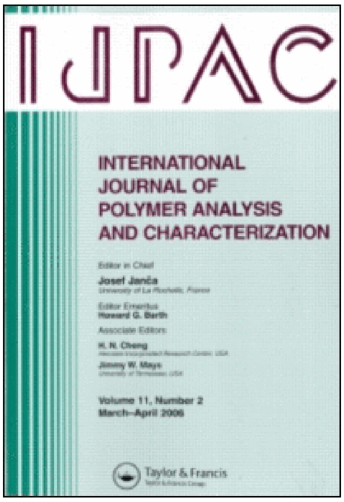

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Micellization of a Novel Type of Hydrophilic/Hydrophobic Block Copolymers

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Hydrophilic/hydrophobic block copolymers, which consist of hydrophilic blocks containing carboxylated polystyrene or poly(4-methylstyrene) chains, resist micellization by routine procedures. Micellization may be achieved in the presence of tris (2-hydroxyethyl)amine (THEA). Apparently, in a THF/water mixture. THEA with carboxyls forms tight ionic pairs that are quite hydrophilic and keep the micelles in solution. The resulting micelles could be transferred into water, aqueous LiCl, and THEA buffer solutions. They were characterized by static and dynamic light scattering and their properties were shown to conform to a typical behavior expected for micellar solutions.

Keywords: Hydrophilic/hydrophobic block copolymers; Polymeric micelles; Static and dynamic light scattering

INTRODUCTION

Hydrophilic/hydrophobic block copolymers can associate in aqueous media into multimolecular, mostly spherical micelles with cores formed by hydrophobic blocks and shells by hydrophilic blocks.[1–3] Various types of block copolymers have been explored, differing in molar mass, composition, glass-transition temperature T_g and polarity

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of hydrophobic blocks, and the chemical nature (neutral, cationic, anionic, or zwitterionic) of the hydrophilic blocks.[4–9] If a water-insoluble block is only slightly hydrophobic (as poly(propylene oxide) in Pluronic® -type copolymers) or is relatively short with respect to the hydrophilic block, then such a copolymer would dissolve directly in water or aqueous buffers and form equilibrium micelles.[1] Otherwise, micelles must first be prepared in a mixture of water with some organic cosolvent and then transferred into water.[8] Micelles prepared this way are in a nonequilibrium 'frozen' state.[1, 10]

In our recent paper,[11] a novel method of the preparation of hydrophilic/hydrophobic block copolymers was described, consisting of a selective multisite substitution in block copolymers with hydrophilic groups (*e.g.*, carboxyls) in the blocks with a higher C—H acidity. The method involves two steps: (i) a multisite metalation of the more reactive block by a Superbase, prepared from 3-(lithiomethyl)-heptane and potassium *tert*-pentoxide in cyclohexane, and (ii) reaction of the metalated intermediate with an electrophile, for example, carbon dioxide, *in situ*.[11, 12] Two types of copolymers were treated this way: Polystyrene-*block*-hydrogenated polydienes and polystyrene-*block*-poly (4-methylstyrene). The polystyrene block in the first copolymer type and the poly(4-methylstyrene) block in the second were selectively substituted with carboxyl groups. The location of the substituents was on the aromatic rings in the polystyrene blocks and on the benzylic sites in 4-methylstyrene blocks.

In this communication we report on the formation and properties of micelles of four block copolymer samples: two diblock copolymers with a hydrogenated polyisoprene (PIH) block and a carboxylated polystyrene (PSC) block (PSC-*b*-PIH(I) and PSC-*b*-PIH(II)), one triblock copolymer with a middle hydrogenated polybutadiene (PBH) block and outer carboxylated polystyrene blocks (PSC-*b*-PBH-*b*-PSC), and one diblock copolymer with a polystyrene block and a carboxylated poly(4-mehyl-styrene) (PMSC) block (PMSC-*b*-PS).

EXPERIMENTAL SECTION

Copolymer Samples

PSC-*b*-PIH(I), PSC-*b*-PIH(II), and PSC-*b*-PBH-*b*-PSC copolymers were prepared from the commercial products (Shell Co., Houston.

Texas) Shellvis® 40, Shellvis 50, and Kraton® G-1650, respectively. PMSC-*b*-PS was prepared from a block copolymer of styrene and 4-methylstyrene. The latter copolymer was synthesized by successive anionic copolymerization in tetrahydrofuran at −78°C using benzylpotassium as an initiator. Characteristics parameters of the carboxylated samples are given in Table I. Metalation and carboxylation of the copolymers are described in Ref. [11] ^{1}H NMR, elemental analysis, and the alkalimetric titration showed that the degree of carboxylation was about 90% of the repeat units susceptible of substitution.[11]

Static Light Scattering (SLS)

Measurements of the molar mass of the micelles were performed on a Sofica instrument equipped with a He-Ne laser. Data were treated by the standard Zimm method. Refractive index increments of micelles in water were determined using a Brice-Phoenix differential refractometer. In LiCl and buffer solutions, refractive index increment values were measured after dialysis equilibrium between a solvent and the solution was established. A custom-made dialyzer was used consisting of two cells having fixed volumes and Spectra/Por® (Houston, Texas) Molecularporous Dialysis Membranes. The procedure was described in detail earlier.[13]

Dynamic Light Scattering (DLS)

Measurements were made using an ALV 5000 (Langen, Germany), multibit, multitau autocorrelator and an argon-ion laser ($\lambda_0 =$ 514.5 nm). The hydrodynamic radii R_H were obtained from diffusion

TABLE I Molar mass, polydispersity, and mass fraction of hydrophobic units of hydrophilic/hydrophobic block copolymers

Sample	$M_w \times 10^{-3}$ $g\ mol^{-1}$	M_w/M_n	w_{hphob}	$M_{hphob} \times 10^{-3}$ $g\ mol^{-1}$
PSC-*b*-PIH(I)	200	1.10	0.69	138
PSC-*b*-PIH(II)	95	1.05	0.51	48
PSC-*b*-PBH-*b*-PSC	84	1.07	0.59	50
PMSC-*b*-PS	143	1.02	0.71	102

w_{hphob} and M_{hphob} are mass fraction and molar mass of hydrophobic units in a copolymer, PS is polystyrene, PSC is carboxylated polystyrene, PMSC is carboxylated poly(4-methylstyrene), PBH is hydrogenated polybutadiene, and PIH is hydrogenated polyisoprene.

coefficients using Stokes–Einstein relation. Polydispersity (PD) was obtained from the second cumulant.[14]

RESULTS AND DISCUSSION

Isolated solid hydrophilic/hydrophobic copolymers under study were not soluble/dispersable either in pure water or in any aqueous buffer. However, the tris(2-hydroxyethyl)amonium (THEA) salt of carboxylated copolymers could be prepared in 50% aqueous THF, giving rise to a micellar solution of the THEA salt. From this THF/water mixture the micelles could be transferred into pure water or an aqueous buffer by a stepwise dialysis as described below.[8, 10]

Micelle solutions of all copolymer samples were prepared as follows: First, stock molecular solutions ($c = 2 \times 10^{-2}\,\mathrm{g\,mL^{-1}}$) of carboxylated copolymers in THF were mixed with an equal volume of an aqueous solution of tris(2-hydroxyethyl)amine (THEA). The amount of THEA in this solution was equal to 1.3 equivalents of the carboxyls. The micelles were formed in this step. During stepwise dialysis, solvent mixtures THF/(THEA/HCl buffer pH 8) with a decreasing THF content were used. Once in a THF-free buffer, the micelles survived with unchanged molar mass (*i.e.*, association number) when transferred into pure water or into a LiCl aqueous solutions by dialysis. Surprisingly, the procedure of the THF removal is successful only when the THEA/HCl buffer (minimum pH 8) was used. When any other buffer (*e.g.*, phosphate or borate) is employed, the copolymer precipitates. Freeze-dried sample of the micellar solution in water after dialysis did not contain any traces of nitrogen, proving that THEA was removed from the micellar solution completely. These micellar solutions were investigated by SLS and DLS. Micelle molar mass M_w, association number n, hydrodynamic radius R_H, and polydispersity of micelle sizes PD, are presented in Table II.

The association numbers of the three samples with micelle cores formed by aliphatic chains are related among themselves as expected. Sample PSC-*b*-PIH(I), which has a high unimer mass and low weight fraction of the hydrophilic block, exhibits a much higher association number than the smaller, more hydrophilic copolymer PSC-*b*-PIH(II). The triblock copolymer PSC-*b*-PBH-*b*-PSC which has a similar mass

TABLE II Micelle molar mass $M_w^{(m)}$, association number n (in 0.1 M LiCl), and hydrodynamic radius R_H and polydispersity PD (from the cumulants method), in three solvents

	$M_w^{(m)} \times 10^{-6}$		R_H *(nm)/PD*		
Sample	*g mol*$^{-1}$	*n*	H_2O	0.1 *M LiCl*	*THEA-buf.*
PSC-*b*-PIH(I)	26.0	130	48/0.10	56/0.06	66/0.05
PSC-*b*-PIH(II)	7.3	76	23/0.08	31/0.06	39/0.04
PSC-*b*-PBH-*b*-PSC	5.2	62	14/0.05	18/0.05	23/0.05
PMSC-*b*-PS	5.6	39	22/0.08	22/0.05	30/0.05

of the core block as the PSC-*b*-PIH(II) sample, but less hydrophilic, shows a smaller association number. This is a clear manifestation of its triblock character. We have observed similar trends in block copolymer micelles formed by copolymers of styrene and methacrylic acid dissolved in dioxane/water mixtures.[15]

The hydrodynamic radii R_H of the three samples also show (in all three solvents) the expected trends. Less massive micelles of PSC-*b*-PIH(II) have smaller R_H than much more massive PSC-*b*-PIH(I) micelles. The triblock micelles have smaller R_H because their shell blocks are less than half as long as the blocks in PSC-*b*-PIH(II).

The micelles formed by the rather large copolymer PMSC-*b*-PS with relatively short shell blocks do not seem to conform to the same picture. However, the chemical nature of this copolymer is quite different from the former three copolymers. Its relevant structural and thermodynamic properties may consequently lead to different micelle sizes. Nevertheless, rather short shell chains manifest themselves in a relatively small R_H.

Besides the fundamental information about the association numbers, our experiments give several interesting insights into the shell–solvent interaction. Let us look first into the process of micelle formation and compare it with the system polystyrene-*b*-poly (methacrylic acid) (PS-*b*-PMA) which we have studied extensively in the past.[15] The present copolymers are molecularly dissolved in pure THF. Similarly, the PS-*b*-PMA copolymers are soluble in pure dioxane. Upon addition of water the mixed solvent becomes a poor solvent for the hydrophobic block (PIH, PBH, or PS in present experiments, PS in PS-*b*-PMA studies)–a precondition for micellization. While micellization occurs readily for the PS-*b*-PMA copolymers, a special procedure using THEA is necessary for the present copolymers. In our opinion, the difference is caused by the interactive properties of the carboxyl-containing blocks. There are only three aliphatic carbons in a monomeric unit of poly(methacrylic acid) (PMA) *per* one carboxyl. Consequently, PMA interacts rather strongly with water, and mixed dioxane/water solvents behave as classical selective solvents for PS-*b*-PMA copolymers. However, in the present copolymers, in addition to two or three aliphatic carbons, a rather hydrophobic phenylene moiety accompanies each carboxyl. Consequently, the so-called hydrophilic block is actually quite hydrophobic and its dissolution in aqueous mixtures must be facilitated.

Seemingly, the obvious choice would be the conversion of the carboxylated chains into polyelectrolytes, for example by adding a high-pH buffer to the solvent mixture. Surprisingly, the addition of phosphate or borate buffers does not help. We assume that this is because of the low dielectric constant in THF/water mixtures as compared to that of pure water. Under these circumstances, the attraction between the ionized carboxyls and the counterions is strong and they have a tendency to form tight pairs. In other words, the system shows something between polyelectrolyte and ionomeric behavior. This situation does not help the dissolution of the carboxylated blocks.

However, when the counterion is THEA, the pair is strongly hydrophilic (it contains three hydroxyls *per* a carboxyl group) and succeeds in keeping the block in solution. However, there is a need to explain the behavior of the copolymers in aqueous solvents in the absence of any organic solvent. The copolymers are not soluble in water or any buffer. This is a behavior common to all block copolymers with hydrophobic blocks that have no affinity to water (PIH, PBH, PS, *etc.*, but not poly(propylene oxide) as in Pluronic® type copolymers). However, the micelles formed in mixed solvents may be freed from the organic co-solvent by dialysis. By extensive dialysis, the THEA buffer is quantitatively removed and the micelles still remain in solution. What prevents their precipitation? Apparently, in water (high dielectric constant) the carboxyls may partially dissociate (probably only to a very small degree), some of the hydroxontum ions may escape into the surrounding water (large increase of translational entropy), and the resulting repulsion of negatively charged micelles may keep them in solution. Nevertheless, the effect is weak as is manifested by small R_H in pure water.

The well-known capability of lithium salts to interact with polar groups makes the carboxylated chains more soluble resulting in an increase of R_H. In buffers with high pH, the micelles behave like other micelles with polyelectrolyte shells (*e.g.*, the PS-*b*-PMA micelles [14]) and their R_H increases significantly. It should be emphasized that aqueous buffers have a dielectric constant close to that of water and that the effect of reduced dielectric constant (that played a role in THF/water mixed solvents) is not present.

CONCLUSIONS

Two diblock copolymers with hydrogenated polyisoprene blocks and carboxylated polystyrene blocks, one triblock copolymer with hydrogenated polybutadiene middle block and carboxylated polystyrene blocks, and one diblock copolymer with polystyrene and carboxylated poly(4-methylstyrene) blocks were induced to form micelles by mixing molecular solutions in THF with aqueous solutions of THEA. These micelles could be transferred into water, LiCl aqueous solution, and THEA buffer by stepwise dialysis. It is assumed that the cores of the micelles are formed by hydrophobic blocks (hydrogenated polydiene or polystyrene) and the shells by carboxylated polystyrene or carboxylated poly(4-methylstyrene) blocks. Static and dynamic light scattering data showed that micelle molar mass depends on both molar mass and chemical composition of the copolymers and that hydrodynamic radii of micelles are determined by the swelling of the shells. An explanation was offered of the peculiar behavior of the copolymers during the micellization process, as well as of the dependence of the expansion of the micelle shells on the nature of the aqueous solvent.

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