BLOCK COPOLYMER MICELLES IN AQUEOUS MEDIA

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Received February 25, 1993
Accepted April 30, 1993

Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Micellization of di- and triblock copolymers, poly(methacrylic acid)-*block*-polystyrene and poly(methacrylic acid)-*block*-polystyrene-*block*-poly(methacrylic acid), varying in molecular weight and composition, has been studied by static and dynamic light scattering, and sedimentation velocity. Micelles with polystyrene cores were prepared in water–dioxane mixtures, rich in dioxane, and transferred into water-rich mixtures, water, and aqueous buffers via stepwise dialysis. It has been shown that, in dioxane-rich mixtures, the micellar system was in dynamic equilibrium, while in water-rich solvents, in water, and in aqueous buffers the micellization equilibrium was frozen and micelles behaved like autonomous particles. Under certain conditions, micelles were accompanied by independent large particles. This phenomenon, known from other micellar systems as an "anomalous micellization", is discussed.

Colloidal properties of block copolymers in selective solvents (thermodynamically good for one block, poor for the other) remind of those known from aqueous solutions of soaps and surfactants. Block copolymers form fairly uniform spherical micelles, the cores of which consist of insoluble blocks, while soluble blocks form protective shells[1]. These micelles can solubilize substances otherwise insoluble in a given solvent, "compatibilize" immiscible substances, both low-molecular-weight and polymeric. Polymer micelles are a specific state of polymeric matter with a number of interesting structural features and properties. They are interesting not only from the viewpoint of academic research, but their properties are operative in, e.g., formulations for motor oil additives, tertiary oil recovery, and compatibilization of polymer blends. Lately, polymer micelles have been explored as a promising material for the uptake and controlled release of organic substances from and into aqueous media, with potential applications in pharmacology, agriculture and ecology[2].

Micellization of block copolymers obeys a model of what is called closed association[3], characterized by an equilibrium between unimer (molecularly dissolved copolymer) and micelles. Micelle association number (i.e., the number of copolymer molecules forming a micelle) is typically from several tens to several hundreds. Micellar static and dynamic parameters, kinetics of micelle formation and dissociation, and the dynamics of micellar equilibria depend on many factors, such as chemical nature and lengths of copolymer blocks, thermodynamic quality (specificity) of the solvent system, copolymer concentration, temperature, etc.[4].

Until recently, most of the studies on polymeric micelles were done using organic selective solvents and block copolymers of styrene and dienes, or styrene and acrylates, which are available as commercial products or can be relatively easily prepared in laboratory[1]. Only in recent years, proper attention has been paid to micelles of hydrophilic/hydrophobic block copolymers in water. Two types of such copolymers have been studied: di- and triblock copolymers of ethylene oxide and propylene oxide (e.g. refs[5,6]) known as commercial products Poloxamers and Pluronics, and laboratory-prepared di- and triblock copolymers of ethylene oxide and styrene (e.g. refs[7,8]). These systems combine the thermodynamic and interfacial properties of strongly hydrophilic/strongly hydrophobic low-molecular weight substances (like soaps and surfactants) with the stability and structures that are based on long polymeric chains.

The aim of this paper is to summarize the results based on a three-years' cooperation of authors' laboratories on the structure and properties of micelles with polystyrene cores and poly(methacrylic acid) shells. New results concerning anomalous micellization are included.

Copolymers

Poly(methacrylic acid)-*block*-polystyrene (AS) and poly(methacrylic acid)-*block*-polystyrene-*block*-poly(methacrylic acid) (ASA) samples were prepared by sequential anionic polymerization[9,10]. First, di- and triblock copolymers of styrene and *tert*-butyl methacrylate were prepared in tetrahydrofuran using cumylpotassium and potassium naphthalenide as initiators, respectively. The *tert*-butyl groups were then hydrolyzed by aqueous hydrochloric acid in dioxane. The resulting AS and ASA copolymers were precipitated in cold hexane, redissolved in dioxane and freeze-dried. The completion of hydrolysis was checked and the mass fraction of styrene units, w_{PS}, was determined by NMR. Molecular weights, M_w, and the M_w/M_n ratio, were determined by static light scattering and size exclusion chromatography, respectively[9,10]. A great number of AS and ASA copolymers were prepared with M_w ranging from $7 . 10^3$ to $1.3 . 10^5$, w_{PS} from 0.41 to 0.80, M_w/M_n for all samples being less than 1.15.

Micelle Formation

As a rule, block copolymers in selective organic solvents form micelles by direct dissolution. In some cases, formation of equilibrium micelles (defined by the minimum of the Gibbs function of a given micellar system) must be assisted by heating the given solutions[1]. Micelles of our samples as well as those of block copolymers of styrene and ethylene oxide, can be obtained by direct dissolution in water only when M_w of the particular copolymer is lower than ca $2.5 \cdot 10^4$ and w_{PS} is lower than ca 0.2. None of our AS and ASA samples could thus form micelles directly in water. However, all samples micellize when dissolved in aqueous mixtures with an organic cosolvent which alone is a good solvent for polystyrene like tetrahydrofuran or dioxane.

The AS and ASA copolymers under study showed similar pattern of solution behaviour in aqueous dioxane[9]: (i) There exists a certain solvent composition range for each sample where equilibrium micelles with polystyrene cores and poly(methacrylic acid) shells are formed. The higher the values of M_w and w_{PS}, the higher content of dioxane is needed. In dioxane-poor solvent mixtures, copolymer samples are insoluble even upon heating. (ii) Although dioxane is a nonsolvent for poly(methacrylic acid), it dissolves practically all copolymer samples molecularly. (iii) In mixtures with 5 to 10 vol.% water, most samples give milky-white solutions which, in some cases, undergo a macrophase separation. This phenomenon is discussed below. (iv) Equilibrium micelles formed in water–dioxane mixtures can be transferred into water or aqueous buffers by stepwise dialysis.

Micelle Structure

Molecular weights of micelles were measured by static light scattering. Refractive index increments were determined by differential refractometry; when mixed solvents were employed, measurements were performed under conditions of dialysis equilibrium between polymer solutions and a mixed solvent[9,11]. Hydrodynamic radii were measured by dynamic light scattering as described in refs[9,12].

Equilibrium micelles in dioxane-rich mixtures were fairly uniform ($M_w/M_n < 1.15$), their association number, n, was determined to range from 40 to 320. Selected results in Table I demonstrate that n is higher for diblock copolymers in comparison with triblock ones of comparable M_w and w_{PS}; for both AS and ASA samples n is the higher, the higher is M_w and w_{PS}, as expected from theory[4,13].

In various water–dioxane solvent mixtures, the hydrodynamic radius, R_h, is controlled by two competing effects: by swelling of polystyrene cores by dioxane and by swelling of the poly(methacrylic acid) shells by water. The first effect seems to be stronger, since R_h decreases with decreasing amount of dioxane in the mixture[9,14] (Table II). In dioxane-free solutions, where polystyrene cores are believed to be in the glassy state[12], R_h values depend on the swelling of the shells only: With increasing pH, the dissociation degree of the carboxyl groups increases and the shell-forming blocks are better solvated (Table II).

Anomalous Micellization

In our first study[9], we reported that micellar solutions in any of the water–dioxane mixtures could not be prepared starting from copolymer solutions in neat dioxane. Both a stepwise dialysis or an addition of water lead to milky-white, unstable, macrophase-separating solutions. Such a behaviour has already been observed (e.g., refs[5,15,16]) and named "anomalous micellization". The effect was explained by the presence of a homopolymer[16] identical with the core-forming blocks, or by the presence of copolymer molecules with a high fraction of the core-forming blocks[5].

TABLE I
Characteristics of poly(methacrylic acid)-*block*-polystyrene (AS) and poly(methacrylic acid)-*block*-polystyrene-*block*-poly(methacrylic acid) (ASA) and association number (n) of their micelles in 80 vol.% aqueous dioxane at 25 °C

Copolymer[a]	M_w	w_{PS}	n
AS-18-0.58	18 700	0.58	59
AS-36-0.77	36 300	0.77	322
AS-40-0.61	40 300	0.61	124
ASA-41-0.79	41 600	0.79	55
ASA-68-0.56	68 700	0.56	44
ASA-68-0.65	68 800	0.65	89

[a] The code numbers denote molecular weight and weight fraction of polystyrene blocks.

TABLE II
Micellar hydrodynamic radii, R_h (nm), of di- and triblock copolymers[a] in various solvents

Solvent	AS-45-0.54	AS-57-0.59	ASA-38-0.57
80% aq. dioxane[b]	24.3	32.7	12.7
60% aq. dioxane[b]	21.8	31.6	13.7
40% aq. dioxane[b]	18.3	26.6	14.2
Water	13.2	23.2	9.7
Citrate buffer, pH 5	25.4	27.2	12.7
Phosphate buffer, pH 7	27.2	35.1	16.8
Phosphate buffer, pH 7.8	29.3	36.1	17.5

[a] See Table I; [b] vol.%.

In the present study we have explored the anomalous micellization with two AS samples AS-35-0.56 and AS-67-0.60 and one ASA sample, ASA-39-0.65 (the first code number is the molecular weight in thousands and the second is w_{PS}). All three samples formed uniform micelles when dissolved directly in 70 – 80 vol.% aqueous dioxane. However, if the copolymers are dissolved in neat dioxane and water is added, the anomaly appears. The following experiment has been performed with each sample: To a dust-free solution ($c = 3 . 10^{-3}$ g/ml) in dioxane, water was added dropwise to obtain mixtures with 95, 90, 85, 80, and 70 vol.% dioxane. Each solution was stirred during the addition of water, left for 15 min, and measured by dynamic light scattering; then more water was added, etc. Measurements were performed with an ALV 5000 multibit multitau correlator. Autocorrelation curves have been treated by an inverse Laplace transform to get spectra of the decay times as described in ref.[17]. Since all three samples showed the same pattern, data for only one sample are given in Fig. 1.

In neat dioxane, only one kind of particles is present in solution, its R_h corresponding to molecularly dissolved copolymer (unimer). In 95 vol.% aqueous dioxane, new particles appear. These particles survive in solutions with increasing content of water, but their relative amount decreases on account of the formation of particles with a size corresponding to regular micelles. R_h values of these micelles decrease with increasing amount of water in a solvent mixture in the same way as with micelles prepared by direct dissolution (cf. Table II). The seemingly contradictory increase of τ with increasing amount of water (Fig. 1) is caused by changes in viscosity and refractive index with

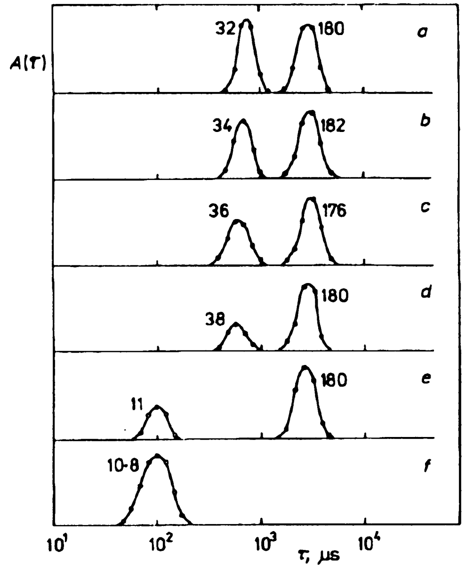

FIG. 1

Distribution of the decay times of copolymer AS-35-0.56 (see Table I) particles prepared by the addition of water to copolymer solutions in dioxane (c 0.003 g/mol) at 25 °C. The curves are denoted by R_h values (nm). ○ Unimer; ● micelles; ◐ large particles. Dioxane (vol.%): *a* 70, *b* 80, *c* 85, *d* 90, *e* 95, *f* 100 the solvent composition. The R_h of all three samples in mixtures with 70 and 80 vol.% dioxane correspond within ±5% to values obtained by direct dissolution of the samples in the respective solvent mixtures. The behaviour described in Fig. 1 did not change even when solutions in sealed ampoules were heated to 100 °C for 30 min and cooled back to 25 °C. When large particles were removed (by spontaneous macrophase separation after several days, by centrifugation or by filtration through 0.2 μm Millipore filters), only regular micelles with unchanged R_h remained in solutions.

Before attempting to interpret the data in Fig. 1, a few facts concerning the large particles should be emphasized: (i) They appear in solutions at a relatively low content of water (5 vol.%) insufficient for regular micellization. (ii) Their polydispersity is comparable with that of regular micelles. (iii) Their R_h does not change with addition of water.

In analogy with our earlier study[16] we assumed that the homopolymer might be responsible for the anomaly. Unfortunately, no homopolymer could be detected in the sample under study by GPC; this means that the content of the homopolymer, if any, must have been below 1 – 2 wt.%. An alternative explanation might be that the large particles are non-equilibrium aggregates that contain a part of the given sample with higher polystyrene content. However, neither hypothesis has been proved, but we work on the solution to this problem. A relatively small polydispersity and a fair stability (for several days) of these particles could be explained by partial steric stabilization by the unimer. The absence of these particles in solutions prepared directly in mixtures with 70 and 80 vol.% of dioxane could be explained by the fact that the macromolecules that aggregated in the absence of regular micelles in 95 vol.% aqueous dioxane, all participated in equilibrium micellization. The existence of dynamic micellar equilibria in 80 vol.% aqueous dioxane has been proved experimentally (see the following section). Experimental evidence of bimodal distributions in a system similar to ours has been reported recently[7].

Dynamics of Micellar Equilibria

The closed association model, confirmed for soaps and surfactants in water[3], as well as for block copolymers in selective organic solvents, implicates a dynamic equilibrium between unimers and micelles. It further implies an exchange of copolymer molecules between unimer and micellar states, and thus also between micelles themselves. Such an exchange has been experimentally proved with polystyrene-*block*-poly(ethylene-*co*-propylene) in aliphatic nonsolvents for polystyrene[18]: Two solutions were prepared, one containing micelles with fluorescence donor-tagged polystyrene blocks, the other with fluorescence acceptor-tagged polystyrene blocks. After mixing, an exchange of unimers led to mixed micelles containing both labels in their cores. The process of mixed micelle formation was monitored as a nonradiative energy transfer. The relaxation time of this process (≈ 10^3 s) was by several orders of magnitude smaller in comparison with that of soaps and surfactants in aqueous solutions.

We assumed[9] that the micelles with polystyrene cores and poly(methacrylic acid) shells prepared by direct dissolution in dioxane-rich solvents were equilibrium structures, while those in water-rich mixtures and in water became frozen during dialysis. In our systems, sedimentation velocity proved to be an effective tool for studying the exchange of unimers between two kinds of micelles with different sedimentation coefficients. Scores of pairs of micelles, including mixtures of diblock and triblock micells, have been studied[14,19]. When mixing two micellar solutions in 80 vol.% aqueous dioxane, one sharp boundary with the value of the sedimentation coeficient in between those of the original micelles appeared in the sedimentation diagram sooner or later (from tens of minutes to tens of days). In solvent mixtures where micelles could not be prepared by direct dissolution but only by dialysis, two sharp boundaries identical with those of parent micelles did not change even during several weeks after mixing the original solutions. This confirmed our idea that micellar equilibria in water-rich mixtures, in water, and in aqueous buffers are kinetically frozen and micelles behave as stable structures.

Some of us (Z. T. and P. M.) acknowledge the support from the Scientific and Environmental Division of the NATO (Collaborative Research Grant # 920166).

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