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Self- and co-assembly of amphiphilic gradient polyelectrolyte in aqueous solution: Interaction with oppositely charged ionic surfactant

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ABSTRACT

Association behavior of the biocompatible amphiphilic cationic gradient polyelectrolyte poly[(2-methyl-2-oxazoline)-*grad*-(2-phenyl-2-oxazoline)-*mod*-(ethylene imine)] (HPPhMeOx) prepared by partial hydrolysis of the gradient copolymer poly[(2-methyl-2-oxazoline)-*grad*-(2-phenyl-2-oxazoline)] and the interaction of HPPhMeOx with the anionic surfactant sodium dodecyl sulfate (SDS) in aqueous solutions were investigated by scattering techniques (SANS, DLS) and by atomic force microscopy. SANS measurements revealed that large particles with the hydrodynamic radius of ca. 500 nm observed in HPPhMeOx aqueous solutions by DLS are formed by a network of physically crosslinked compact hydrophobic domains with the mean radius of ca. 10 nm. Upon addition of sodium dodecyl sulfate (SDS), the size of the domains increases at low amounts of the added SDS due to hydrophobic interaction of the single surfactant ions with the aggregates. Further addition of SDS leads to the formation of the co-assembled polyelectrolyte–surfactant complex manifested in SANS by the presence of the correlation peak from the densely packed SDS micelles as well as by partial disruption of the domains.

1. Introduction

Block copolymers (BC) have been a subject of numerous studies in connection with their ability to form self-assembled core–shell nanoparticles in selective solvents, such as micelles or vesicles, with the core formed by the collapsed insoluble blocks and the shell (also referred to as corona) of soluble blocks swollen by the solvent [1–3]. Amphiphilic BC nanoparticles have been extensively investigated as potential vessels for the controlled release and delivery of hydrophobic drugs [4,5].

In contrast to block copolymers, much less attention has been paid so far to the association behavior of gradient copolymers (GC) in selective solvents [6–10]. In the case of an amphiphilic GC, instead of micelles which possess a well-defined core–shell structure with segregated blocks, one can expect the formation of particles in which the GC chain ends rich in the hydrophobic units will assemble in the inner parts of the associate, and the shell rich in the hydrophilic units in the outer part. The structure of such particles resembles that of block copolymer micelles with no sharp interface between the core and the shell.

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The self-assembly behavior of amphiphilic GC in aqueous solutions depends both on the solvent interaction parameters of the monomeric units in the GC chain and on the steepness of the gradient. It has been reported that the presence of poly (acrylic acid) (PAA) hydrophilic units in the polystyrene (PS) core of PAA-*b*-(PAA-*grad*-PS) micelles causes the swelling of the core with water and makes the core softer so that the micelles are in dynamic equilibrium with the unimers although micelles of the BC counterpart of this copolymer, PAA-*b*-PS, are kinetically frozen [11,12].

On the other hand, the shell of the amphiphilic GC micelles has partly hydrophobic character due to the presence of hydrophobic units. This may lead to secondary association of the micelles into larger aggregates and to the formation of physical network [11,12].

Here we focus on the amphiphilic cationic gradient polyelectrolyte poly[(2-methyl-2-oxazoline)-*grad*-(2-phenyl-2-oxazoline)-*mod*-(ethylene imine)] (HPPhMeOx) [13] prepared by partial hydrolysis of the gradient copolymer poly(2-methyl-2-oxazoline)-*grad*-poly(2-phenyl-2-oxazoline) (PPhMeOx) [14,15]. Derivatives of poly(2-oxazoline)s have proved to be promising polymers for biomedical applications due to their biocompatibility and tunable hydrophobicity [16,17] (some of them exhibiting the critical solution temperature behavior in water and alcohols) [18,19]. The partial hydrolysis of 2-methyl-2-oxazoline and 2-phenyl-2-oxazoline to ethylene imine units converts the PPhMeOx copolymer to biocompatible amphiphilic cationic polyelectrolyte HPPhMeOx, the structure of which mimics a positively charged protein with hydrophobic and hydrophilic domains. It was reported that HPPhMeOx formed electrostatically stabilized complexes with DNA [13].

In this article, we focus on electrostatic coassembly behavior of HPPhMeOx and report on the formation of the polyelectrolyte–surfactant complexes (PE–S) of HPPhMeOx with sodium dodecyl sulfate (SDS) in aqueous solutions. PE–S have attracted attention of many researchers in the past two decades due to general interest in nanostructured self-assembled systems, as well as due to applications of these systems [20–22]. It has been found that the oppositely charged surfactant condenses on the polyelectrolyte chains and forms micelles at concentrations below the critical micelle concentration (cmc) of the surfactant [23] and that water-insoluble stoichiometric PE–S with zero net charge form various water-insoluble ordered crystalline-like phases [24]. While there are a number of papers about co-assembly of block copolymers consisting of a neutral block and a polyelectrolyte block (so-called double hydrophilic block polyelectrolytes, DHBP) with oppositely-charged surfactants in core–shell particles [25–27], the interaction of the hydrophobic–hydrophilic gradient polyelectrolyte with oppositely charged surfactant has not yet been studied so far.

In this study, we use both scattering techniques (static and dynamic light scattering, SANS) and atomic force microscopy to investigate structure of HPPhMeOx and HPPhMeOx/SDS aggregates in aqueous solutions.

2. Experimental

2.1. Materials

HPPhMeOx (Fig. 1) was prepared by partial hydrolysis of the precursor gradient copolymer PPhMeOx synthesized by ring opening cationic polymerization according to the procedure described in Ref. [14]. PPhMeOx (1 g) was then dissolved in 16 ml of ethanol, 6.2 ml of 37% HCl were added to the solution and the reaction mixture was left to stand for 3 h. After hydrolysis, the mixture was cooled in an ice bath and the pH was adjusted to 3 using NaOH solution and dialyzed against deionized water. The resulting HPPhMeOx copolymer was isolated using a rotary evaporator and further dried in a vacuum oven. The number-averaged molar mass of HPPhMeOx according to a SEC analysis of the precursor was, $M_n = 3400\ \text{g mol}^{-1}$, taking into account the mass composition according to ^{1}H NMR, which was 39, 37 and 24 wt.% of ethylene imine, 2-methyloxazoline and 2-phenyloxazoline units, respectively [13].

2.2. Preparation of samples

For light scattering and AFM measurements, 10 mg of HPPhMeOx copolymer were dissolved in 10 ml of deionized water. The pH and conductivity of the resulting 1 mg/ml solution were 3.5 and 0.8 mS cm^{-1}, respectively, which correspond to the

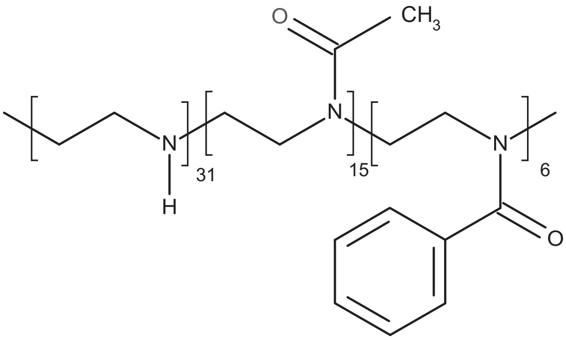

Fig. 1. Structure of HPPhMeOx copolymer.