}	186	19.5	36.7	0.51	18.0	37.5	1.02
67/33	67.4	2829	1.0×10^{-4}	301.5	23	46.0	0.85	15.0	40.65	0.88
PS(PI) ₂	49.0	611.0	6.2×10^{-6}	66	19	31.3	0.62	22.0	27.7	1.12
PSPI	50.0	2400	2.1×10^{-6}	243	0	45.7	1.2	27.1	46.9	1.03

Abbreviations: PI, polyisoprene; PS, polystyrene.

^aBy LALLS.

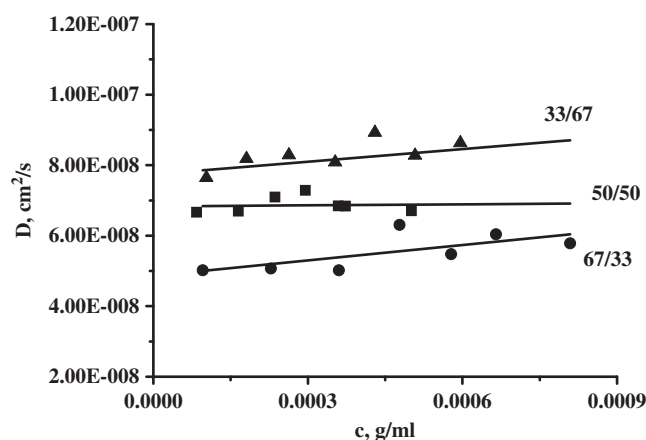
^bBy DLS.

^cBy dilute solution viscometry.

Table 3 Solution properties of the miktoarm stars in THF

Sample	D_0 , $\text{cm}^2 \text{s}^{-1}$	k_d	R_h , nm	k_H	$[\eta]$, dl g^{-1}	R_v , nm
10/90	3.79×10^{-7}	42	10.7	0.55	0.60	23.6
33/67	2.70×10^{-7}	30	9.96	0.27	0.48	19.5
50/50	5.30×10^{-7}	35	7.64	0.41	0.51	20.1
67/33	3.34×10^{-7}	23	13.9	0.41	0.42	18.6
90/10	2.45×10^{-7}	9×10^{-2}	15.1	0.37	0.42	20.0

Abbreviation: THF, tetrahydrofuran.

**Figure 2** Diffusion coefficient vs concentration plots for samples 33/67 (▲), 50/50 (■) and 67/33 (●) in *n*-decane at 25 °C.

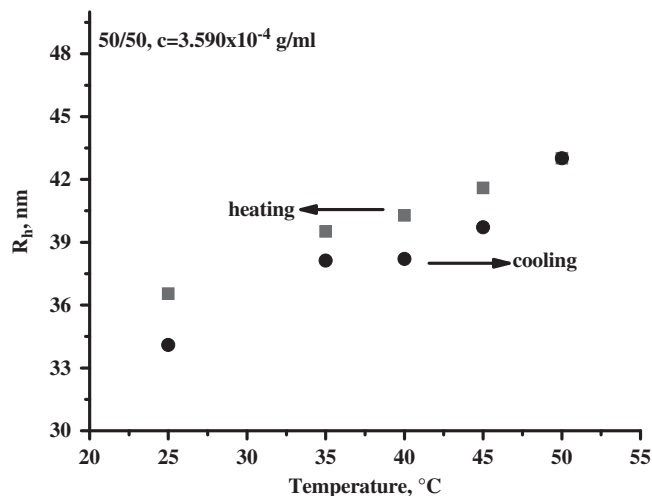
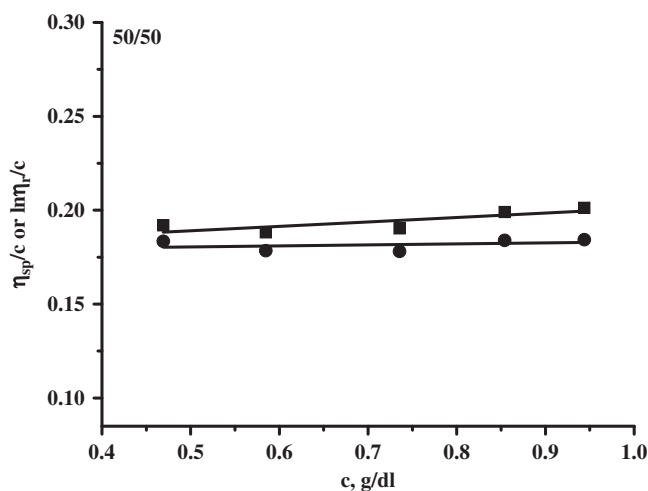
metric miktoarm stars can be envisioned as intermediate structures, compared with diblocks and symmetric miktoarm stars.

The LALLS results were further confirmed by DLS measurements. Results were obtained both in tetrahydrofuran (THF), a common good solvent for PS and PI arms (incorporated in Table 3), and *n*-decane. Characteristic plots in *n*-decane are given in Figure 2. In THF, reasonably low R_h values were obtained. CONTIN analysis revealed the existence of only one population in solution. The polydispersity factor μ_2/Γ^2 , where Γ is the decay rate of the correlation function and μ_2 is the second moment of the cumulant analysis, was always <0.1 , indicating the presence of monodisperse structures in agreement with the narrow molecular-weight distribution and the structural homogeneity by which the samples are characterized.

In *n*-decane, the plots were linear in the whole concentration range, showing that stable micellar structures exist. The R_h values were higher than those measured in THF and were found to increase upon increasing aggregation numbers. Measurements were conducted at three different angles (45, 90 and 135°). However, the angular dependence was negligible. This result, in association with the rather small R_h values of the micelles, indicates that the supramolecular structures are more or less spherical. In addition, the k_D values were smaller than in THF, as expected from the small A_2 values (LALLS) and in agreement with the Equation:¹⁰¹

$$k_D = 2A_2M + k_f - u \quad (7)$$

where M is the micellar molecular weight (the average molecular weight is most commonly used for light-scattering techniques), k_f is the coefficient of the concentration dependence of the friction coefficient and u is the partial specific volume of the polymer. k_d is a dynamic interaction parameter incorporating both thermodynamic interactions, manifested in A_2 , and hydrodynamic interactions, manifested in k_f .¹⁰¹ The combination of the low A_2 values along

**Figure 3** R_h vs temperature plots for sample 50/50 in *n*-decane, $c = 3.590 \times 10^{-4} \text{ g ml}^{-1}$: heating cycle (■) and cooling cycle (●). A full color version of this figure is available at *Polymer Journal* online.**Figure 4** Viscometry plots for sample 50/50 in *n*-decane at 25 °C.

with the rather low degrees of association, N_w , in *n*-decane is responsible for the low k_d values. CONTIN analysis revealed the existence of only one population, further confirming the presence of stable micellar structures in solution. The polydispersity factor μ_2/Γ^2 was always <0.1 , indicating the presence of monodisperse micelles.

DLS measurements were also conducted at different temperatures from 25 to 55 °C. Characteristic plots of the variation of the hydrodynamic radii and the scattered light intensity with temperature are given in Figure 3 and Supplementary Information (Supplementary Figure SI-1). CONTIN analysis showed that at all temperatures only one population exists, with the polydispersity factor μ_2/Γ^2 being always <0.1 . In addition, the intensity of the scattered light did not change appreciably with temperature for the same sample concentration. The R_h values were found to slightly increase upon increasing the temperature, and this behavior was reversible. All these results indicate that the micellar structures are thermally stable up to 55 °C, without any evidence of decomposition to unimers or further aggregation to clusters. The small increase of the R_h values can be attributed to the gradual swelling of the corona chains, due to the increased interactions with the solvent by raising the temperature.

A similar behavior has been observed for other micellar systems having PS chains at their core.^{102,103}

Viscometry measurements were also performed both in THF and *n*-decane. The results are given in Tables 2 and 3, respectively, whereas representative plots are displayed in Figure 4.

The existence of micelles is confirmed from the increased R_v values in *n*-decane, compared with those obtained in THF. The high values of the Huggins coefficients, due to increased hydrodynamic interactions of the polymeric chains in the aggregates, lead to the same conclusion. The intrinsic viscosity is, in almost all cases, lower in *n*-decane than in THF. Comparing this result with the higher R_v values obtained in the selective solvent, it can be concluded that the micelles are more compact than the free copolymeric chains in THF, a common good solvent for all the blocks. The only exception is sample 10/90 because of the low aggregation number, which leads to less compact structures. It is observed that the R_v values are in close agreement with the corresponding R_h values. Therefore, the ratio R_v/R_h is close to unity, indicating that rather stable micellar structures are obtained. However, for the samples 10/90 and 33/67 with the lowest PS content, the R_v/R_h ratios were sufficiently lower than unity, indicating that partial deassociation may be effective, due to the application of the shear forces in the capillary tube of the viscometer. The rather low PS content leads to less stable supramolecular structures, which are susceptible to deaggregation. Comparing the R_h and R_v values of the asymmetric miktoarm star 50/50 with the corresponding linear diblock and symmetric miktoarm star PS(PI)₂, having similar compositions and molecular weights, the following relationship is revealed: $(R_h)_{SI} > (R_h)_{50/50} > (R_h)_{I2S}$.

Further insight into the micellar structure can be obtained from the values of the core radius, calculated by the Equation (8):

$$R_c = (3M_{w,mic}wt_{PS}/4\pi N_A d_{PS} \varphi_{PS})^{1/3} \quad (8)$$

where $M_{w,mic}$ is the micellar molecular weight, wt_{PS} is the weight fraction of the core-forming block, d_{PS} is the density of PS ($d_{PS} = 1.05 \text{ g mL}^{-1}$) and φ_{PS} is the volume fraction of PS in the core. Two limiting cases can be considered—the dry core ($\varphi_{PS} = 1$) and the

swollen core ($\varphi_{PS} = 0.5$). It is evident that the case of the dry core is much closer to reality, taking into account the incompatibility between PS and *n*-decane, and the results of previous studies as well. The results taking $\varphi_{PS} = 1$ are reported in Table 4. The corona thickness, L , is defined as:

$$L = R_h - R_c \quad (9)$$

The area of the core-corona interface, A_c , occupied per the copolymer chain is given by Equation (10):

$$A_c = 4\pi R_c^2 / N_w \quad (10)$$

The L and A_c values for the dry core case are also incorporated in Table 6. It is obvious that the R_c values increase upon increasing the PS copolymer content. It can also be observed that the R_c values are relatively low compared with the corresponding R_h values or, in other words, that the micellar core is rather compact, in agreement with that usually observed in block copolymer micelles. However, it is clear that the samples with the lower PS content, that is, 10/90 and 33/67, have less compact cores, taking into account the relative size of the R_c over the R_h with the PS content of the asymmetric stars. This result supports the conclusion derived from the viscometry measurements, where partial deaggregation was observed for the specific samples.

The A_c values decrease upon increasing the PS content of the asymmetric miktoarm stars, with the change being rather small for samples 50/50 and 67/33. This result indicates that the lower PS content stars form less compact micelles, in agreement with the previous observations.

Comparing the A_c values with the corresponding symmetric miktoarm star and the diblock copolymer, the following order was observed: $(A_c)_{I2S} > (A_c)_{50/50} > (A_c)_{SI}$. The presence of the two PI chains per junction point increases the core-corona interface. In the case of the asymmetric miktoarm stars, the crowding effect around the junction point is less important compared with the symmetric one, so that an intermediate behavior between that of the diblock and the symmetric miktoarm star is obtained.

A schematic illustration of the micellar structures derived from the diblock copolymer, the symmetric and asymmetric miktoarm stars is given in Scheme 2.

Table 4 Structural characteristics of the micellar structures in *n*-decane

Sample	R_h , nm	R_c , nm	L , nm	A_c , nm ²
10/90	18.8	2.55	16.2	38.9
33/67	30.7	7.73	23.0	19.6
50/50	36.7	15.7	21.0	16.7
67/33	46.0	19.3	26.7	15.5
PS(PI) ₂	31.3	10.4	20.9	20.6
PSPI	45.7	16.5	29.2	14.1

Abbreviations: PI, polyisoprene; PS, polystyrene.

Table 5 Micellization properties of the miktoarm stars in DMA

Sample	% wt PS	$M_w \times 10^{-4a}$	A_z^a	N_w	k_d^b	R_h , nm ^b	k_H^c	$[\eta]$ mL g ⁻¹ c	R_v , nm ^c	R_v/R_h
33/67	29.1	3239	-1.4×10^{-5}	335	-114	69.0	0.32	5.52	30.5	0.44
50/50	51.5	1275	7.0×10^{-6}	128	-13	47.8	0.76	17.24	32.6	0.68
67/33	67.4	879.8	3.0×10^{-6}	93.8	25	41.4	0.84	24.11	32.3	0.78
88/12	80.1	489.8	-4.0×10^{-5}	41.5	15	36.1	1.72	35.45	30.2	0.84

Abbreviation: DMA, *N,N*-dimethylacetamide.

^aBy LALLS.

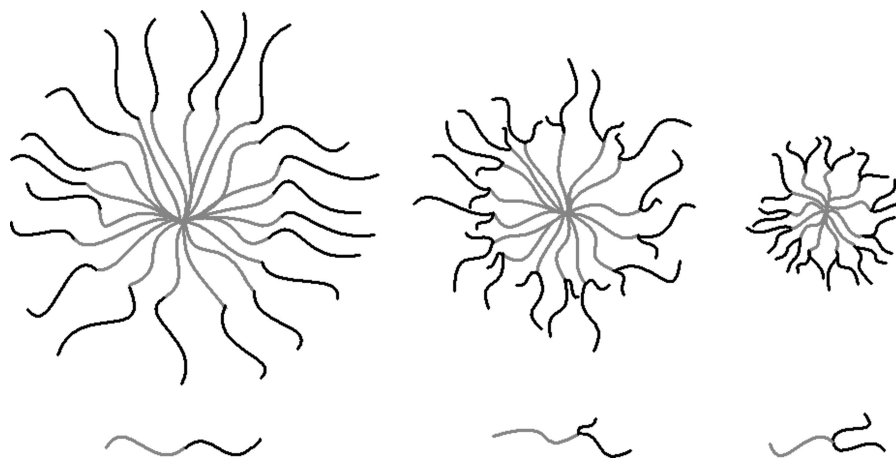
^bBy DLS.

^cBy dilute solution viscometry.

Table 6 Structural characteristics of the micellar structures in DMA

Sample	R_h , nm	R_c , nm	L , nm	A_c , nm ²
33/67	69.0	21.2	47.8	16.9
50/50	47.8	14.1	33.7	19.5
67/33	41.4	10.8	30.6	15.8
88/12	36.1	6.4	29.8	12.3

Abbreviation: DMA, *N,N*-dimethylacetamide.



Scheme 2 Schematic representation of the micellar structures formed by the block copolymer (left), the asymmetric (center) and the symmetric miktoarm star (right) copolymers in *n*-decane. A full color version of this figure is available at *Polymer Journal* online.

Micellization behavior in DMA

DMA is a selective solvent for the PS chains. Therefore, in this case the micellar structures consist of a PI core surrounded by a PS corona. The sample with the highest PI content (sample 10/90) was not soluble in DMA. PI is a very flexible polymer having a very low glass-transition temperature, much lower than room temperature. It is therefore much easier in this case to achieve equilibrium micellar structures. However, for safety reasons, the micellar solutions were heated at 60 °C for several hours and were allowed to equilibrate for more than 12 h at room temperature.

The LALLS data of the asymmetric miktoarm star copolymers in DMA are given in Table 5, whereas characteristic $Kc/\Delta R_\theta$ vs c plots are provided in Supplementary Information (Supplementary Figure SI-2). The plots were linear in the concentration range studied, except sample 88/12 for which the plot was curved to higher $Kc/\Delta R_\theta$ values at lower concentrations. Because of the low PI content, higher concentrations were needed in this case to form stable equilibrium micellar structures. However, in all cases no indication of critical micelle concentration was obtained. The A_2 values were very low for reasons already explained in the discussion regarding the micellization behavior in *n*-decane.

The aggregation numbers, N_w , were found to increase upon increasing the PI content, which is the core-forming block. It is interesting to note that the N_w values in DMA are slightly higher than those in *n*-decane, comparing samples with similar compositions in soluble and insoluble components. This behavior may be attributed to differences in the quality of the solvents, but, in addition, it may reflect the general conclusion drawn in graft copolymers that the degrees of aggregation are reduced upon increasing the number of soluble chains.¹⁰⁴

The micellization behavior of a PS–PI diblock copolymer with $M_w = 80\,700$ and 54% wt PS was reported in the literature in DMA and thus can be compared with sample 50/50.¹⁰⁵ It is obvious that the diblock copolymer has a much higher N_w value compared with the corresponding asymmetric miktoarm star, because of the difference in polymer topology.

Additional data were obtained by DLS measurements, given in Table 5. The D vs c plots (Supplementary Information, Supplementary Figure SI-3) were linear for all samples, and the k_D values were very low, even negative in some cases, in agreement with the low A_2 values measured by LALLS. No angular dependence was observed and, in association with the relatively low R_h values, it can

be concluded that the micelles should be spherical. The existence of stable micellar structures was revealed by CONTIN analysis. Unimers or micellar aggregates were not present in solution. The micelles were near monodisperse, because the μ_2/Γ^2 values were <0.1 for all samples and concentrations, further confirming a spherical structure of the micelles.

The hydrodynamic radii generally increase with increasing aggregation numbers. The R_h values in DMA are substantially higher than those in *n*-decane, when comparing samples with similar compositions in soluble and insoluble components. This result reflects the same behavior obtained from LALLS measurements regarding the aggregation numbers, and may also indicate that the micellar structures, with the two insoluble blocks incorporated in the same core, are not very compact as in the case of the micelles obtained in *n*-decane. The same conclusion can be reached taking into account the higher R_h value of the asymmetric miktoarm star compared with the R_h value of the diblock copolymer, even though the latter has a higher N_w value.

Measurements were also conducted at different temperatures from 25 to 55 °C. For all samples and concentrations examined, the pattern was the same. No angular dependence was observed at any temperature, and CONTIN analysis revealed the existence of single peaks. The only change was that the apparent R_h value for each concentration slowly decreased upon increasing the temperature. Characteristic examples are given in Supplementary Information (Supplementary Figures SI-4 and SI-5). This decrease in dimensions was reversible. Upon cooling the solution, the R_h values increased according to approximately the same temperature dependence. In addition, the μ_2/Γ^2 values were very low at 25 °C but were found to slightly increase upon increasing the temperature up to 55 °C. From these results, it can be concluded that the micelles may be thermally sensitive and susceptible to decomposition to smaller structures. The effect is not so pronounced to lead to bimodal distributions in the CONTIN analysis but is evidenced by the increase of the polydispersity factor with increasing temperature.

Dilute solution viscometry was also employed in order to obtain additional information on the hydrodynamic behavior of the micelles. The results are reported in Table 5, and characteristic plots are illustrated in Supplementary Information (Supplementary Figure SI-6). As in the case of the micellar structures formed in *n*-decane, the intrinsic viscosities are lower than those measured in THF, and they also decrease upon increasing aggregation numbers. This is a direct indication that the higher the N_w value, the more compact the micellar structure. The R_v values were sufficiently lower than the corresponding R_h values, revealing that the macromolecular structures

are not connected by strong intermolecular forces and that shear thinning is observed in the viscometry tube, leading to considerable deaggregation. The effect is much more pronounced for the micelles having the higher N_w values, as was judged by the low R_v/R_h ratios. This result is in agreement with the DLS observations regarding the slight decrease of R_h upon increasing the temperature.

Using Equations (8–10), the structural parameters R_c , L and A_c were calculated, and the results are given in Table 6. The micellar corona is very extended compared with the structures obtained from the same samples in *n*-decane. This can be attributed to the different topology of the soluble component. In *n*-decane, the corona consists of branched PI chains of low molecular weight, whereas in DMA, the corona consists of linear PS chains, which can be more readily expanded. For the calculation of the R_c values, the following equation was employed:

$$R_c = (3M_{w,mic}wt_{PI}/4\pi N_A d_{PI} \phi_{PI})^{1/3} \quad (11)$$

where, $M_{w,mic}$ is the micellar molecular weight, wt_{PI} is the weight fraction of the core-forming block, d_{PI} is the density of PI ($d_{PI}=0.90$ g ml⁻¹) and ϕ_{PS} is the volume fraction of PS in the core.

CONCLUSIONS

Static and DLS techniques along with dilute solution viscometry were utilized to study the micellization behavior of model asymmetric miktoarm star copolymers of the type AA'B, where A and A' are PIs and B is deuterated PS. The study was performed in *n*-decane, a selective solvent for the PI blocks, and DMA, selective for the PS blocks. The comparison between linear PS-PI diblocks, symmetric PS(PI)₂ and asymmetric PS(PI)(PI') miktoarm stars confirms that the micellar properties can be manipulated at will, and tailor-made micelles can be constructed changing the macromolecular architecture. The micellar structures, formed in *n*-decane, are thermally stable. However, in DMA there is a slight tendency toward decomposition upon increasing the temperature and applying shear forces to the polymer solutions.

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