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Doubly-grafted copolymers with hydrophilic and thermosensitive side chains: Thermosensitivity and complexation with surfactants

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ABSTRACT

The behavior in aqueous solution of the doubly-grafted anionic polyelectrolyte poly(sodium 2-acrylamido-2-methylpropanesulfonate-*co*-sodium acrylate-)-*g*-poly(*N*-isopropylacry-lamide)-g-poly(N,N-dimethylacrylamide), P(AMPSNa-co-ANa)-g-PNIPAM-g-PDMAM, was compared to that of the single-grafted anionic polyelectrolyte poly(sodium 2-acrylamido-2-methylpropanesulfonate-*co*-sodium acrylate)-*g*-poly(*N*-isopropylacrylamide), P(AMPSNa-co-ANa)-g-PNIPAM. The investigation through turbidimetry, pyrene fluorescence probing, viscometry and dynamic light scattering revealed that the existence of the hydrophilic poly(N,N-dimethylacrylamide), PDMAM, side chains in the doubly-grafted copolymer P(AMPSNa-co-ANa)-g-PNIPAM-g-PDMAM did not perturb the thermoresponsiveness of the poly(*N*-isopropylacrylamide), PNIPAM, side chains, but favoured the stabilization in water of the core-corona nanoparticles, formed upon heating the aqueous solution above the Lower Critical Solution Temperature (LCST) of PNIPAM chains. In a similar manner, the complexes formed between the cationic surfactant N,N,N,N-dodecyltrimethylammonium chloride, DTAC, and the oppositely charged backbone of the doubly-grafted copolymer P(AMPSNa-co-ANa)-g-PNIPAM-g-PDMAM were stabilized in water by the PDMAM side chains. Thus, phase separation was prevented upon heating the aqueous solution above LCST. Moreover, the ^{1}H NMR study revealed that the fraction of PNIPAM chains forming solid-like aggregates at high temperature increased substantially in the presence of DTAC, as a consequence of the net charge decrease of the backbone due to the polymer/DTAC complexation.

1. Introduction

The formation of the so-called polyelectrolyte/surfactant complexes upon mixing polyelectrolytes with oppositely charged surfactants in water is a well-known phenomenon, extensively studied during the past decades [1–14]. Such complexes remain always appealing, since they find a wide range of applications (cosmetics, paints, detergents, pharmaceutics, rheology control, etc.). Electrostatic interactions between the oppositely charged species, in combination with hydrophobic association, are at the origin of the surfactant/polymer association, usually taking place at a critical aggregation concentration (CAC) which is much lower than the critical micelle concentration (CMC) of the surfactant alone in aqueous medium [1,2,15].

As the binding process evolves and the net charge of the polyelectrolyte/surfactant complex decreases, approaching zero, phase separation is observed and the formed complex becomes hydrophobic, being no longer soluble in water [1,2,6,16–18]. An efficient methodology to effectively inhibit phase separation and obtain water-dispersible surfactant/polymer complexes even at charge stoichiometry is by designing the macromolecular architecture. For example, such architectures are those of double hydrophilic block copolymers [19–28], consisting of a polyelectrolyte block and a nonionic hydrophilic block, and graft copolymers [29–34], consisting of a polyelectrolyte backbone and nonionic hydrophilic side chains. In the presence of an oppositely charged surfactant, these systems are usually stabilized in water as core–corona nanoparticles, where the complex of the surfactant with the polyelectrolyte blocks (or backbone) forms the water-insoluble core and the nonionic hydrophilic blocks (or side chains) form the water-swelled corona [11].

Having in mind thermosensitivity, the association of cationic surfactants with poly(*N*-isopropylacrylamide)-containing block or graft copolymers has been also investigated during the last decade [28,34,35–37]. In fact, PNIPAM is a broadly studied thermoresponsive polymer known for its characteristic Lower Critical Solution Temperature behavior in water (LCST) at ~31–33 °C. Below LCST, PNIPAM is easily dissolved water, while above LCST it becomes water insoluble and phase separation takes place [38–41]. As a

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consequence of this thermoresponsiveness, the complexes formed between surfactants and oppositely charged PNIPAM-containing copolymers are enriched with temperature-sensitive properties.

Based on the graft copolymer approach, earlier in our group [33] we were able to stabilize in water complexes of N,N,N,N-dodecyltrimethylammonium bromide (DTAB) with graft copolymers comprised by a charged poly(sodium-2-acrylamido-2-methylpropanesulfonate-*co*-sodium acrylate) backbone (P(AMPSNa-co-ANa)) and highly hydrophilic nonionic poly(N,N-dimethylacrylamide) (PDMAM) side chains. At a next step, we replaced the PDMAM side chains with PNIPAM ones. However, turbidity was not avoided upon heating the aqueous solution of the complex formed between DTAB and the synthesized P(AMPSNa-co-ANa)-g-PNIPAM graft copolymer, for surfactant concentrations below CMC [34].

Our intention in the present study was to combine both kinds of side chains, PDMAM and PNIPAM, resulting potentially in novel thermoresponsive surfactant/polymer complexes with improved solubility. To achieve this goal, we proceeded to the synthesis of a doubly-grafted copolymer P(AMPSNa-co-ANa)-g-PNIPAM-g-PDMAM, based on a highly charged P(AMPSNa-co-ANa) backbone grafted with both hydrophilic PDMAM and thermosensitive PNIPAM chains (see Fig. 1). Reports concerning the synthesis of doubly-grafted copolymers are scarce [42–44]. Thus, the first section of the present work is devoted to the synthesis and the thermoresponsive behavior of this copolymer in aqueous media, as compared to the behavior of the respective single-grafted one, P(AMPSNa-co-ANa)-g-PNIPAM. In the second section, the association behavior of these copolymers with the cationic surfactant N,N,N,N-dodecyltrimethylammonium chloride (DTAC) is discussed, as a function of charge mixing ratio and temperature.

2. Materials and methods

2.1. Materials

The monomers, acrylic acid (AA), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA), *N*-isopropylacrylamide (NIPAM), and N,N-dimethylacrylamide (DMAM) were purchased from Aldrich. Potassium metabisulfite (KBS), 2-aminoethanethiol hydrochloride (AET), 1-(3-(dimethylamino) propyl)-3-ethyl-carbodiimide hydrochloride (EDC), dodecyl trimethylammonium chloride (DTAC) and deuterium oxide (D_2O) were also obtained from Aldrich. Ammonium persulfate (APS) was purchased from Serva. Pyrene (Py) was purchased from Fluka. Ultra-pure water was obtained by means of a SG apparatus water purification unit.

2.2. Synthesis and characterization of the graft copolymers

The synthetic procedure for the preparation of the single-grafted P(AMPSNa-co-ANa)-g-PNIPAM copolymer has been described elsewhere. [34] Briefly, the backbone P(AMPSNa-co-ANa) was first synthesized via free radical copolymerization of 0.02 mol AA and 0.08 mol AMPSA at 35 °C in water (100 mL), using the redox couple APS/KBS (0.001 mol/0.001 mol) as initiator. Before initiation the monomers were partially neutralized with NaOH (pH ~ 6). The final product was fully neutralized, dialysed and recovered through freeze-drying. The composition of the product was determined by acid–base titration and ^{1}H NMR analysis. As a second step, amine-terminated PNIPAM and PDMAM chains, PNIPAM-NH_2 and PDMAM-NH_2, were synthesized via free radical telomerization in water at 29 °C and 35 °C, respectively, using APS as initiator and AET as telogen. The APS/AET/monomer molar ratio was 2/1/100, while the monomer concentration was 1 M. The products were purified through dialysis and obtained by freeze-drying. At a third step, the PNIPAM-NH_2 chains (1.5 g) were grafted onto the carboxylic groups of the P(AMPSNa-co-ANa) copolymer (4.5 g) in aqueous solution and at room temperature, using EDC as a condensing agent. The mixture was left under gentle stirring for three days, while a quantity of ~0.1 g of EDC was added daily. Then, the solution was fully neutralized with a large excess of NaOH, and the final product, P(AMPSNa-co-ANa)-g-PNIPAM, was recovered by freeze-drying, after purification through ultrafiltration (Masterflex 1/P, Millipore, a membrane with a cutoff of 100 kDa was used). Finally, the doubly-grafted copolymer P(AMPSNa-co-ANa)-g-PNIPAM-g-PDMAM was obtained by grafting the PDMAM-NH_2 chains (0.74 g) onto the carboxylic groups of the backbone of the P(AMPSNa-co-ANa)-g-PNIPAM copolymer (1.5 g), in water and at room temperature, using EDC as condensing agent. The final product was purified through ultrafiltration and freeze-dried.

2.3. Polymer characterization

^{1}H NMR spectra of the copolymers in D_2O were obtained on a Bruker Advance DPX 400 MHz spectrometer. The number average molecular weight of the amine-terminated PDMAM and PNIPAM chains was determined by acid–base titration.

2.4. Turbidimetry

The optical density at 500 nm was measured using the HITACHI U-1800 UV–Vis spectrophotometer equipped with a circulating water bath. The polymer solution was placed in a 10 mm path-length quartz cuvette.

2.5. Viscometry

The reduced viscosity studies were carried out using an automated viscosity measuring system (Schott-Gerate AVS 300, Germany), equipped with a micro-Ostwald viscometer.

2.6. Pyrene fluorescence probing

All fluorescence studies were performed using a Perkin Elmer LS50B luminescence spectrometer, equipped with a circulating water bath. A stock ethanolic solution of 1×10^{-3} M pyrene was used and the final concentration was fixed at 8×10^{-7} M. The excitation wavelength was set at 334 nm and the intensity ratio I_1/I_3 of the first (I_1) and third (I_3) vibronic bands of the emission spectrum of pyrene, at 373 and 384 nm, respectively, was used to detect the formation of hydrophobic microdomains. The excitation and emission slits were set, respectively, at 2.5 nm and 0 (an apparatus setting giving a resolution <2 nm).

2.7. Dynamic light scattering (DLS)

The size of the copolymers nanoparticles formed in aqueous solutions at various temperatures was determined by means of a NanoZetasizer, Nano ZS Malvern apparatus. The excitation light source was a 4 mW He–Ne laser at 633 nm, and the intensity of the scattered light was measured at 173°. From the relaxation time determined, the apparent diffusion coefficient at the actual polymer concentration was estimated and, then, the apparent hydrodynamic diameter (D_H) of the particles was calculated through the Stokes–Einstein equation:

$$D_H = kT/3\pi\eta D \quad (1)$$

where k is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the solvent and D is the apparent diffusion coefficient.