Macromolecules **2002,** *35,* 834−840

Controlling Micellar Properties of Styrene/Isoprene Copolymers by Altering the Monomer Arrangement along the Chain

P. Hodrokoukes, S. Pispas, and N. Hadjichristidis*

Department of Chemistry, University of Athens, Panepistiomiopolis Zografou, 15771 Athens, Greece

Received July 26, 2001; Revised Manuscript Received October 23, 2001

ABSTRACT: By using appropriate anionic polymerization high-vacuum techniques, novel triblock copolymers of styrene and isoprene with normal tapered (TMB), inverse tapered (ITMB), and random (RMB) middle blocks were synthesized. In addition, diblock copolymers (SI) as reference materials and normal tapered (TBC) and random (RC) were prepared. All copolymers have practically the same composition (~50 wt % PS). Their micellization behavior was investigated in dilute solutions in *n*-decane, a selective solvent for the isoprene part of the macromolecules, by static and dynamic light scattering as well as viscometry. Experiments were directed toward the determination of the micelles fundamental properties (average aggregation number, critical micelle concentration, critical micellization temperature) and compared with those obtained for pure diblock copolymers. No considerable differences, compared to the pure diblock copolymers, were observed for triblocks having a normal tapered middle block (TMB). A considerable decrease in the aggregation number and a corresponding decrease in the critical micellization temperature were found for the triblock copolymers having an inverse tapered middle block (ITMB) with length comparable to the length of the outer pure blocks. A similar decrease in the aggregation number was also observed in the case of a normal tapered copolymer. The differences in behavior are attributed to the different arrangement of the segments, which seems to have a considerable effect on the solubility characteristics of these copolymers.

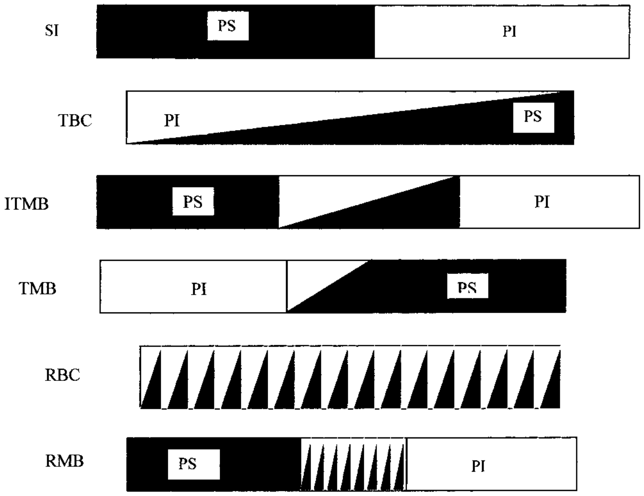
Introduction

Micelle formation from block copolymers, dissolved in a selective solvent for one of the blocks, has been the subject of intense experimental and theoretical work in recent years.[1−4] These intensive studies were triggered by the many possible uses of these self-organizing systems in fields of academic and technological interest like colloid stabilization and drug delivery, in coating and microreactors applications, and in cosmetic technology.[3]

Micelles formed by block copolymers are usually multimolecular having a spherical core−shell structure. The core, formed by the insoluble blocks, is stabilized in solution by the presence of the soluble corona chains. It has been experimentally verified that, in most cases, the micellization of block copolymers obeys the model of closed association characterized by an equilibrium between molecular dissolved unimers and well-defined, narrow size distributed, micelles.[1] The core−shell microstructure of the micelles, their usually low critical micelle concentration compared to low molecular weight surfactants, their stability over a broad range of concentration and temperature, and their narrow size distribution together with the ability to tailor micellar properties by variation of the molecular characteristics of the block copolymer chains are the main factors leading to the numerous applications of polymeric micellar systems.

It has been found that the structural parameters of the micelles (overall size, core and shell dimensions, microstructure) and their fundamental properties (aggregation number and critical micelle concentration) are influenced by many factors such as chemical nature and molecular weight of the blocks, solvent−blocks interactions, concentration, temperature, and architecture of the copolymer.[1−19] However, much experimental work is still needed in order to elucidate the influence of the different molecular characteristics of the block copolymers 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 various types of micelles, giving great possibilities in fine-tuning the final properties of the micellar systems according to the desired application.

Scheme 1



In this paper we extend the micellization studies to novel copolymer architectures of styrene and isoprene in *n*-decane, a selective solvent for the polyisoprene blocks (Scheme 1). In the series of samples studied the arrangement of the styrene and isoprene segments was varied in a systematic manner, taking advantage of the different reactivity ratios of the two monomers, in hydrocarbon solvents, as well as using different addition sequences of monomers during the polymerization process. In this way, because of the synthetic capabilities

10.1021/ma011331e CCC: $22.00

of the anionic polymerization of styrene and isoprene, simple diblock and normal tapered diblock copolymers and triblock copolymers with a normal or inverse tapered and random middle block can be synthesized.

The presence of a middle block with variable composition, between the pure styrene and isoprene blocks, in the case of triblock copolymers is expected to alter the micellization behavior (aggregation number and size of the micelles formed as well as the critical micelle concentration) of the system in a way analogous to the changes observed in the microphase separation behavior in the bulk state.[20−26] All samples have the same composition and overall molecular weights. 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 the fundamental properties of the micelles formed by different copolymers are discussed.

Experimental Section

Synthesis of Block Copolymers. All copolymers of styrene (S) and isoprene (I) have been prepared by anionic polymerization high-vacuum techniques.[27] *sec*-Butyllithium was the initiator and benzene the solvent in all cases. Polymerizations were terminated with degassed methanol. In each step of the synthesis samples were withdrawn from the reaction medium and characterized. The targeted composition of the copolymers was 50 wt % PS.

The various synthetic schemes followed in order to obtain the different block copolymer architectures are outlined in the following:

(a) Pure Block Copolymers (SI). These materials, used as reference, were synthesized by sequential addition of styrene (S) and isoprene (I) to a *sec*-BuLi solution in benzene. Two samples having different molecular weight of the two blocks were prepared.

(b) Normal Tapered Diblock Copolymer (TBC). For the preparation of this architecture advantage was taken from the different reactivity ratios of S and I, toward anionic polymerization, in hydrocarbon solvents ($r_I = 14.6$, $r_S = 0.046$).[28] Isoprene is polymerized first until its concentration becomes relatively low. At this point S starts incorporating in the polymer chain in increasing amounts as the reaction continues. After complete consumption of I, a pure PS block is formed. The part of the chain between the pure blocks has a gradient of composition in either monomer.

(c) Triblock Copolymer with a Normal Tapered Middle Block (TMB). This material was prepared by a procedure involving a three-step addition of monomers. Polymerization has been initiated by addition of isoprene to *sec*-BuLi followed by addition of a mixture of the two monomers (S and I in a 50:50 weight ratio) and then addition of styrene. The molecular weight of each pure block and that of the tapered part in the copolymer can be controlled by the amount of the initiator and the quantity of the monomers added.

(d) Triblock Copolymers with an Inverse Tapered Middle Block (ITMB). A similar strategy with the one in (c) was followed with the only difference being the inversion of the order of monomer addition; i.e., S was polymerized first followed by the addition of the S/I mixture and finally the I. Using this procedure, the gradient of the composition in the middle block is inverted. In this case an amount of blocky PI is connected to the PS block whereas an amount of blocky PS is next to the PI block. This inversion can produce some frustration in the organization of block copolymer chains into micelles. Three copolymers with different length of the middle block but having outer blocks of the same length were synthesized.

(e) Random Copolymer (RC). Random copolymers of styrene and isoprene can be obtained if a small amount of a polar compound is added to the system.[29] Unfortunately, the polar compounds result in formation of PI having a high vinyl content (1,2 or 3,4 microstructure). Recently, it has been reported that the random copolymerization of S/I mixtures via anionic polymerization will be successful by using a potassium alkoxide additive.[20b] The potassium alkoxide used in this case was generated by the reaction of excess pure potassium metal with 2,3-dimethyl-3-pentanol. It was found that a 30:1 ratio of Li:OK gives very good results in terms of polydispersity. The random copolymer was synthesized by simultaneous polymerization of a S/I (50:50 wt) mixture in the presence of the alkoxide at the above Li:K ratio.

Table 1. Molecular Characteristics of the Different Copolymers of Styrene and Isoprene

	precursors M_n [a] ($\times 10^{-3}$)			final copolymer			
sample[e]	first block	second block	third block	M_w[b] ($\times 10^{-3}$)	M_n[a] ($\times 10^{-3}$)	M_w/M_n[c]	wt % PS[d]
SI-1	8.0	8.7		18.7	16.7	1.03	49.8
SI-2	12.4	17.2		33.3	29.6	1.04	50.9
TBC				26.5	23.1	1.03	51.9
TMB	7.8	5.5	9.5	27.1	22.8	1.02	56.8
ITMB-1	8.6	2.0	7.9	22.5	18.5	1.02	50.8
ITMB-2	7.8	5.2	9.8	25.7	22.8	1.03	51.4
ITMB-3	8.5	8.7	9.2	31.9	26.4	1.03	51.8
RC				26.7	24.3	1.03	53.6
RMB	9.7	5.6	9.7	29.2	25.0	1.03	52.0

[a] By membrane osmometry in toluene at 37 °C. [b] By low-angle laser light scattering in THF at 25 °C. [c] By size exclusion chromatography in THF at 30 °C. [d] By ^1H NMR spectroscopy in $CDCl_3$ at 30 °C. [e] For the structures of each sample see Scheme 1.

(f) Triblock Copolymer with a Random Middle Block (RMB). The synthetic course is also based on a three-step anionic polymerization procedure. The first step was the addition of styrene, followed by an addition of the two monomers and the alkoxide and then the addition of isoprene in the third step. By this way in the obtained triblock copolymer the first block was PS, the middle was a random P(S/I) copolymer, and the third block was PI.

Molecular Characterization. All samples were characterized by a variety of methods. The molecular weight distribution and compositional homogeneity of the final and intermediate products were obtained by size exclusion chromatography (SEC) at 30 °C in THF at a flow rate of 1 mL/min, using a Waters system composed of a Waters 600 pump controller, a set of four Styragel columns (continuous porosity range 10^3−10^6 Å), a Waters 410 differential refractometer, and a Waters 996 photodiode array UV detector interfaced with a computer. The instrument was calibrated with nine linear polystyrene standards having molecular weights in the range 4000−900 000. Number-average molecular weights and second virial coefficients were determined by membrane osmometry (MO) in toluene, refluxed over CaH_2 and distilled prior to use, at 37 °C, using a Jupiter Instruments Co. model 231 membrane osmometer. Weight-average molecular weights and second virial coefficients were obtained by low-angle laser light scattering (LALLS) using a Chromatix KMX-6 low-angle laser light scattering photometer equipped with a He−Ne laser operating at 633 nm. THF, refluxed over sodium metal and distilled just prior to use, was the solvent at 25 °C. The required specific refractive index increments, dn/dc, were determined with a Chromatix KMX-16 laser differential refractometer operating at the same wavelength/temperature and calibrated with aqueous NaCl solutions. The average composition of the copolymers was determined by ^1H NMR spectroscopy using a Varian 200 MHz instrument in $CDCl_3$ at 30 °C. The molecular characteristics of the copolymers are given in Table 1. The characterization results indicate a high degree of molecular weight and compositional homogeneity for all samples.

Micellization Studies. Analytical grade *n*-decane was first dried over CaH_2 under reflux for 24 h, and it was fractionally distilled just before use. Stock solutions were prepared by dissolving a weighted amount of sample in the appropriate volume of dried solvent with occasional stirring. The stock

Table 2. Static Light Scattering Results for the Different Copolymers of Styrene and Isoprene in *n*-Decane at 25 °C

sample[a]	$M_{\mathrm{w,mic}} \times 10^{-6}$	$A_2 \times 10^6$	N_{w} ($M_{\mathrm{w,Dec}}/M_{\mathrm{w,THF}}$)
SI-1	0.43	136	23
SI-2	2.1	8.6	63
TMB	1.9	1.5	70
ITMB-1	0.63	23.3	28
ITMB-2	1.7	34.1	66
ITMB-3	0.51	39.1	16
RMB	1.84	13.5	63
TBC	0.45	64.3	17

[a] For the structures of each sample see Scheme 1.

solutions were heated at 70 °C overnight before the measurements to ensure complete dissolution of the samples and removal of possible memory effects. The characteristic bluish tint related to the presence of micelles was present in the stock solutions. No polymer precipitation was observed from these solutions after standing at room temperature for several weeks. Solutions of lower concentrations were obtained by subsequent dilutions of the stock solutions. Before light scattering measurements the solutions were filtered through 0.45 μm nylon filters whereas for viscosity measurements 1.2 μm nylon filters were used. Measurements by the different methods were carried out in the broader concentration range possible determined by experimental accuracy (in the case of low concentrations).

Apparent weight-average molecular weights, M_{w}, of the micelles and second virial coefficients, A_2, in *n*-decane, were obtained from linear part of the concentration dependence of the reduced scattering intensity at high concentrations, using a Chromatix KMX-6 low-angle laser light scattering photometer.

Dynamic light scattering experiments were carried out at 25 °C, using a Series 4700 Malvern system composed of a PCS5101 goniometer interfaced with a PCS7 stepper motor controller, a Cyonics variable power Ar^+ laser, operating at 488 nm. A 192-channel correlator was used for accumulation of the data. Correlation functions were analyzed by the cumulant method, and the Contin software was provided by the manufacturer. The correlation functions were collected at angles between 45° and 135°. The viscosity of the solvent was determined at different temperatures using a Cannon-Ubbelohde viscometer.

For the viscosity measurements Cannon-Ubbelohde dilution viscometers were used in a temperature-controlled bath (at 25 ± 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 and Kraemer equations. More details on the procedures and methods used have been given elsewhere.[19]

Results and Discussion

The results obtained by static light scattering are given in Table 2. It is clear that all the copolymers investigated form multimolecular micelles in *n*-decane as evidenced by the increase in the molecular weights compared with the ones obtained in THF a nonselective and good, for both components, solvent. This is also supported by the low values of the second virial coefficient, A_2, due to the increase in the molecular weight and the unfavorable core–solvent interactions. An exception is the random copolymer which forms unimolecular micelles since the molecular weight determined in *n*-decane is similar to the molecular weight determined in THF.

The value of the weight-average aggregation number, N_{w} (the number of polymer chains per micelle), for sample TMB is practically equal to that of sample SI-2 (Table 2). These samples have similar molecular weights and composition. It turns out that the normal tapered middle block of TMB does not make any difference in the way micelles are formed by the two copolymers. Experimental results for sample RMB lead to the same conclusion. Comparison with sample SI-2 shows no difference in the aggregation number. Again, the random middle block in sample RMB does not seem to alter the characteristics of the micelles formed.

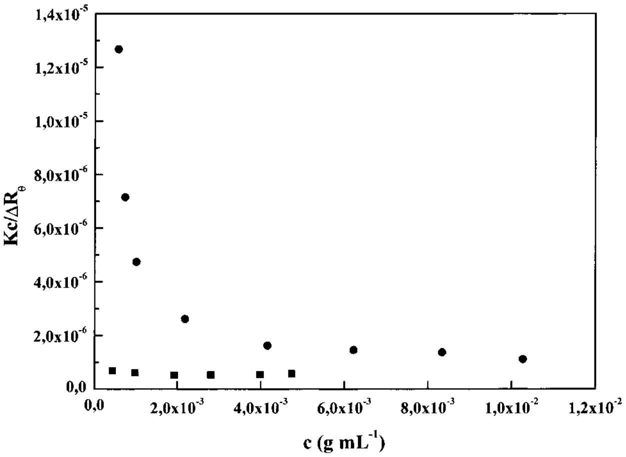


Figure 1. $Kc/\Delta R_\theta$ vs concentration plot for sample SI-2 (■) and sample ITMB-3 (●) in *n*-decane at 25 °C.

In the case of sample TBC N_{w} is lower than that of SI-1 and considerably lower than that of SI-2. One would expect at least in terms of molecular weight, since all samples have the same overall composition, that TBC would form micelles having an aggregation number intermediate between the two pure block copolymers. Generally, N_{w} depends primarily on the length of the insoluble block, i.e., increases as the length of the insoluble block increases.[1-4] Its dependence on the length of the soluble block is the opposite but much weaker. Obviously, the tapered nature of the copolymer, i.e., the existence of shorter pure blocks in the chain, enhances the solubility of the whole molecule.

The behavior of the ITMB copolymers, i.e., the ones having an inverse tapered middle block, deserves special attention. Samples ITMB-1 and ITMB-2 have similar aggregation numbers with the corresponding pure diblock copolymers SI-1 and SI-2 within experimental error. Apparently even an inverse tapered middle block of 5000 molecular weight is not enough to impart any changes in micelle formation of the block copolymer. However, when the inverse tapered middle block becomes about 10 000 in molecular weight, the aggregation number decreases considerably, below the values for ITMB-1 and ITMB-2, despite the fact that total molecular weight increases and composition remains the same. Direct comparison with the diblock sample SI-2, which has similar molecular weight and composition with ITMB-3, leads to the same conclusion.

A comparative plot of $Kc/\Delta R_\theta$ for samples SI-2 and ITMB-3 is given in Figure 1. For sample SI-2 the concentration dependence of the reduced scattering intensity in the whole concentration range studied is linear, and the extrapolated value at zero concentration leads to the determination of the molecular weight of the micelles. The corresponding plot for sample ITMB-3 shows an upward curvature at the low concentration range, indicative for the approach to a cmc. In the concentration range from 5.6×10^{-4} to 4×10^{-3} g/mL obviously micelles and unimers coexist. At concentra-

Table 3. Dynamic Light Scattering Results for the Different Copolymers of Styrene and Isoprene in *n*-Decane at 25 °C

sample[a]	$D_0 \times 10^{-7}$ (cm^2/s)	k_D	$R_{h,0}$ (nm)
SI-1	1.95	0	13.0
SI-2	1.41	8	18.0
TMB	1.33	6	19.1
ITMB-1	1.53	5	16.6
ITMB-2	1.49	0	17.0
ITMB-3	1.86	0	13.6
RMB	1.40	11	18.1

[a] For the structures of each sample see Scheme 1.

Table 4. Viscometric Results for the Different Copolymers of Styrene and Isoprene Studied in *n*-Decane at 25 °C

sample[a]	[η] (mL/g)	k_H	R_v (nm)	R_v/R_h
SI-1	13.2	1.3	9.6	0.73
SI-2	15.3	1.3	17.2	0.96
TMB	13.5	1.2	16.0	0.84
ITMB-1	14.1	1.2	11.2	0.67
ITMB-2	14.1	1.3	15.6	0.92
ITMB-3	15.8	1.2	10.8	0.79
RMB	15.2	1.5	16.6	0.92

[a] For the structures of each sample see Scheme 1.

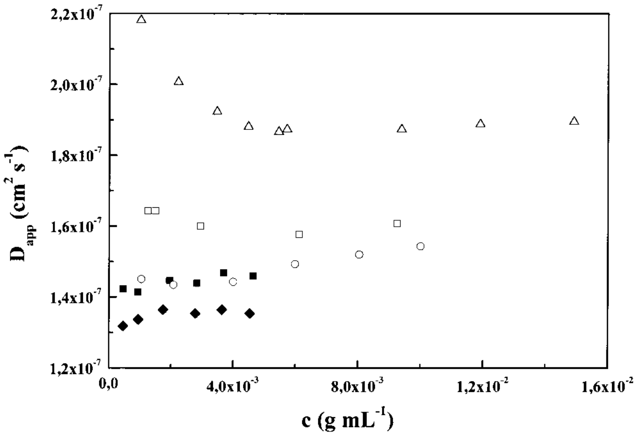


Figure 2. Comparative plot of D_{app} vs concentration for (a) sample SI-2 (■), (b) sample TMB (◆), (c) sample ITMB-2 (□), (d) sample ITMB-3 (△), and (e) sample RMB (○) in *n*-decane at 25 °C.

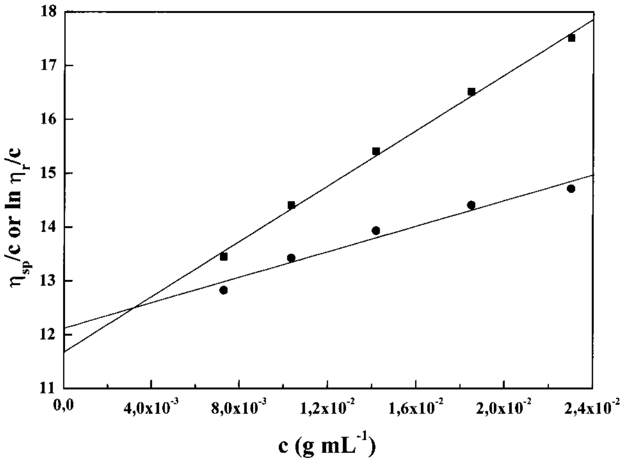


Figure 3. η_{sp}/c (■) and ln η_r/c (●) vs concentration plots for sample ITMB-3 in *n*-decane at 25 °C.

tions higher than 4×10^{-3} g/mL micelles dominate the scattering profile, and the concentration of the unimers is low as indicated from the linear concentration dependence of $Kc/\Delta R_\theta$. This difference in the light scattering plots also indicates that sample ITMB-3 must have a higher cmc than SI-2. We will return to this point later.

The experimental results from dynamic light scattering, aiming to the determination of the hydrodynamic size of the micelles and their size polydispersity, are given in Table 3.

The results show the same general trend as those from static light scattering. Hydrodynamic size increases as the aggregation number increases in all cases. The small values of k_D must be a result of the predominance of hydrodynamic friction factors over thermodynamic ones as well as a result of the low A_2 values obtained for these systems.[18,19]

A characteristic diagram depicting the concentration dependence of the apparent diffusion coefficient, D_{app}, for a number of samples is shown in Figure 2. For all samples, except sample ITMB-3, there is a linear dependence of D_{app} on concentration leading to the conclusion that micelles are predominately present in the solutions of these samples at the concentration range studied. This conclusion is supported by the low size polydispersity values ($\mu_2/\Gamma^2 < 0.1$), through the second cumulant, determined for the same concentration range.

On the other hand, the concentration dependence of *D* for sample ITMB-3 is not linear. Furthermore, size polydispersity decreases as concentration increases and acquires values typical for the other samples ($\mu_2/\Gamma^2 <$ 0.1) at concentrations higher than about 5.5×10^{-3} g/mL. Unfortunately, because of the small difference in hydrodynamic sizes between micelles and unimers, two separate peaks could not be resolved by Contin. Apparently, for $c < 5.5 \times 10^{-3}$ g/mL there is a coexistence of micelles and molecular dispersed chains according to the model of closed association.[1,2] This observation is in agreement with the results from static light scattering for sample ITMB-3 and supports the conclusion that this sample may has a higher critical micelle concentration than the rest of the samples and specifically from the corresponding pure diblock (sample SI-2).

Complementary information concerning the size and structure of the micelles was obtained by dilute solution viscometry. The results are given in Table 4. A representative plot is given in Figure 3.

Measurements were conducted in the same solvent in order to determine the intrinsic viscosity of the micellar systems, a parameter associated with the rheological characteristics of these systems, the viscometric radius of the micelles, R_v, and the Huggins coefficient, k_H, a parameter connected to the hydrodynamic interactions between polymeric chains. The variation in [η] reflects the variation in the aggregation number and consequently the variation in size of the micelles, determined by light scattering. [η] increases as N_w and size increase. The k_H values are high and reflect the increased hydrodynamic interactions in the system due to the incorporation of copolymer chains into micelles and the unfavorable interactions between solvent and styrene segments that form the core of the micelles. The k_H values are higher from the theoretical value of 0.99 calculated for hard spheres,[30,31] indicating that the micelles have compact structures. The viscometric radii calculated by aid of the equation

$$R_v = (3/10\pi N_A)^{1/3}([\eta]M_w)^{1/3}$$

where M_w is the molecular weight of the micelles calculated from static light scattering show a trend similar to that of R_h. They increase as the aggregation number increases. The ratio R_v/R_h is close to unity as expected for hard spheres.[30,31] Therefore, the shape of the micelles formed by these copolymers must be spherical. Some deviations from unity may be understood on the basis that the micelles in a capillary tube experience shear forces that may sometimes disrupt partially or totally them, leading to lower R_v experimental values. It has to be noted that the larger deviations from unity are observed in the case of micelles of low aggregation number. This can be attributed to a looser structure of smaller micelles that can be disrupted more easily by a shear field than more compact micelles of larger aggregation number.

One of the questions that have to be answered, especially for micellar systems with cores containing high-T_g material, like in the case of PS, is whether the micelles formed by direct dissolution of the material in the selective solvent are the equilibrium ones.[3−5,32] To avoid the presence of thermodynamically nonequilibrium or kinetically frozen superstructures in the investigated solutions, the solutions were heated overnight at 70 °C to ensure complete dissolution of the material and erase any sample history effects associated with nonequilibrium structures before the measurements. Additionally, solutions of certain concentrations were subjected to continuous heating and cooling cycles, within the light scattering cell, with simultaneous measurements of the scattered intensity as a function of temperature. Measurements were obtained in the range 25−55 °C. A representative example is given in Figure 4 for sample ITMB-3.

The intensity measurements were reproducible at the same temperature within subsequent heating−cooling cycles. Since the scattering intensity is analogous to the molecular weight of the micelles, the variation of the number of chains within the micelles as a function of temperature can be followed, i.e., micelle formation, during cooling, and micelle decomposition, during heating can be observed. At the same time measurements of R_h at each temperature where conducted which where also reproducible. The fact that the intensity and R_h values are reproducible shows that one can arrive to the same micellar state either by cooling or by heating. This in turn leads to the conclusion that the structures formed in the solutions of these copolymers are equilibrium ones and interconversion between different species is possible and can be accomplished reversibly by changing temperature.

Another important parameter of micellar systems following the model of closed association is the existence of a critical micelle concentration (cmc).[1−3] Below this concentration only unimers (unimolecular dissolved chains) exist whereas beyond cmc micelles and unimers can be found in the block copolymer solution. Conversely, the observation of a cmc is evidence that the system follows the closed association model of micellization. Unfortunately, a cmc observation was not possible although measurements where extended to the lowest concentrations possible as determined by the accuracy of the techniques used. Apparently all systems studied have a very low cmc, outside the experimentally accessible concentration range. Indirect evidence of the existence of a cmc was observed only in the case of sample ITMB-3 based on the upward curvature of the static and dynamic light scattering plots at lower concentrations, typical for systems following the closed association model, as mentioned earlier. Although the upward curvature in Figures 1 and 2 for sample ITMB-3 does not necessarily indicate a closed association mechanism (this pattern can be also observed in systems following the open association model), an open association mechanism is highly improbable in this case, if one takes into account the experimental results on other block copolymer systems.[1,2] The observation of a cmt also supports the assumption of a closed association mechanism being operative in the systems under study, as explained below.

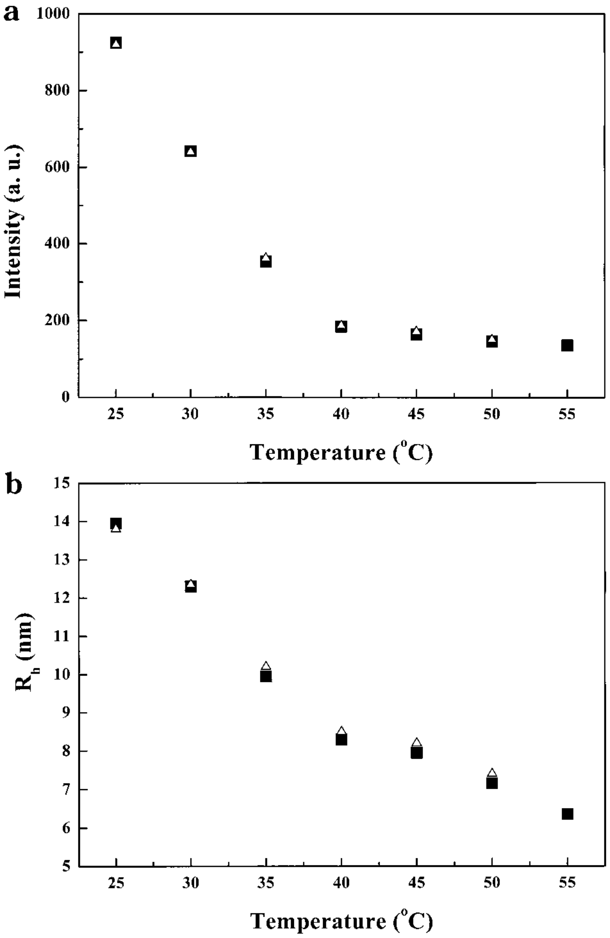


Figure 4. (a) Intensity vs temperature plot for sample ITMB-3 in *n*-decane: (■) heating, (△) cooling. (b) R_h vs temperature plot for the same sample: (■) heating, (△) cooling. The concentration of the solution is 1×10^{-2} g/mL.

Alternatively, the critical micellization temperature (cmt) can be determined. The cmt can be defined as the temperature at which micelles no longer exist at a certain concentration. In principle, if the cmts for two samples are determined at the same concentration and the cmt for the first is larger than that of the second, it is expected that the cmc for the first is lower than the cmc of the second.[1−3] The determinations of cmt for samples SI-2 and ITMB-3 are shown in Figures 5 and 6, respectively. It can be seen that the micelles of the normal diblock copolymer show a cmt of ~46 °C whereas the cmt for ITMB-3 is ~40 °C although the concentration is almost 3 times higher in the second case. This is another experimental evidence that the cmc of ITMB-3 must be larger than the cmc of SI-2. This finding supports the conclusions drawn from the static and dynamic light scattering diagrams vs concentration.

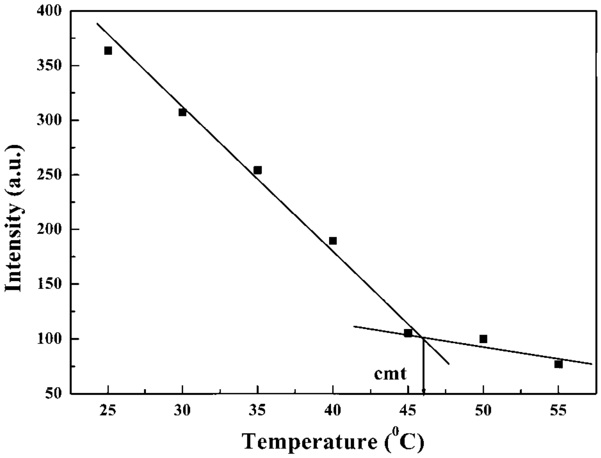


Figure 5. Intensity vs temperature plot, during heating, for sample SI-2 ($c = 3 \times 10^{-3}$ g/mL in *n*-decane).

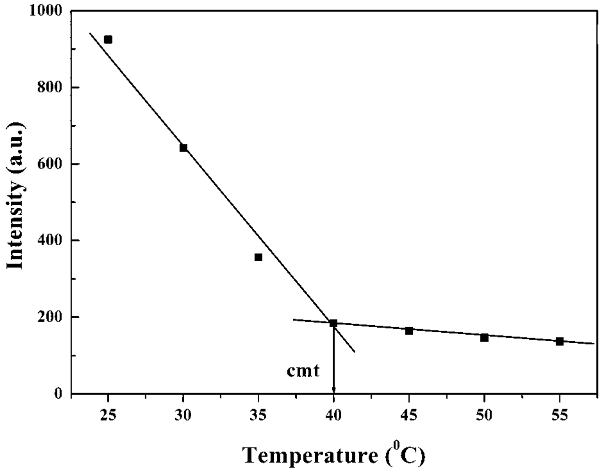
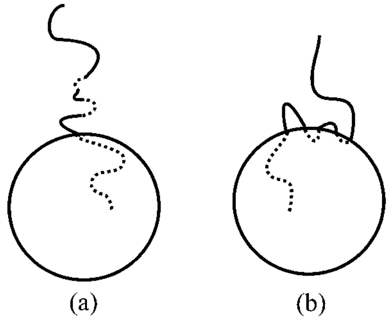


Figure 6. Intensity vs temperature plot, during heating, for sample ITMB-3 ($c = 1 \times 10^{-2}$ g/mL in *n*-decane).

The observations reported so far lead to the conclusion that the differences in the monomer arrangement of the linear copolymers studied can induce differences in the micellization behavior. The way styrene and isoprene segments are arranged in the macromolecular chain produces, when these chains are dissolved in a selective solvent, micelles with different aggregation numbers and sizes. However, no change in the shape of the micelles formed is supported by the results presented. The micelles remain spherical in all cases. Presumably, the existence of a middle block with variable composition between the pure PS and PI blocks makes the interfacial region between the core and the shell of the micelles more diffuse in comparison with pure PS-PI micelles. This enables solvent molecules to penetrate easier in this region and alter the solubility behavior of the whole chain. This in turn has a noticeable effect on the characteristic properties of the micelles, i.e., decreases the aggregation number and their size. The phenomenon is more pronounced in the case of block copolymers with a long inverse tapered middle block due to the dissymmetry in the placement of segments. In this case long sequences of styrene monomers are close to pure PI block, and long sequences of isoprene monomers are close to the PS pure block. A similar effect must be present in the case of sample TBC. However, despite the fact that the aggregation number is lower in the latter case, the increase in cmc is not found to be so much different as in the case of ITMB-3. In the case of triblock copolymers with a normal tapered middle block the composition variation is more gradual, causing less frustration to the chains in the micelles.

Scheme 2



Coming back to the case of inverse tapered block copolymer micelles, one would wonder about the specific conformation of an individual chain within a micelle. Although drawing direct conclusions about this question from the experimental evidence at hand is not possible, we will try to come to a semiqualitive conclusion by comparing the data on SI-1, SI-2, and ITMB-3 micelles. In principle, two different conformations are possible for an ITMB chain: either an extended conformation (Scheme 2a) or the one where the middle block forms loops at the core–corona interfacial region (Scheme 2b). In the first case the blocky sequences of styrene are brought in contact with *n*-decane, a situation that is energetically unfavorable due to the fact that *n*-decane is a bad solvent for PS. In the second case the formation of loops increases the free energy of the system, due to loss in configurational entropy, but the incorporation of the blocky styrene sequences into the micellar core may compensate for at least some of this free energy increase. Using this simple way of thinking, the second possibility (Scheme 2b) seems more probable.

In terms of micellar characteristics (aggregation number and size of the micelles formed in each case) the experimental data are in summary $N_{\mathrm{w,ITMB-3}} < N_{\mathrm{w,SI-1}} < N_{\mathrm{w,SI-2}}$ for the aggregation numbers (Table 2) and $R_{\mathrm{h,ITMB-3}} \sim R_{\mathrm{h,SI-1}} < R_{\mathrm{h,SI-2}}$ in terms of micellar radii (Table 3), while from the molecular characterization and synthesis $M_{\mathrm{total,ITMB-3}} \sim M_{\mathrm{total\ SI-2}}$ and $M_{\mathrm{PI,ITMB-3}} \sim M_{\mathrm{PI,SI-1}}$ and $M_{\mathrm{PS,ITMB-3}} \sim M_{\mathrm{PS,SI-1}}$ (i.e., SI-1 equals the molecular weight of ITMB-3 without the middle tapered block, Table 1). One can assume that both chain conformations are associated with a smaller aggregation number, compared to the case of a pure diblock (SI-2). In the case of Scheme 2a, the situation resembles that of a diblock copolymer with a PS core forming block equal to the PS block of ITMB-3 and a corona forming block (soluble part) equal to the sum of the tapered middle block and the pure PI block of ITMB-3. According to the scaling laws,[2] this copolymer would form micelles having a lower aggregation number than those of SI-2. In the case of Scheme 2b, the aggregation number should be smaller due to the additional constrains imposed by the looped conformation (similar to the case of triblock[1−3] and H and π-shaped copolymers[14]). Therefore, the relation for aggregation numbers found by experiment maybe fulfilled for both situations. At this point one should also have in mind the similarity between star polymers and starlike spherical micelles. In the case of star polymers with high functionality ($f > 6$) the overall size depends on the length of the arms comprising the star molecule and not the number of arms.[30,33] Consequently, one would expect that the overall size of starlike spherical micelles would be primarily determined by the length of the unimer chain (to be more exact, by the length of the soluble block, i.e., the thickness of the corona) and to a lesser extent by the aggregation number. (Of course, in the case of micelles the size of the core also contributes to the overall size, but its dependence on the number of monomers in the chain is weaker.[2]) In light of these arguments, one arrives at the rough conclusion that the size of the micelle where the ITMB-3 chains form loops should be smaller than that of SI-2 micelles and actually closer to the size of SI-1 micelles, where the middle block is absent. This is truly the case (Table 3). In other words, if the middle block of ITMB-3 forms loops, it would not contribute significantly to the size of the micelles. The size of these micelles should be close to the size of the pure diblock SI-1 micelles having the same length of pure blocks. Therefore, it seems likely to us that the preferred conformation of an individual chain in an ITMB-3 micelle is that depicted in Scheme 2b.

Conclusions

A series of tapered block copolymers of styrene and isoprene with different arrangement of the segments were synthesized by anionic polymerization high-vacuum techniques. Molecular characterization of the materials showed their low degree of molecular weight and compositional heterogeneity. The experimental results on the micellization behavior of these block copolymers in *n*-decane, a selective solvent for the polyisoprene blocks, tend to the conclusion that aggregation number and size of the micelles decrease in the case of a triblock copolymer having an inverse tapered middle block (sample ITMB-3) and of a tapered copolymer (sample TBC) compared to a pure diblock copolymer of similar molecular weight and composition (sample SI-2). The cmt for ITMB-3 was also found to be increased compared to the SI-2 case. Undoubtedly, by altering the sequence of the segments in the macromolecular chains, control over the size, and possibly the microstructure of the micelles formed, can be exercised.

Acknowledgment. Financial support from the European TMR network “Complex Architectures in Diblock Copolymer Based Polymer Systems” (Contract FMRX-CT97-0112, DG 12-DLCL) and the Graduate Educational Program on “Polymer Science and its Applications” financed by the Greek Ministry of Education is gratefully acknowledged.

References and Notes

(1) Tuzar, Z.; Kratochvil, P. *Surf. Colloid Sci.* **1993**, *15*, 1.
(2) Hamley, I. A. *The Physics of Block Copolymers*; Oxford University Press: Oxford, 1998.
(3) Webber, S. E.; Munk, P.; Tuzar, Z. *Solvents and Self-Organization of Polymers*; NATO ASI Series, Vol. E327; Kluwer Academic Publishers: Dordrecht, 1996.
(4) Moffitt, M.; Khougaz, K.; Eisenberg, A. *Acc. Chem. Res.* **1996**, *29*, 95.
(5) Stejskal, J.; Hlavata, D.; Sikora, A.; Konak, C.; Plestil, J.; Kratochvil, P. *Polymer* **1992**, *33*, 3675.
(6) Bahadur, P.; Sastry, N. V.; Marti, S.; Riess, G. *Colloids Surf.* **1985**, *16*, 337.
(7) Oranli, L.; Bahadur, P.; Riess, G. *Can. J. Chem.* **1985**, *63*, 2691.
(8) Antonietti, M.; Heinz, S.; Schmidt, M.; Rosenauer, C. *Macromolecules* **1994**, *27*, 3276.
(9) Forster, S.; Zisenis, M.; Wenz, E.; Antonietti, M. *J. Chem. Phys.* **1996**, *104*, 9956.
(10) Calderara, F.; Riess, G. *Macromol. Chem. Phys.* **1996**, *197*, 2115.
(11) Antonietti, M.; Forster, S.; Oestreich, S. *Macromol. Symp.* **1997**, *121*, 75.
(12) Prochaska, K.; Glocker, G.; Hoff, M.; Tuzar, Z. *Makromol. Chem.* **1984**, *185*, 1187.
(13) Bayer, U.; Standler, R. *Macromol. Chem. Phys.* **1994**, *195*, 2709.
(14) Pispas, S.; Hadjichristidis, N.; Mays, J. W. *Macromolecules* **1996**, *29*, 7378.
(15) Iatrou, H.; Willner, L.; Hadjichristidis, N.; Halperin, A.; Richter, D. *Macromolecules* **1996**, *29*, 581.
(16) Tsitsilianis, C.; Papanagopoulos, D.; Lutz, P. *Polymer* **1995**, *36*, 3745.
(17) Ramzi, A.; Prager, M.; Richter, D.; Efstratiadis, V.; Hadjichristidis, N.; Young, R. N.; Allgaier, J. B. *Macromolecules* **1997**, *30*, 7171.
(18) Pispas, S.; Poulos, Y.; Hadjichristidis, N. *Macromolecules* **1998**, *31*, 4177.
(19) Pispas, S.; Hadjichristidis, N.; Potemkin, I.; Khokhlov, A. *Macromolecules* **2000**, *33*.
(20) Smith, S. D.; Ashraf, A.; Clarson, S. J. *Polym. Prepr.* **1993**, *34*, 672; **1994**, *35*, 467. (b) Ashraf, A.; Smith, S. D.; Satkowski, M. M.; Spontak, R. J.; Clarson, S. J.; Lipscomb, G. G. *Polym. Prepr.* **1994**, *35*, 581. (c) Smith, S. D.; Ashraf, A.; Satkowski, M. M.; Spontak, R. J. *Polym. Prepr.* **1994**, *35*, 651.
(21) Tsukahara, Y.; Nakamura, N.; Hashimoto, T.; Kawai, H. *Polym. J.* **1980**, *12*, 455.
(22) Hashimoto, T.; Tsukahara, Y.; Kawai, H. *Polym. J.* **1983**, *15*, 699.
(23) Hashimoto, T.; Thukahara, Y.; Tachi, K.; Kawai, H. *Macromolecules* **1983**, *16*, 648.
(24) Annighofer, F.; Gronski, W. *Colloid Polym. Sci.* **1983**, *261*, 15.
(25) Laurer, J. H.; Smith, S. D.; Samseth, J.; Mortensen, K.; Spontak, R. J. *Macromolecules* **1998**, *31*, 4975.
(26) Hodrokoukes, P.; Floudas, G.; Pispas, S.; Hadjichristidis, N. *Macromolecules* **2001**, *34*, 650.
(27) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211.
(28) Morton, M.; Elis, F. R. *J. Polym. Sci.* **1962**, *61*, 25. (b) Morton, M.; Fetters, L. *J. Rubber Chem. Technol.* **1975**, *48*, 359.
(29) Antkowiak, T. A.; Oberster, A. E.; Halasa, A. F.; Tate, D. P. *J. Polym. Sci., Part A-1: Polym. Chem.* **1972**, *10*, 1319. (b) Wofford, C. F.; Hsieh, H. L. *J. Polym. Sci., Part A-1: Polym. Chem.* **1969**, *7*, 461.
(30) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(31) Roovers, J.; Martin, J. E. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 2513.
(32) Khougaz, K.; Astafieva, I.; Eisenberg, A. *Macromolecules* **1995**, *28*, 7135.
(33) Roovers, J., Mishra, M. K., Kobagashi, S., Eds.; *Star and Hyperbranched Polymers*; Marcel Dekker: New York, 1998.

MA011331E