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Temperature-Sensitive Water-Soluble Polyelectrolyte/Surfactant Complexes Formed between Dodecyltrimethylammonium Bromide and a Comb-Type Copolymer Consisting of an Anionic Backbone and Poly(*N*-isopropylacrylamide) Side Chains

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ABSTRACT: The properties of the complexes formed in water between the cationic surfactant dodecyltrimethylammonium bromide (DTAB) and the comb-type anionic polyelectrolyte poly(sodium acrylate-*co*-sodium 2-acrylamido-2-methylpropanesulfonate)-*g*-poly(*N*-isopropylacrylamide) (P(NaA-*co*-NaAMPS)-*g*-PNIPAM) were investigated in dilute aqueous solutions and compared to the properties of the complexes formed between DTAB and poly(sodium acrylate-*co*-sodium 2-acrylamido-2-methylpropanesulfonate)-*g*-poly(*N*,*N*-dimethylacrylamide) (P(NaA-*co*-NaAMPS)-*g*-PDMAM). It was found that, contrary to the water-insoluble complexes formed between the linear polyelectrolyte P(NaA-*co*-NaAMPS) and the oppositely charged DTAB, the complexes formed between DTAB and the comb-type copolymers, either P(NaA-*co*-NaAMPS)-*g*-PNIPAM or P(NaA-*co*-NaAMPS)-*g*-PDMAM, maintain water solubility at room temperature. In both cases, complexation is accompanied by charge neutralization, formation of hydrophobic microdomains, and a substantial decrease of the reduced viscosity of the aqueous solution. Contrary to the P(NaA-*co*-NaAMPS)-*g*-PDMAM/DTAB complexes, the P(NaA-*co*-NaAMPS)-*g*-PNIPAM/DTAB complexes separate out from water upon heating, due to the lower critical solution temperature behavior of the PNIPAM side chains. At high DTAB concentrations, mixed aggregates between the PNIPAM side chains and DTAB cations are formed, leading to the indirect introduction of positive charges in the complex and to the elevation of the phase separation temperature.

Introduction

The investigation of the interactions between polyelectrolytes and oppositely charged surfactants, leading to the formation of the so-called polyelectrolyte/surfactant complexes,[1−3] represents an intensive research field during the past decades. Usually, binding of the surfactant molecules to the oppositely charged polyelectrolyte is characterized by an important cooperativity and starts at a critical surfactant concentration, termed critical aggregation concentration (cac), at concentrations well below the critical micelle concentration of the surfactant (cmc).[2] As the surfactant binding increases and the net charge of the polyelectrolyte/surfactant complex approaches zero, the complex formed is usually not soluble anymore in water.[1,2,4−11]

To avoid phase separation and maintain water solubility even at electroneutrality, polyelectrolytes of an adequately designed block or comb-type architecture may be used. Thus, Kabanov and co-workers[12−15] have prepared water-soluble oppositely charged polyelectrolyte/surfactant complexes using block copolymers, where the polyelectrolyte block is covalently attached to a nonionic hydrophilic block. Alternatively, comb-type copolymers may be used, consisting of a polyelectrolyte backbone, onto which the nonionic hydrophilic chains are grafted.[14,16−18]

Recently,[19] we have applied this second approach using comb-type polyelectrolytes based on a highly charged poly(sodium acrylate-*co*-sodium 2-acrylamido-2-methylpropanesulfonate) backbone (P(NaA-*co*-NaAMPS)), while the side chains consisted of the highly hydrophilic nonionic polymer poly(*N*,*N*-dimethylacrylamide) (PDMAM). It was shown that these comb-type copolymers, P(NaA-*co*-NaAMPS)-*g*-PDMAM, do form water-soluble complexes with the cationic surfactant dodecyltrimethylammonium bromide (DTAB), while the polyelectrolyte/surfactant complex is characterized by a cac value about 2 orders of magnitude lower than the cmc of DTAB.

Our intention in the present study was to provide these water-soluble polyelectrolyte/surfactant complexes with temperature-sensitive properties. To succeed with this goal, we used a comb-type copolymer consisting of an identical charged backbone, but we have replaced the PDMAM side chains with the thermosensitive poly(*N*-isopropylacrylamide), PNIPAM, ones. The chemical structure of this comb-type product, P(NaA-*co*-NaAMPS)-*g*-PNIPAM, is presented in Scheme 1. In the first part of the present study the behavior of the complexes formed between DTAB and P(NaA-*co*-NaAMPS)-*g*-PNIPAM is compared to the behavior of the corresponding complexes formed between DTAB and P(NaA-*co*-NaAMPS)-*g*-PDMAM, while the second part focuses on the thermosensitive properties of the former complexes.

As is known, the thermosensitivity of PNIPAM arises from its lower critical solution temperature (LCST) behavior in water: the polymer separates out from water upon heating above ∼33 °C.[20,21] When the PNIPAM chains are attached to a highly hydrophilic backbone,[22−34] this phase separation is confined at a local scale, leading to temperature-induced formation of hydrophobic PNIPAM aggregates in dilute solution and to temperature-induced thickening aqueous formulations in semidilute solutions. In addition, PNIPAM is reported to associate weakly with cationic surfactants, like DTAB or dodecyltrimethylammonium chloride (DTAC), as evidenced from various studies, including swelling equilibrium of PNIPAM gels,[35] dilute solution viscometry,[36] pyrene fluorescence probing,[36] and isothermal titration calorimetry.[37] These studies revealed that PNIPAM/DTAB (or DTAC) association occurs at a surfactant

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Scheme 1. Chemical Structure of the Comb-Type Copolymer P(NaA-*co*-NaAMPS)-*g*-PNIPAM

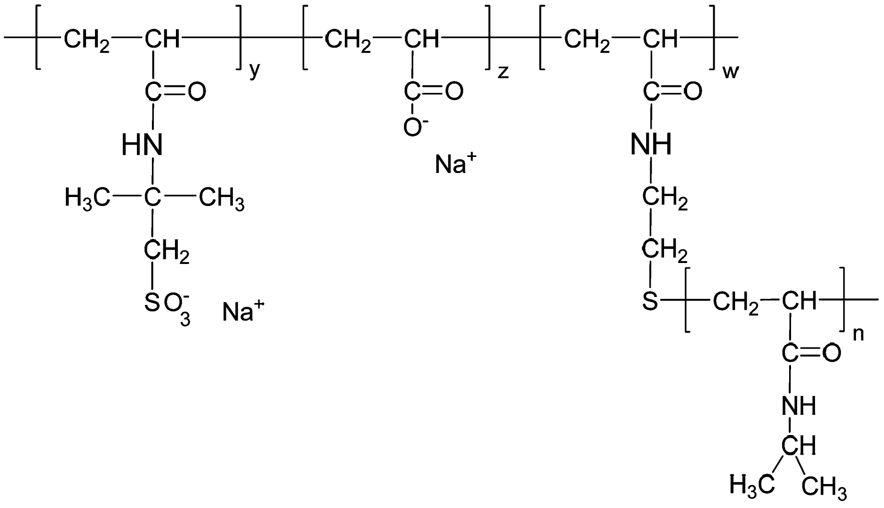

Table 1. Chemical Characterization of the Anionic Polyelectrolytes

copolymer	feed composition	^{1}H NMR analysis	mol wt × 10^{-5}
P(NaA-*co*-NaAMPS)	80 mol % NaAMPS	84 mol % NaAMPS	3.2[a]
P(NaA-*co*-NaAMPS)-*g*-PDMAM	50% (w:w) PDMAM	58% (w:w) PDMAM	7.6[b]
P(NaA-*co*-NaAMPS)-*g*-PNIPAM	50% (w:w) PNIPAM	53% (w:w) PNIPAM	6.8[b]

[a] From static light scattering measurements. [b] Calculated from the molecular weight of the backbone and the composition of the copolymer.

concentration close to the cmc of the pure surfactant[36,37] and leads to a moderate increase of the transition temperature of PNIPAM in water.[35] As a consequence, association of DTAB with the comb-type copolymer P(NaA-*co*-NaAMPS)-*g*-PNIPAM is expected to be rather complicated, as it may combine the interactions of surfactant both with the negatively charged backbone and with the nonionic PNIPAM side chains. In fact, because of these reasons, a two-step surfactant binding process has been suggested for the interactions of DTAB with P(NIPAM-*co*-NaAMPS) random copolymers of *N*-isopropylacrylamide, NIPAM, and sodium 2-acrylamido-2-methylpropanesulfonate, NaAMPS.[38]

Experimental Section

Materials. Ammonium persulfate (APS) was purchased from Serva, while acrylic acid (AA), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA), *N*-isopropylacrylamide (NIPAM), potassium metabisulfite (KBS), aminoethanethiol hydrochloride (AET), 1-(3-(dimethylamino)propyl)-3-ethyl-carbodiimide hydrochloride (EDC), and dodecyltrimethylammonium bromide (DTAB) were purchased from Aldrich. Water was purified by means of a Seralpur Pro 90C apparatus combined with an USF Elga water purification unit.

Synthesis and Characterization of the Copolymers. The synthetic procedure for the preparation of the backbone P(NaA-*co*-NaAMPS) and the comb-type copolymer P(NaA-*co*-NaAMPS)-*g*-PDMAM has been described elsewhere.[19,39] A similar synthetic procedure was applied for the preparation of the comb-type P(NaA-*co*-NaAMPS)-*g*-PNIPAM copolymer. Briefly, amine-terminated PDMAM or PNIPAM chains were synthesized via free radical telomerization in water at 35 or 30 °C, respectively, using APS as initiator and AET as telogen. The number-average molecular weight were determined to be 11 000 and 23 000 for PDMAM and PNIPAM, respectively, by acid−base titration in water. As a second step, the backbone P(NaA-*co*-NaAMPS) was synthesized via free radical copolymerization of AA and AMPSA in water, using the redox couple APS/KBS as initiator. The composition of the product, recovered in the sodium salt form, was determined by acid−base titration and ^{1}H NMR spectroscopy analysis. It was found that the copolymer contains 84 mol % NaAMPS units. The molecular weight of the backbone P(NaA-*co*-NaAMPS) was determined by static light scattering measurements in 0.1 M NaCl. Finally, the amine-terminated PDMAM or PNIPAM chains were grafted to the carboxylic groups of the copolymer by a grafting reaction in water at room temperature, using the water-soluble EDC as condensing agent. The composition of the comb-type copolymers was determined by ^{1}H NMR spectroscopy analysis, while their molecular weights were calculated from their composition and the molecular weight of the backbone. The results of the characterization are reported in Table 1.

Turbidimetry. The optical density of dilute aqueous polymer−surfactant solutions was monitored at 490 nm by means of a Hitachi spectrophotometer, model U 2001, equipped with a circulating water bath.

Viscometry. Reduced viscosity studies were carried out with an automated viscosity measuring system (Schott-Geräte AVS 300, Germany), equipped with a micro-Ostwald viscometer.

Pyrene Fluorescence Probing. Steady-state fluorescence spectra of pyrene were recorded on a Perkin-Elmer LS50B luminescence spectrometer, equipped with a circulating water bath. A stock ethanol solution, containing 1×10^{-3} M pyrene, was used. The final concentration of the probe was 6×10^{-7} M, and the excitation wavelength was 334 nm. The intensity ratio (I_1/I_3) of the first (I_1) over the third (I_3) vibronic band of the emission spectrum of pyrene, at 373 and 384 nm, respectively, was used to detect the formation of hydrophobic microdomains.[40,41]

ζ-Potential Measurements. The ζ-potential of dilute aqueous polymer−surfactant solutions at room temperature was measured by means of a Zetaseizer 5000 (Malvern Instruments Ltd.), equipped with a cell type ZET 5104 (cross-beam mode).

Results and Discussion

Properties of the Polymer−Surfactant Complexes at T = 25 °C. In Figure 1, we present the dependence of the optical density on the surfactant concentration of aqueous solutions of mixtures of DTAB with either the backbone P(NaA-*co*-NaAMPS) or the two comb-type copolymers, P(NaA-*co*-NaAMPS)-*g*-PDMAM and P(NaA-*co*-NaAMPS)-*g*-PNIPAM. The polymer concentration is constant and adequately chosen, so that in all mixtures the concentration of negatively charged groups, originating from the backbone, is in all cases ~1 mM. As seen, the association of the positively charged DTAB cations

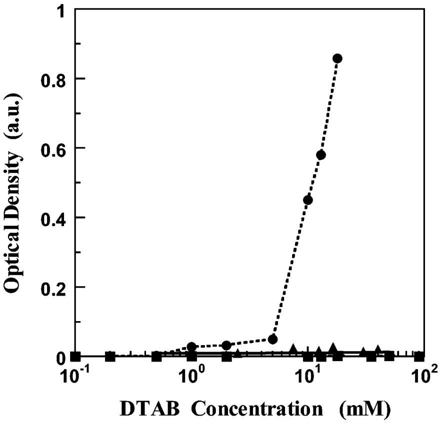

Figure 1. Variation of the optical density of aqueous solutions of mixtures of DTAB with (a) P(NaA-*co*-NaAMPS) (●), (b) P(NaA-*co*-NaAMPS)-*g*-PDMAM (■), and (c) P(NaA-*co*-NaAMPS)-*g*-PNIPAM (▲) as a function of the concentration of DTAB. The concentration of P(NaA-*co*-NaAMPS) is 0.025% (w:w), while the concentration of the comb-type copolymers is 0.050% (w:w). $T = 25$ °C.

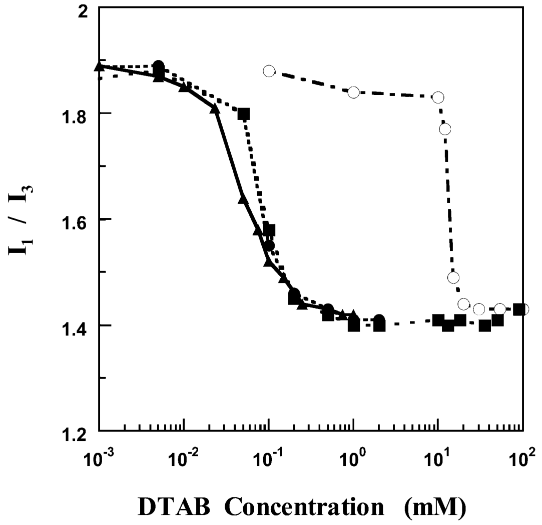

Figure 2. Variation of the ratio I_1/I_3 of aqueous DTAB solutions (○) or of aqueous mixtures of DTAB with (a) P(NaA-*co*-NaAMPS) (●), (b) P(NaA-*co*-NaAMPS)-*g*-PDMAM (■), and (c) P(NaA-*co*-NaAMPS)-*g*-PNIPAM (▲) as a function of the concentration of DTAB. The polymer concentrations are as in Figure 1. $T = 25$ °C.

with the negatively charged P(NaA-*co*-NaAMPS) copolymer leads to phase separation: the aqueous mixtures turn slightly turbid at a surfactant concentration of ∼1 mM, while turbidity becomes strong when the surfactant concentration exceeds the value of ∼4 mM. On the contrary, when the comb-type copolymers are used, no phase separation is observed, and the solutions remain clear, regardless of the surfactant concentration, varying from 0 up to 50 mM. As has been explained in the case of the P(NaA-*co*-NaAMPS)-*g*-PDMAM/DTAB system,[19] the hydrophilic PDMAM chains stabilize the complex formed in water between the backbone and the surfactant, probably in the form of core−corona nanoparticles. Apparently, this is also the case for the P(NaA-*co*-NaAMPS)-*g*-PNIPAM/DTAB system at 25 °C, although the PNIPAM side chains are less hydrophilic and rather hydrophobic as compared to the PDMAM side chains.

The polyelectrolyte/surfactant complexes formed are significantly hydrophobic, comparable to the hydrophobic nature of pure DTAB micelles. This is revealed by the pyrene fluorescence probing study, reported in Figure 2. As seen in this figure, for all the three polyelectrolyte/surfactant systems we obtain similar sigmoidal curves, displaced about 2 orders of magnitude

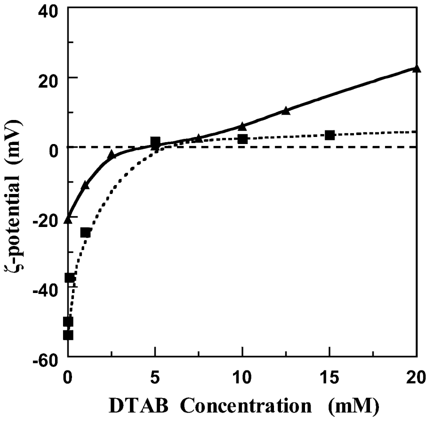

Figure 3. Variation of the ζ-potential of the polyelectrolyte/surfactant complexes formed in water between DTAB and P(NaA-*co*-NaAMPS)-*g*-PDMAM (■) or P(NaA-*co*-NaAMPS)-*g*-PNIPAM (▲) as a function of the concentration of DTAB. The polymer concentration is 0.050% (w:w). $T = 25$ °C.

to lower DTAB concentrations, as compared to the corresponding curve of pure DTAB. Thus, the critical aggregation concentration (cac), determined as the inflection point of the corresponding curve, is estimated to be ∼0.2 mM for the mixtures of DTAB with P(NaA-*co*-NaAMPS) or P(NaA-*co*-NaAMPS)-*g*-PDMAM, whereas the critical micelle concentration (cmc) of DTAB is found to be ∼14 mM, in a rather good agreement with the values reported in the literature.[2] Furthermore, when the copolymer P(NaA-*co*-NaAMPS)-*g*-PNIPAM is used, we observe that the curve is displaced to somewhat lower DTAB concentrations (the cac of this system is estimated to be ∼0.1 mM). Although the difference is not very significant, it is possible that mixed PNIPAM/surfactant aggregates are formed due to the moderately hydrophobic nature of the PNIPAM chains, in contrast to the hydrophilic nature of the PDMAM ones.

We can obtain important information on the association of DTAB with our copolymers from the variation of the ζ-potential of the polyelectrolyte/surfactant complexes formed with the DTAB concentration, presented in Figure 3. As seen, ζ-potential is negative at low DTAB concentration, originating from the negatively charged backbone of the comb-type copolymers. Upon addition of DTAB, ζ-potential approaches zero, as a result of charge neutralization during complexation. When the copolymer P(NaA-*co*-NaAMPS)-*g*-PDMAM is used, further addition of DTAB does not influence at all the ζ-potential of the complex, remaining constant to values close to zero. On the contrary, when the copolymer P(NaA-*co*-NaAMPS)-*g*-PNIPAM is used, ζ-potential is stabilized to values close to zero within the DTAB concentration region ∼2.5 to 10 mM, while it deviates to significantly positive values for higher DTAB concentrations. We should note that association between PNIPAM and DTAB, characterized by a cac value ∼11.4 ± 0.3 mM at 25 °C,[37] is reported to take place in this concentration region. As a result, after charge neutralization, the net charge of the P(NaA-*co*-NaAMPS)-*g*-PNIPAM/DTAB complex is very low for surfactant concentrations lower than 10 mM, while at higher surfactant concentrations it turns to positive values due to the association between the DTAB cations with the uncharged PNIPAM chains. On the other hand, no association can take place between DTAB and the hydrophilic PDMAM chains when the comb-type copolymer P(NaA-*co*-NaAMPS)-*g*-PDMAM is used and the ζ-potential remains constant to values close to zero, after charge neutralization, regardless of the surfactant concentration. It is noteworthy that the polyelectrolyte/surfactant

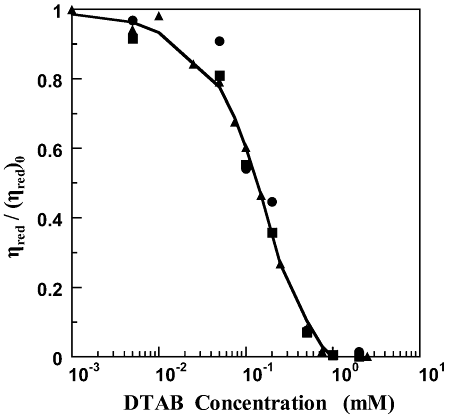

Figure 4. Variation of the ratio $\eta_{red}/(\eta_{red})_0$ of aqueous solutions of mixtures of DTAB with (a) P(NaA-*co*-NaAMPS) (●), (b) P(NaA-*co*-NaAMPS)-*g*-PDMAM (■), and (c) P(NaA-*co*-NaAMPS)-*g*-PNIPAM (▲) as a function of the concentration of DTAB. The polymer concentrations are as in Figure 1. $T = 25$ °C.

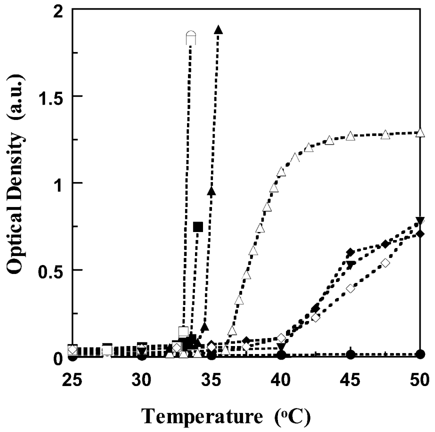

Figure 5. Temperature dependence of the optical density of aqueous solutions of mixtures of P(NaA-*co*-NaAMPS)-*g*-PNIPAM with DTAB. The concentration of the polymer is 0.050% (w:w), while the concentration of DTAB is 0.5 (●), 2.5 (○), 7.5 (■), 12.5 (□), 16.5 (▲), 20 (△), 30 (◆), 40 (◇), and 50 mM (▼).

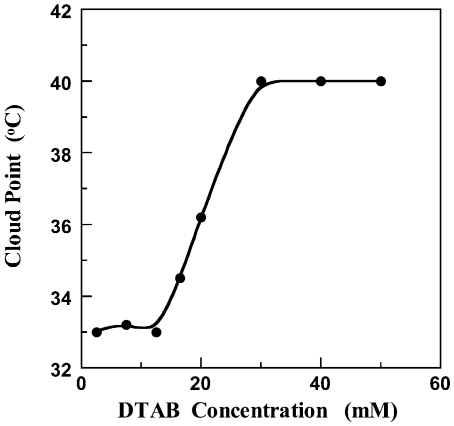

Figure 6. Variation of the cloud point of aqueous solutions of mixtures of P(NaA-*co*-NaAMPS)-*g*-PNIPAM with DTAB as a function of the DTAB concentration. The concentration of the polymer is 0.050% (w:w).

complexes appear to be electroneutral at a DTAB concentration much higher than the concentration of the anionic groups of the copolymers (~1 mM). This deviation from stoichiometry may possibly indicate that the complexation process is not characterized by an important cooperativity, thus allowing to some negative charges of the copolymer backbone to be uncomplexed even if the surfactant is in excess.

The viscometric study in dilute aqueous solution of these systems is presented in Figure 4, using the normalized term $\eta_{red}/(\eta_{red})_0$, where η_{red} is the reduced viscosity of the polyelectrolyte/surfactant mixture and $(\eta_{red})_0$ is the reduced viscosity of the polyelectrolyte in the absence of DTAB. As seen, the ratio $\eta_{red}/(\eta_{red})_0$ decreases drastically as the DTAB concentration exceeds ~0.1 mM, a concentration close to the critical aggregation concentration estimated for these systems. The drastic reduced viscosity decrease apparently originates from the decrease of the net charge (discussed in Figure 3) of the polyelectrolyte/surfactant complexes and the enhancement of their hydrophobic nature as the surfactant molecules bind to the polyelectrolyte chain. It is noteworthy that all three curves practically coincide, indicating that the side PDMAM or PNIPAM chains do not significantly perturb the association of the positively charged surfactant with the negatively charged backbone. They just prevent the further aggregation of the compact particles formed to large precipitates, as is observed for the P(NaA-*co*-NaAMPS)/DTAB mixtures.

Temperature Sensitivity of the P(NaA-*co*-NaAMPS)-*g*-PNIPAM/DTAB Complexes. In Figure 5, we present the variation of the optical density of aqueous P(NaA-*co*-NaAMPS)-*g*-PNIPAM/DTAB solutions with the temperature for several DTAB concentrations, covering the range 0−50 mM. In these solutions, the polymer concentration is always 0.05% (w:w). As known, the attachment of the PNIPAM chains to a very hydrophilic backbone restricts the phase separation of PNIPAM in water to a microscopic level. As a result, the aqueous solution of the pure copolymer P(NaA-*co*-NaAMPS)-*g*-PNIPAM remains transparent for the whole temperature range studied, 25−50 °C. Similar is the behavior for the polymer/DTAB mixtures with low DTAB concentration (for instance, 0.5 mM). With increasing the DTAB concentration, however, the solutions turn turbid upon heating; i.e., a lower critical solution temperature (LCST)-type phase separation behavior is observed. As seen, both the cloud point (defined as the temperature where the onset of the curve is observed) and the level of turbidity depend strongly on the DTAB concentration.

The cloud point diagram of the P(NaA-*co*-NaAMPS)-*g*-PNIPAM/DTAB system for these conditions is presented in Figure 6. The solutions containing DTAB at a concentration less than 2.5 mM remain transparent in the whole temperature range studied, and no cloud point is detected. For the DTAB concentration region 2.5−13 mM, the solutions turn strongly turbid upon heating, while the cloud point is, more or less, constant at 33 °C. As discussed in Figure 3, at this surfactant concentration region, the complex is practically uncharged (and the polymer backbone is not hydrophilic anymore, due to the electrostatic binding of the surfactant dodecyl groups), thus allowing the LCST-type phase separation of the PNIPAM side chains to be evidenced. The formation of mixed aggregates between the DTAB cations and the PNIPAM side chains introduces indirectly negative charges to these chains, leading to the cloud point increase upon further addition of DTAB. The plateau value observed at high surfactant concentrations (>30 mM) could probably attributed to the saturation of PNIPAM chains with surfactant, similarly to the association of PNIPAM with anionic surfactants[42] or hydrophobically modified polymers.[43] To our knowledge, no systematic study is reported on the cloud point behavior of the PNIPAM/DTAB system. However, the behavior observed here qualitatively resembles the dependence reported for the swelling−deswelling transition temperature of PNIPAM gels upon addition of DTAC.[35]

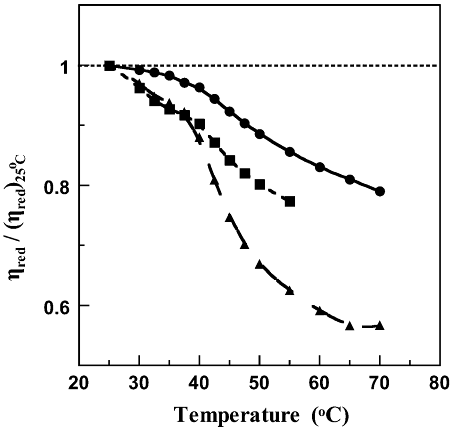

Figure 7. Temperature dependence of the ratio $\eta_{\mathrm{red}}/(\eta_{\mathrm{red}})_{25\,^{\circ}\mathrm{C}}$ of aqueous solutions of mixtures of P(NaA-*co*-NaAMPS)-*g*-PNIPAM with DTAB. The concentration of the polymer is 0.050% (w:w), while the concentration of DTAB is 0 (●), 0.25 (■), and 0.5 mM (▲).

The low DTAB region, where no macroscopic phase separation is observed upon heating, was studied in more detail by dilute solution viscometry. As discussed in Figure 4, the reduced viscosity of the P(NaA-*co*-NaAMPS)-*g*-PNIPAM/DTAB mixtures changes drastically with the DTAB concentration. For this reason, the viscometric results in Figure 7 are presented in terms of the normalized ratio $\eta_{\mathrm{red}}/(\eta_{\mathrm{red}})_{25\,^{\circ}\mathrm{C}}$, where η_{red} is the reduced viscosity of the system at the actual temperature and $(\eta_{\mathrm{red}})_{25\,^{\circ}\mathrm{C}}$ is the reduced viscosity of the same system at 25 °C. As seen, in the absence of surfactant the ratio $\eta_{\mathrm{red}}/(\eta_{\mathrm{red}})_{25\,^{\circ}\mathrm{C}}$ of the comb-type copolymer P(NaA-*co*-NaAMPS)-*g*-PNIPAM initially decreases slightly upon heating, while a more substantial decrease is observed when temperature increases above 35−40 °C. This is probably due to the shrinkage of the PNIPAM side chains at high temperature. Nevertheless, as these chains are attached to the polyelectrolyte backbone, this shrinkage does not influence significantly the reduced viscosity of the copolymer, so that the ratio $\eta_{\mathrm{red}}/(\eta_{\mathrm{red}})_{25\,^{\circ}\mathrm{C}}$ remains at values higher than ~0.8 even at 70 °C. Similar trends are also observed when the solution contains DTAB at low concentration (0.25 and 0.5 mM). However, the observed phenomena are now more pronounced. Thus, when the concentration of DTAB is 0.5 mM, an important decrease is observed at high temperature, and the value of the ratio $\eta_{\mathrm{red}}/(\eta_{\mathrm{red}})_{25\,^{\circ}\mathrm{C}}$ at 70 °C is just 0.55, almost half of that measured at 25 °C. Apparently, because of polyelectrolyte/surfactant complexation, the contribution of the backbone to the overall reduced viscosity is much smaller (this is also verified by the results reported in Figure 4). As a consequence, the shrinkage of the PNIPAM side chains at high temperature has a significant effect in the measured $\eta_{\mathrm{red}}/(\eta_{\mathrm{red}})_{25\,^{\circ}\mathrm{C}}$ ratio.

Conclusion

In the present study we investigated the polymer/surfactant complexation between the cationic surfactant DTAB and the anionic comb-type polyelectrolyte P(NaA-*co*-NaAMPS)-*g*-PNIPAM. Contrary to the complexes formed between DTAC and P(NaA-*co*-NaAMPS), the P(NaA-*co*-NaAMPS)-*g*-PNIPAM/DTAB complexes are water-soluble at room temperature, due to the stabilizing effect of the nonionic side chains, as is also the case for the P(NaA-*co*-NaAMPS)-*g*-PDMAM/DTAB complexes. Nevertheless, the well-known thermosensitive properties of PNIPAM and its ability to form mixed aggregates with DTAB introduce new interesting characteristics in the polymer/surfactant complexes formed, when the copolymer P(NaA-*co*-NaAMPS)-*g*-PNIPAM is used. First, the relatively hydrophobic character of PNIPAM seems to enhance somewhat the association of DTAB with the oppositely charged backbone, as evidenced by the smooth decrease of the cac for the P(NaA-*co*-NaAMPS)-*g*-PNIPAM/DTAB complexes, in relation to the identical cac of the P(NaA-*co*-NaAMPS)/DTAB and P(NaA-*co*-NaAMPS)-*g*-PDMAM/DTAB complexes. Furthermore, DTAB associates with P(NaA-*co*-NaAMPS)-*g*-PNIPAM probably by a two-step association process: the first step is association of the cationic surfactant with the negatively charged backbone, characterized by a very low cac, while at higher DTAB concentrations the surfactant forms mixed aggregates with the PNIPAM chains.

The second, more essential, characteristic of the P(NaA-*co*-NaAMPS)-*g*-PNIPAM/DTAB complexes is that they are provided with temperature-sensitive properties. This temperature sensitivity in the present system was manifested as a macroscopic LCST-type phase separation. The corresponding cloud point diagram depends significantly on the DTAB concentration. Thus, a cloud point close to the cloud point of PNIPAM is found within the DTAB concentration region where the net charge of the complex is close to zero, while a cloud point elevation is observed when DTAB starts to form mixed aggregates with the PNIPAM side chains.

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References and Notes

(1) Hayakawa, K.; Kwak, J. In *Cationic Surfactants: Physical Chemistry*; Rubingh, D., Holland, P. M., Eds.; Surfactant Science Series; Marcel Dekker: New York, 1991.
(2) Lindman, B.; Thalberg, K. In *Interactions of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananathapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1993.
(3) Langevin, D. *Adv. Colloid Interface Sci.* **2001**, *89−90*, 467.
(4) Dubin, P. L.; Oteri, R. *J. Colloid Interface Sci.* **1983**, *95*, 453.
(5) Dubin, P. L.; Rigsbee, D. R.; McQuigg, D. W. *J. Colloid Interface Sci.* **1985**, *105*, 509.
(6) Thalberg, K.; Lindman, B.; Bergfelt, K. *Langmuir* **1991**, *7*, 3.
(7) Piculell, L.; Lindman, B. *Adv. Colloid Interface Sci.* **1992**, *41*, 149.
(8) Piculell, L.; Lindman, B.; Karlstrom, G. In *Polymer-Surfactant Systems*; Kwak, J. C. T., Ed.; Marcel Dekker: New York, 1998.
(9) Yoshida, K.; Sokhakian, S.; Dubin, P. L. *J. Colloid Interface Sci.* **1998**, *205*, 257.
(10) Wang, Y.; Kimura, K.; Dubin, P. L.; Jaeger, W. *Macromolecules* **2000**, *33*, 3324.
(11) Hansson, P. *Langmuir* **2001**, *17*, 4167.
(12) Bronich, T. K.; Kabanov, A. V.; Kabanov, V. A.; Yu, K.; Eisenberg, A. *Macromolecules* **1997**, *30*, 3519.
(13) Kabanov, A. V.; Bronich, T. K.; Kabanov, V. A.; Yu, K.; Eisenberg, A. *J. Am. Chem. Soc.* **1998**, *120*, 9941.
(14) Bronich, T. K.; Nehls, A.; Eisenberg, A.; Kabanov, V. A.; Kabanov, A. V. *Colloids Surf., B* **1999**, *16*, 243.
(15) Bronich, T. K.; Popov, A. M.; Eisenberg, A.; Kabanov, V. A.; Kabanov, A. V. *Langmuir* **2000**, *16*, 481.
(16) Bronich, T. K.; Cherry, T.; Vinogradov, S. V.; Eisenberg, A.; Kabanov, V. A.; Kabanov, A. V. *Langmuir* **1998**, *14*, 6101.
(17) Nisha, C. K.; Basak, P.; Manorama, S. V.; Maiti, S.; Jayachandran, K. N. *Langmuir* **2003**, *19*, 2947.
(18) Nisha, C. K.; Manorama, S. V.; Kizhakkedathu, J. N.; Maiti, S. *Langmuir* **2004**, *20*, 8468.
(19) Balomenou, I.; Bokias, G. *Langmuir* **2005**, *21*, 9038.
(20) Heskins, M.; Guillet, J. E. *J. Macromol. Sci., Chem.* **1968**, *A2*, 1441.
(21) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.
(22) Chen, G.; Hoffman, A. S. *Nature (London)* **1995**, *373*, 49.
(23) Chen, G.; Hoffman, A. S. *Macromol. Rapid Commun.* **1995**, *16*, 175.
(24) Kurisawa, M.; Yui, N. *Macromol. Chem. Phys.* **1998**, *199*, 2613.
(25) Durand, A.; Hourdet, D. *Polymer* **1999**, *40*, 4941.
(26) Huh, K. M.; Hashi, J.; Ooya, T.; Yui, N. *Macromol. Chem. Phys.* **2000**, *201*, 613.
(27) Durand, A.; Hourdet, D. *Polymer* **2000**, *41*, 545.
(28) Durand, A.; Hourdet, D. *Macromol. Chem. Phys.* **2000**, *201*, 858.

(29) Durand, A.; Hourdet, D.; Lafuma, F. *J. Phys. Chem. B* **2000**, *104*, 9371.

(30) Sudor, J.; Barbier, V.; Thirot, S.; Godfrin, D.; Hourdet, D.; Millequant, M.; Blanchard, J.; Voily, J.-L. *Electrophoresis* **2001**, *22*, 720.

(31) Bokias, G.; Mylonas, Y.; Staikos, G.; Bumbu, G. G.; Vasile, C. *Macromolecules* **2001**, *34*, 4958.

(32) Wang, L. Q.; Tu, K.; Li, Y.; Zhang, J.; Jiang, L.; Zhang, Z. *React. Funct. Polym.* **2002**, *53*, 19.

(33) Konak, C.; Reschel, T.; Oupicky, D.; Ulbrich, K. *Langmuir* **2002**, *18*, 8217.

(34) Chourdakis, N.; Bokias, G.; Staikos, G. *J. Appl. Polym. Sci.* **2004**, *92*, 3466.

(35) Kokufuta, E.; Zhang, Y. Q.; Tanaka, T.; Mamada, A. *Macromolecules* **1993**, *26*, 1053.

(36) Mylonas, Y.; Karayanni, K.; Staikos, G. *Langmuir* **1998**, *14*, 6320.

(37) Loh, W.; Teixeira, L. A. C.; Lee, L. T. *J. Phys. Chem. B* **2004**, *108*, 3196.

(38) Matsukata, M.; Hirata, M.; Gong, J. P.; Osada, Y.; Sakurai, Y.; Okano, T. *Colloid Polym. Sci.* **1998**, *276*, 11.

(39) Sotiropoulou, M.; Bokias, G.; Staikos, G. *Macromolecules* **2003**, *36*, 1349.

(40) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039.

(41) Lianos, P.; Viriot, M.-L.; Zana, R. *J. Phys. Chem.* **1984**, *88*, 1098.

(42) Schild, H. G.; Tirrell, D. A. *Langmuir* **1991**, *7*, 665.

(43) Mylonas, Y.; Bokias, G.; Iliopoulos, I.; Staikos, G. *Eur. Polym. J.*, in press.

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