Polymer Colloids*

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ABSTRACT

Polymer colloids cover a broad spectrum of polymeric materials like macrolattices, microlattices, polymeric membranes, etc. The most important polymer colloids are block and graft copolymer micelles which represent a specific state of polymeric matter with a number of interesting structural features and properties. In this paper, recent development in the field of polymeric micelles is discussed, namely, problems of micelle formation, micelle structure, hydrodynamic properties, micellar equilibria, and solubilization.

Key Words

block copolymer micelles, micellar equilibria, kinetics of micelle formation, solubilization, Hydrodynamic behavior

INTRODUCTION

The term "polymer colloids" may sound controversial. At the beginning of the existence of the polymer science as a new field of chemistry, most chemists claimed that large organic molecules, i.e., macromolecules or polymers, do not exist. 70 years ago, even the most enlightened organic chemists believed that cellulose, proteins and polymers synthesized in laboratory were only colloids, i.e., aggregates of small organic molecules. Later, when the existence of macromolecules was undisputably recognized, polymer science was treated, e.g., in textbooks of physical chemistry, in colloids chapters. That is why some polymer scientists became allergic to the word "colloid" and are reluctant to accept the name of a 30 years old branch of polymer science, polymer colloidics.

Polymer colloids cover a broad field of self-assembling or self-organizing polymeric systems in solutions that possess surface-active or colloidal properties. Basic polymer compounds in polymer colloidics are block and graft copolymers. In selective solvents (good solvents for one block and bad for the other), block and graft copolymers self-assemble into various organized structures, the most prominent ones being multimolecular spherical micelles, cores of which are formed by insoluble blocks and shells by soluble blocks. These micelles can solubilize otherwise insoluble substances, both low-molecular and polymeric. Micelles with extremely swollen cores form microemulsions, microlattices, or stable polymer dispersions.

Due to increasing interest in this field of both experimentalists and theoreticians, the amount of relevant papers has been increasing in the last several years. Various aspects of polymer colloidics have been surveyed from both experimental [1,2] and theoretical [3] point of view. In this article colloidal behavior of block and graft copolymers will be reviewed with the emphasis on the development in the last years.

MICELLE FORMATION

When a typical diblock copolymer, AB, where A and B are blocks differing in chemical nature, each having a molar mass of several tens of thousands, is dissolved in a selective solvent, thermodynamically good for the blocks A and poor for the blocks B, micelles are formed with insoluble blocks B in the core and soluble blocks A in the shell. Numerous

Table 1. Some typical micellar systems.

Copolymer	Solvent (selectively good for)
PS-PMMA	p-xylene (PS)
	aceton (PMMA)
PS-PI	dimethylformamide (PS)
	hexane (PI)
PS-g-PI	decane (PI)
	tetrahydrofuran/heptane (PI)
PS-PB-PS	methyl ethyl ketone
PS-PDMS	decane (PDMS)
PS-hPI	heptane (PhI)
	1,4-dioxane/heptane (PS)
PS-hPB-PS	1,4-dioxane (PS)
PEO-PPO-PEO	water (PEO)
PS-PEO	water (PEO)
PS-PMAc	water (PMAc)

PS..polystyrene, PMMA..poly(methyl methacrylate), PI..polyisoprene, PB..polybutadiene, PDMS..poly(dimethylsiloxane),hPI..hydrogenated polyisoprene, hPB..hydrogenated polybutadiene, PEO..poly(ethylene oxide), PPO..poly(propylene oxide), PMAc..poly(methacrylic acid) -g- stands for graft.

block and graft copolymers have been used in micellar studies [2]. Typical systems are listed in Table 1. Various experimental techniques havebeen employed for their characterization [2] (Table 2).

Like soaps and surfactants in water, block copolymers in selective solvents form micelles via the so-called closed association, characterized by a certain critical micelle concentration (CMC) below which only molecularly dissolved copolymer (called usually unimer in this context) is present in solution and above which multimolecular spherical micelles are in a dynamic equilibrium with the unimer (Fig. 1). In comparison with soaps and surfactants, CMC in block copolymer micellar systems is very small, in most cases even imperceptible [2].

Micellar molar mass or association number, n, (i.e., the number of copolymer molecules in a micelle), core and shell dimensions, dynamics of the micellar equilibrium, and other properties, depend on the chemical nature and lengths of the blocks, on the thermodynamic quality (selectivity) of the given solvent towards both blocks, and on the copolymer architecture. General rules based on theory and confirmed by numerous experiments can be roughly summarized as follows:

- The larger is the number of copolymer blocks, the lower is the association number, n. While diand triblock copolymers AB and ABA in selective solvents for block A form micelles with n typically of several tens or hundreds, multiblock copolymers, e.g., ABABA, or graft copolymers with a backbone A and higher number of grafts B, form micelles with n below 10, or in some cases assume a conformation of so-called unimolecular micelles.

- n increases with increasing molar mass of a given copolymer or with decreasing mass fraction (i.e., the relative block length) of soluble blocks.

- n decreases with increasing solvent power towards insoluble blocks, e.g., in most micellar systems with increasing temperature.

The micellar equilibrium state is given by a minimum of the Gibbs energy of the system. It has been found that polymer micelle formation in organic selective solvents is an enthalpy-driven

Table 2. Experimental methods for micelle characterization.

| Method	Information obtained
(a) Static light scattering	Mass-average molar mass-Radius of gyration
(b) Small-angle X-ray	Weight-average molar mass-Radius of gyration
and neutron scattering	Core radius-Macrolattice structure
(c) Dynamic light scattering	Diffusion coefficient-Hydrodynamic radius
(d) Electron microscopy	Size and shape
(e) Sedimentation velocity	Micelles/unimer mass ratio
(f) Size exclusion chromatography	Dynamics of micellar equilibrium
(g) Stopped flow	Kinetics of micelle formation and dissociation
(h) Steady-state and time-resolved fluorescence	Dynamics of micellar equilibrium-Dynamics on segmental level
(i) Nuclear magnetic resonance	Dynamics on segmental level
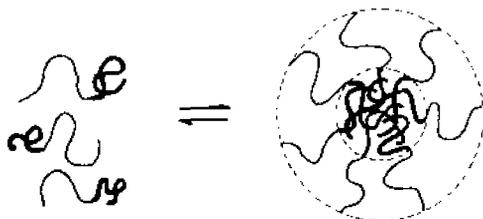
Fig.1. Unimer-micelle equilibrium.

and entropy-controlled process. Surfactant micelle formation is, on the other hand, an entropy-driven process, due to the effect of hydrophobic interactions and the consequent change of water structure [2].

KINETICS OF MICELLE FORMATION

Kinetics of micelle formation and dissociation has been studied by the stopped-flow technique with light scattering detection on di- and triblock copolymers AB and ABA, A being polystyrene and B hydrogenated polybutadiene [4]. Micelle formation was realized by fast mixing of a molecular solution in a good solvent with a precipitant so that the resulting solvent mixture became selectively poor for blocks B. Micelle dissociation was realized by fast mixing of a micellar solution with a good solvent, so that the final solvent mixture became thermodynamically good for both blocks; micelle formation or dissociation were monitored as a build-up or decrease of light scattering intensity, respectively, in time. The results can be summarized as follows:

The relaxation time of micelle formation was on the time scale of tens of ms for both samples. Relaxation time of micelle dissociation for the diblock copolymer was shorter than the dead time of the instrument (1 ms), while for the triblock copolymer it was over 100 ms. The much slower dissociation of triblock copolymer micelles in comparison with diblock copolymer micelles is due to the necessity for one of the outer blocks of leaving triblock molecule to pass through the highly viscous medium of the core, which is moreover incompatible with the side blocks.

DYNAMICS OF THE MICELLIZATION EQUILIBRIUM

Unimer-micelle equilibrium represents a dynamic process, in which copolymer molecules migrate at a given rate between micellar and unimer states, i.e. also, between micelles themselves. Two

experiments have been done so far, probing the dynamics of micellization equilibria, employing the steady-state fluorescence and the sedimentation velocity method.

In the first study [5], diblock copolymer micelles having polystyrene cores and hydrogenated polyisoprene shells with polystyrene blocks labeled by fluorescence donor, were mixed with identical micelles (in the same solvent) labeled by fluorescence acceptor. Exchange of copolymer molecules between micelles was monitored as the nonradiative energy transfer from donor to acceptor moieties. Equilibration process proved to be very complex, and was roughly characterized by two relaxation times: a faster (on the scale of minutes) and a slower one (hours), the concrete values of which depended on the degree of swelling of polystyrene cores.

In the second study [6], two kinds of micelles with different molar masses and sizes (and thus with different sedimentation coefficients) were mixed, and the formation of mixed micelles with an intermediate sedimentation coefficient was monitored with an analytical ultracentrifuge. Two different original concentration boundaries, approaching each other in time, indicated that the equilibration process via exchange of copolymer molecules between smaller and larger micelles proceeds on the time scale of hours.

MICELLE STRUCTURE

Spherical shape and a very narrow size distribution of polymer micelles as well as their core/shell structure have been confirmed directly by electron microscopy [7]. Small-angle x-ray and neutron scattering methods proved that micellar cores are homogeneous spheres [8,9]. Unlike hydrophobic cores of surfactant micelles in water, cores of polymer micelles are practically always swollen. There are exceptions, e.g., polystyrene cores in water. However, such copolymer micelles cannot be prepared directly but, like in case of polystyrene-poly(methacrylic acid), micelles with swollen polystyrene cores are formed by dissolution in a water/organic solvent mixture and then

transferred into water by a stepwise dialysis [10,11].

Micelles with an atypical behavior are formed in solutions of a triblock copolymer ABA (where A is polystyrene and B hydrogenated polybutadiene) in a selective solvent for the middle block, heptane can serve as an example. A thorough study of this system [12] leads to a model in which ca. 30 copolymer molecules are accommodated in a micelle in such a way that the end blocks are in the core and the middle blocks form loops in the shell, and only a few copolymer molecules assume a conformation with one end block in the core and the other stretched out as a tentacle (Fig. 2). This model explained all unusual properties of such systems, like high viscosity and spatial ordering of micelles at relatively low concentrations, complicated spectra of relaxation times, etc. Recently, the proposed model of "tentacled micelles" has been corroborated by Monte Carlo calculations [13].

HYDRODYNAMIC BEHAVIOR

Generally, micellization of block copolymers induced by a change in the thermodynamic quality of solvent is accompanied by a decrease in the solution viscosity due to the compact structure of micelles. This phenomenon is of considerable practical importance. For instance, in solutions of polystyrene-hydrogenated polydiene copolymers in
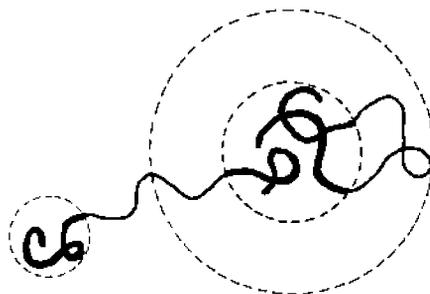

Fig.2. Model of a micelle formed by a triblock copolymer in a selective solvent for the middle block.

mineral oils micellization induced by lowering temperature is accompanied by a drop of the intrinsic viscosity by a factor of five or more. Copolymers of this type are being exploited as viscosity improvers for engine oils.

There is a strong evidence that polymer micelles in dilute solutions behave like hydrodynamic hard spheres: (a) The ratio of the hydrodynamic radius to the radius of gyration of micelles for various systems has been found close to the theoretical value of 1.3 for the hard sphere model [14]. (b) The diffusion virial , coefficient k_D from the equation $D_c/D_o = 1 + k_D \phi$, where D_c and D_o are values of the diffusion coefficient at a at infinite dilution, respectively, and of micelles, also concentration c and is the volume fraction assume the theoretical values for the hard sphere model [15]. Surprisingly, theoretical values have been experimentally found even for micelles with highly swollen shells [15].

Unlike soap micelles, polymer micelles in semidilute solutions do not form rods or lamellae but keep their spherical shape and the same association number as in dilute solution in a given solvent. In comparison with linear polymers, the dilute solution regime, characterized by a small viscosity and a small change of diffusion coefficient with concentration, is for polymer micelles rather broad, often approaching 10 wt.%. A further increase in concentration is accompanied by a steep increase in zero-shear viscosity caused by the formation of the so-called macrolattice. Such a dependence is curve (a) in Fig. 3.

Tentacled micelles in solutions of triblock copolymers in a selective solvent for the middle block show strikingly different hydrodynamic behavior in semidilute solutions. Due to attractive forces between tentacles (i.e., collapsed copolymer blocks in a poor solvent), the cross-over between the dilute and semidilute regimes (indicated by a steep increase in viscosity) (Fig. 3, curve (b)) is much smaller in comparison with the case of ordinary micelles. Like ordinary micelles, "tentacled" ones keep their core/shell structure and dimensions in semidilute solutions. From the practical point of view, systems with tentacled

micelles can be used in cases, where high viscosities at relatively low polymer concentrations are desirable.

SOLUBILIZATION

Solubilization means an enhanced solubility of some compounds (solubilizates) brought about by the presence of other compounds (solubilizers). The phenomenon of solubilization was studied mostly in aqueous solutions of soaps and surfactants. Solutions of these compounds above CMC dissolve a certain amount of hydrocarbons, which are only sparingly soluble in water. Molecules of the solubilizate enter into micelles, increasing somewhat their association number.
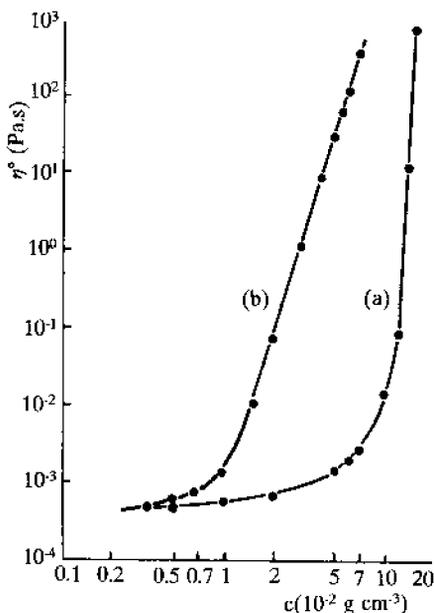

Fig.3. Concentration dependences of zero-shear viscosity of micelles of η^o for solutions of micelles of polystyrene-hydrogenated polybutadiene- polystyrene (molar mass 7×10^4 g/mol, 28 wt.% polystyrene) at 25°C in (a) a selective solvent for polystyrene, 1,4-dioxane/25 vol.% heptane; (b) a selective solvent for the middle block, heptane.

Further addition of the solubilizate above an amount called the saturation limit leads to the formation of an additional phase, as a rule, in the form of macroemulsion. A macroemulsion is also formed by the solubilizate (hydrocarbon) in the presence of a solubilizer (surfactant) with a concentration below CMC. Such a case can be documented by the behavior of aqueous solutions of poly(ethylene oxide)- poly(propyleneoxide)-poly(ethylene oxide), which can be regarded as both non-ionic surfactant and block copolymer, with a small amount of hexane [16]. At 25°C, when the copolymer was dissolved molecularly, solutions were cloudy due to the presence of a macroemulsion, i.e., unsolubilized hexane droplets. At 35°C micellization of the copolymer took place, and hexane solubilized in micelles in an amount up to the saturation limit. Unlike micelles with a solubilizate below the saturation limit, which are thermodynamically stable under given conditions, the macroemulsions are unstable.

In a comprehensive study dealing with the solubilization by block copolymer micelles, poly(ethylene oxide)- poly(propylene oxide) and poly(N-vinylpyrrolidone)-polystyrene were employed as solubilizers and a series of aliphatic and aromatic hydrocarbons as solubilizates [17]. A comparison of the solubilization by surfactants and by both above copolymers leads to an important conclusion: Unlike surfactants, block copolymers show a high specificity towards solubilizates. The amount of a solubilized compound is controlled by the Flory-Huggins parameter characterizing the interaction between the solubilizate and the core-forming copolymer blocks. Thus, aromatic hydrocarbons were solubilized in micelles with polystyrene cores to a much greater extent than aliphatic ones. When a mixture of benzene and heptane was solubilized, the block copolymer micelles selectively solubilized benzene. Hence, block copolymer micelles may become an effective material for separation of various low-molar-mass mixtures.

Polymer micelles have lately been considered as a potential vehicle for controlled release of organic substances into aqueous media. Prior to release, it is desirable to solubilize the maximum possible amount of a given substance in micellar cores. In a recent study [18], the system of micelles with polystyrene cores and poly(methacrylic acid) shells, and a model solubilizate, pyrene, was explored. It has been shown that the amount of solubilized pyrene depended on the method of loading. When the process was performed in an aqueous solution, the maximum amount solubilized was ca. 250 pyrene molecules per one polystyrene core containing 23000 styrene units. When pyrene was loaded into the same micelles (having the same association number) but with swollen cores in a water/1,4-dioxane mixture, the amount of solubilized pyrene was several times higher. After 1,4-dioxane had been removed by a stepwise dialysis, still the triple amount of pyrene, i.e., 800 molecules, was found in a polystyrene core. In the first method, 250 pyrene molecules per one core can be considered an equilibrium amount. In the second method, the enhanced "solubilization" is caused by trapping pyrene molecules during dialysis in the glassy cores of the non-equilibrium, frozen micelles. The process of release of pyrene into water was studied by fluorescence methods. The release was found to proceed on the time scale of thousands of seconds.

NEW TRENDS

Micellar models are still too simplified to be able to predict micellar parameters of a given block copolymer in a given selective solvent [2]. Two approaches will help to solve the problem: New experimental data using a variety of tailor-made block copolymers and a computer modelling using the Monte Carlo method [19, 20].

A deeper interest will be shifted from block copolymers in selective organic solvents to hydrophilic/hydrophobic block copolymers in aqueous media. These systems will be tested for an uptake and release of organic substances, scarcely soluble in water, from and into aqueous environment [e.g. 21]. Block copolymer micelles thus might become a material with potential practical applications in pharmacology, agriculture

and ecology.

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