Colloid solution of surfactant monomers and polyelectrolyte: Polymerization and properties of the resulting interpolyelectrolyte complexes

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ABSTRACT

In the present work, we suggest a novel method for obtaining interpolyelectrolyte complex (IPEC) by free radical polymerization in water–salt dispersions of polyelectrolyte complexes (PECs) based on an anionic polyelectrolyte (sodium salt of poly (2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS-Na)) and a cationic surfactant ((11-acryloyloxy) undecyl)-trimethylammonium bromide (AUTAB), as well as on PAUTAB cationic comb-like polyelectrolyte and AMPS-Na monomer. IPEC consisting of PAMPS and PAUTAB was obtained by two ways. The first one is polymerization of surface active monomers AUTAB in the presence of PAMPS, and the second one is polymerization of AMPS monomers in the presence of PAUTAB. Molecular hydrodynamics methods were used to determine the molecular properties of initial components, polyelectrolyte complexes (PECs), and IPECs. Analysis of the dependence between translational friction coefficient of macromolecules and their molecular masses (which takes into account excluded-volume effects) allowed us to determine the Kuhn segment length of PAMPS-Na macromolecule ($A = 6$ nm). Stable polyelectrolyte complexes, PEC, (PAMPS–AUTAB and PAUTAB–AMPS) were obtained by mixing solutions of components at low concentrations in equimolar ratios; polymerization of their low molecular weight components was carried out for the purpose of preparing IPECs. Comparison between scattered light intensity distributions measured for PEC and IPEC demonstrated that in IPEC solutions, only large aggregates of complex molecules are present, while in PEC solutions, two peaks were observed (those corresponding to diffusion of individual PECs and their aggregates). When concentrations of PEC components exceed 3.4 mM, polymerization results in the formation of IPEC precipitate which was studied by small angle X-ray scattering. It was found that the IPEC based on PAMPS-Na forms a film with hexagonal packing, and the PAUTAB-based IPEC forms a lamellar film.

1. Introduction

Interaction between polyelectrolytes and oppositely charged surfactants leads to the formation of polyelectrolyte complexes (PECs). The structure of PEC is influenced by forces of electrostatic interaction arising between oppositely charged fragments of polyelectrolyte and surfactant as well as by hydrophobic interactions between aliphatic surfactant tails [1]. Hydrophobic surfactant associates (the so-called intramolecular micelles) are formed on polyelectrolyte chain. In the condensed state, PECs may form liquid crystalline phases where these intramolecular micelles are arranged differently (lamellar, hexagonal or cubic packing) [2–6]. Binding between surfactant molecule and polyelectrolyte is accompanied by a cooperative effect which is observed when surfactant concentration exceeds the critical aggregation concentration (CAC). This effect manifests itself in the dramatic increase in degree of surfactant–polyelectrolyte binding [7].

Typical values of CAC are several orders of magnitude lower than the critical micellar concentration (CMC) values for the corresponding surfactants [6]. After reaching stoichiometric composition of a complex, the ζ-potential of PEC dispersions decreases, thus leading to the formation of a precipitate [8,9]; however, if the total concentration of PEC in the dispersion is lowered, precipitation can be avoided at stoichiometric ratio of the components [10].

Use of surface-active monomers provides the possibility of carrying out polymerization in nanostructured PEC ensembles at concentrations close to CAC. This polymerization yields an interpolyelectrolyte complex (IPEC). Radiation polymerization of PEC films in condensed state has been performed in [11,12]. The authors have demonstrated the possibility of fixating PEC structure by polymerization of surface-active monomers; however, high radiation doses led to destruction of the complex.

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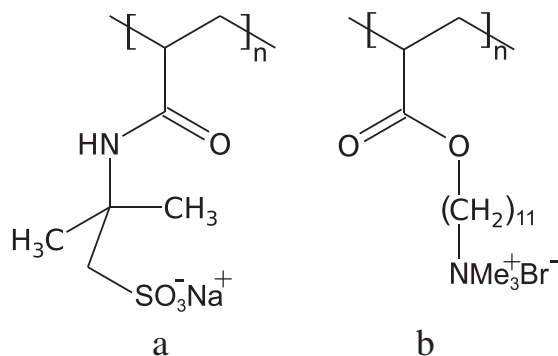 E-mail address: n.tsvetkov@spbu.ru (N.V. Tsvetkov).

Fig. 1. Chemical structure of PAMPS-Na (a) and PAUTAB (b) macromolecules.

Fig. 2. Distributions of hydrodynamic radii obtained from the light scattering data for investigated samples dissolved in 0.05 M NaCl solution at a scattering angle of 90°. (a) corresponds to PAMPS-Na; (b) corresponds to PAUTAB-1 (solid line), PAUTAB-2 (dashed line). Curve numbers in the plots correspond to sample numbers in Table 1.

In the present work, we suggest a novel method for obtaining IPECs by free radical polymerization in water–salt dispersions of PECs based on an anionic polyelectrolyte (sodium salt of poly (2-acrylamido-2-methyl-1-propanesulfonic acid), PAMPS-Na) and a cationic surfactant ((11-acryloyloxy) undecyl)-trimethylammonium bromide (AUTAB), as well as on PAUTAB cationic comb-like polyelectrolyte and AMPS-Na monomer. Several methods, such as dynamic light scattering, viscometry and velocity sedimentation, were used for determining molecular characteristics of PAMPS-Na and PAUTAB polymers and PEC (IPEC) complexes (in 0.05 M NaCl solutions). The samples of IPEC including PAMPS-Na were studied by atomic force microscopy (AFM) on mica substrate. Small-angle X-ray scattering was used for comparison between molecular packing of IPECs based on PAMPS-Na and PAUTAB.

2. Experimental section

2.1. Synthesis of monomers

The synthesis of ((11-acryloyloxy)undecyl)-trimethylammonium bromide (AUTAB) is described in detail elsewhere [13]. The authors used the two-stage method involving acylation of 11-bromoundecanol by acryloyl chloride, chromatographic isolation of the product and subsequent quaternization reaction (with N(Me)₃). We used a similar technique in the synthesis of AUTAB; however, the use of freshly distilled N-methylpyrrolidone as a solvent in acylation allowed us to replace the laborious stage of product isolation (preparative chromatography) with rather easy extraction using petroleum ether. Acylation was performed in the following manner: acryloyl chloride (15% excess) distilled over CuCl at 73–74 °C was added to the solution of 3 g of 11-bromoundecanol (Aldrich, 98%) in 25 mL of freshly distilled N-methylpyrrolidone. The reaction was carried out at −18 °C for 72 h; then the reaction mixture was poured into HCl solution (0.5 M). The product was extracted with petroleum ether and isolated after removing the solvent. In quaternization reaction, a polar solvent (acetonitrile) was used, this allowing shortening the reaction time from 53 h to 24 h.

AMPS-Na monomer was obtained by pH titration of 0.1 M water solution of AMPS-Na (Merck).

PAMPS-Na polyelectrolytes (see Fig. 1a) were prepared by free radical polymerization of AMPS-Na in aqueous solution. In all experiments, the "extra-pure grade" water with a resistivity of 16–18 MΩ·m was used (it was obtained using a UWOI-MF-1NA(18)-4 water purifier, Scientific and Production Corporation "Mediana Filter"). Low molecular weight impurities were removed from the prepared polymer by dialysis; the polymer was isolated by precipitation with acetone. In the case of PAUTAB polyelectrolytes (see Fig. 1b), the polymers were isolated by precipitation with dioxane and washed with diethyl ether. The solutions of PAMPS-Na and PAUTAB in 0.05 M NaCl were prepared at room temperature.

The ionic strength of solution can affect complex formation dramatically. The binding affinity between surfactants and opposite charged polyelectrolytes is reduced with the increase of the ionic strength but it increases the cooperative of the interaction [1]. Aqueous 0.05 M NaCl was used as "salt buffer" for complex formation in this work, such concentration is sufficient to eliminate large change in ionic strength of solution during the addition of the initiator. Also such concentration is sufficient to overcome the polyelectrolyte effects for PAMPS-Na macromolecules [34].

Polyelectrolyte complexes (PECs) of PAMPS–AUTAB and PAUTAB–AMPS composition were prepared by simple mixing equimolar amounts of monomer and polyelectrolyte in 0.05 M aqueous solution of NaCl. PEC polymerization was carried out in no less than 24 h after complex preparation in argon atmosphere (C_i = 1 g/L, T = 60°Ñ, 3 h) with $K_2S_2O_8$ and 2,2′-azobis(2-methylpropanamidine) dihydrochloride initiators (Aldrich) in the cases of PAMPS–AUTAB and PAUTAB–AMPS, respectively. If a precipitate was formed, the product was centrifuged, decanted and dried under vacuum using an oil pump; otherwise the complex was studied without isolation.

2.2. Methods

Size-exclusion chromatography (SEC) was performed using a Shimadzu LC-20 Prominence instrument (Shimadzu, Japan) equipped

Table 1
Molecular characteristics of PAMPS-Na and PAUTAB samples obtained using their solutions in 0.05 M NaCl.

Sample	$[\eta]$, cm³/g	k'	$D_0 \times 10^7$, cm²/s	s, Sv	$M_W \times 10^{-3}$	$A_2 \times 10^4$, mol g² cm³	$M_{sD} \times 10^{-3}$	$M_{D\eta} \times 10^{-3}$	M_W/M_N	R_h, nm	Z[a]
PAMPS-1	68	0.18	2.52	4.49	100	26.0	116	110	3.6	10	503
PAMPS-2	270	0.17	0.92	7.94	500	15.0	517	600	4.4	27	2240
PAMPS-3	450	0.28	0.67	10.29	900	9.5	1005	900	7.0	37	4352
PAUTAB-1	134	0.08	2.22 0.504[b]				80			11	229
PAUTAB-2	122	0.08	2.15 0.669[b]				100			11	277

[a] The degree of polymerization Z was determined as a M_{sD}/M_0 ratio for PAMPS-Na macromolecules (M_0 PAMPS = 231) and as a $M_{D\eta}/M_0$ ratio for PAUTAB macromolecules (M_0 PAUTAB = 364).

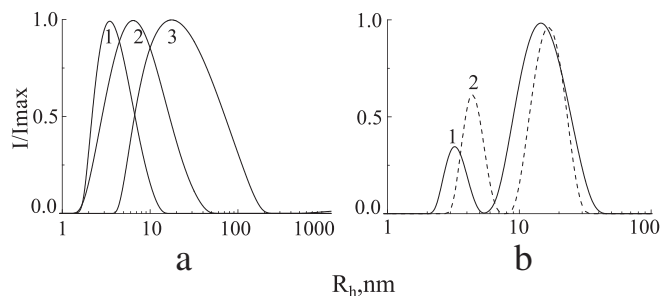[b] The scattered light distributions of PAUTAB solutions consisted of two peaks, with the second component having the corresponding diffusion coefficient.