Interactions of a Smart Cationic Polyelectrolyte Based on Hydroxypropylcellulose with an Anionic Surfactant

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ABSTRACT: Novel thermosensitive, cationic polyelectrolyte was obtained by grafting *N*-vinylformamide onto hydroxypropylcellulose followed by the hydrolysis of the formamide groups to the amine groups. The effect of the ionic strength on the lower critical solution temperature of the polymers was studied. The interactions of the polymers with sodium dodecyl sulfate (SDS) as a model anionic surfactant were studied. It was found by the measurements of the light scattering and fluorescence spectroscopy that the graft copolymers obtained strongly interact with SDS with the formation of polymer-surfactant complexes. The values of critical association concentration (cac) of these polymer-surfactant systems were found to be of the order of 10^{-5} mol/dm^3 at pH = 6.5 and of the order of 10^{-6} mol/dm^3 at pH = 2.5. The polymer was shown to be potentially useful for the purification of water from anionic surfactants. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3184–3189, 2008

Key words: fluorescence; gel permeation chromatography (GPC); polysaccharides; stimuli-sensitive polymers; surfactants

INTRODUCTION

Annual world production of surfactants is estimated to be several million tons. That production is growing because there are more and more practical applications of these compounds. They are widely used in household products, detergents, pesticide formulations and are applied in many industrial processes, e.g., oil recovery, paper, mining, cosmetic, and food industries.[1] Unfortunately, that leads quite often to the pollution of water with surfactants. Many of currently used surfactants are not biodegradable and they can be harmful for aquatic fauna and flora.[2–5] For example, in aquatic plants they break-up chlorophyll-protein complex, damage cell membrane, and delay metabolism and growth.[6] Also, their presence in biological treatment plants is often undesired (toxicity for microorganisms, gas exchange inhibition etc). These adherent effects are already induced by surfactants at very low concentrations when the classical methods used for their removal from water such as adsorption on activated carbon[7] and coagulation/precipitation[8] and are not very effective.

Moreover, some of the surface active agents are very expensive, and they are lost when classical, irreversible methods are applied for the water treatment.

Interactions between ionic surfactants and polyelectrolytes have attracted both scientific and industrial interest which is reflected in many scientific papers concerning this field.[9–14] In particular, using smart polymers which are capable of strongly interacting with surfactants, on one hand, and can be easily removed from water upon application of a stimulus, e.g., temperature, on the other hand, seems to be an attractive alternative method of surfactant removal. Moreover, the reversibility of the response of smart polymers to stimuli may allow recovering the surfactant. We have obtained both synthetic[15] and modified natural polymers[16,17] which were found to form complexes with a cationic surfactant. Our next goal was to synthesize a smart polymer which could be able to form complexes with an anionic surfactant. We propose to use environmentally friendly, water-soluble polymer for that purpose. This report presents the results of our studies on novel, thermosensitive, biodegradable, cationic polyelectrolyte, and its interactions with a model anionic surfactant.

EXPERIMENTAL

Materials

Hydroxypropylcellulose (HPC, Aldrich, M_w = 90,000), *N*-vinylformamide (NVF, Aldrich, 99%), sodium

$$R_1 = -(\!-CH_2CHO\!-)_{\overline{n}} \ H \quad or \quad H \quad \textbf{(HPC)}$$

(with CH_3 above)

$$R_2 = -(\!-CH_2CH\!-)_{\overline{m}} \quad \textbf{(HVF)}$$

(with $O=CH$, NH above)

$$R_3 = -(\!-CH_2CH\!-)_{\overline{m}} \quad pH{=}10 \quad \textbf{(HVA)}$$

(with NH_2 above)

$$R_4 = -(\!-CH_2CH\!-)_{\overline{m}} \quad pH{=}2.5 \quad \textbf{(HVA)}$$

(with NH_3^+ above)
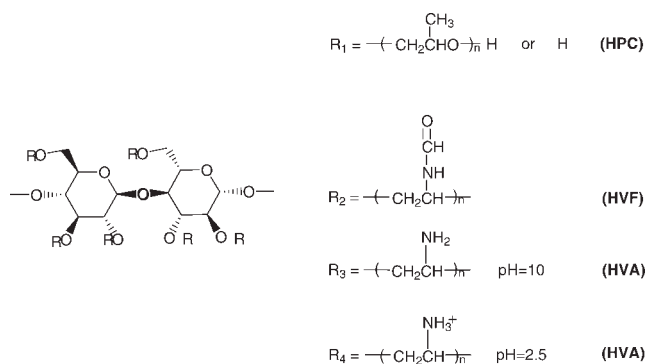
Scheme 1 Structure of HPC before (R_1) and after grafting (R_2) and after hydrolysis pH > 4.5 (R_3), pH < 4.5 (R_4).

dodecyl sulfate (SDS, Fluka, 99%), benzoyl peroxide (BPO, POCH Gliwice, analytical grade), sodium hydroxide (POCH Gliwice, analytical grade), hydrochloric acid (POCH Gliwice, analytical grade), dimethylformamide (DMF, POCH, Gliwice, reagent grade) were used as received. Water was distilled twice. Pyrene was recrystallized twice from methanol.

Polymer synthesis

In a 250-mL three-necked flask 3 g (~ 0.01 mol of repeating unites of glucose) of HPC were dissolved in 30 mL of DMF. The solution was degassed by bubbling with nitrogen for 30 min and 2.7 g (11.16 mmol) of BPO dissolved in 15 mL of DMF was added. After 5 min 12.19 g (171.50 mmol) of NVF was added. The reaction mixture was heated at 70°C for 3 h under constant mixing with a magnetic stirrer and under bubbling with nitrogen. Then the mixture was cooled down and dialyzed for 1 week, first against DMF, and then against distilled water. Next 20 mL of the solution and 10 mL of concentrated hydrochloric acid were poured to a 50-mL three-necked flask. The solution was degassed by bubbling nitrogen and constantly mixed with a magnetic stirrer under room temperature for 72 h. Then the solution was dialyzed for one week against distilled water and freeze-dried.

Apparatus

The elemental analysis (C, H, and N) was performed with an Euroea 3000 elemental analyzer. GPC analyses were performed using a Waters chromatographic system equipped with a Waters Ultrahydrogel Linear column and a Waters 2996 PDA detector. The eluent was 0.1M NaCl and the flow rate was 1 mL/min. Fluorescence emission spectra of pyrene were measured with an SLM-AMINCO spectrofluorimeter using the excitation wavelength of λ_{ex}=320 nm. The widths of the excitation and emission slits were 8 and 2 nm, respectively. The spectra were corrected

for the apparatus response using the function supplied by the manufacturer. Dynamic light scattering measurements were performed using Malvern Nano Zetasizer at the scattering angle of 173° at 25°C. Scattering data were analyzed using Malvern software.

LCST measurements

The LCST values of the polymeric solutions were measured using a Hewlett-Packard 8452A spectrophotometer equipped with a Hewlett-Packard 89090A Peltier temperature control accessory, as described elsewhere.[15] In short, the solution was heated with the Peltier accessory within the range 15–70°C. The solution was heated at the rate of about 0.5°C/min and stirred at the rate of 5 s^{-1}. The LCST values were determined from the changes in the turbidity with temperature, expressed as $1 - T$ (absorptance) where T was apparent transmittance of the polymer solutions at 400 nm.

RESULTS AND DISCUSSION

HPC is a thermosensitive derivative of cellulose, one of the most abundant natural polymers. It shows the lower critical solution temperature (LCST) in aqueous solution. In dilute solution (0.1 g/dm^3) of HPC its LCST falls around 41°C.[18] The purpose of the present study was to modify HPC to obtain a thermosensitive cationic polyelectrolyte. The modification was meant to introduce positive charges to the HPC chain so that the polymer was able to form complexes with negatively charged surfactants, on one hand, and be easily separable by precipitation, on the other. This would offer an alternative way of removing surfactants from aqueous media. However, LCST of the polymers is known to increase with increasing charge on the polymeric chain so the modification had to be limited to avoid considerable rising of LCST. This is important in view of potential practical applications of such systems for removal of surfactants from water.

TABLE I
Characteristics of the Polymers

	HPC	HVF	HVA
m_{NVF}/m_{HPC} [a]	–	0.17	–
n_{NVF}/n_{Glu} [b]	–	0.68	–
LCST [c]	45	42	47

[a] m_{NVF}/m_{HPC} is the weight ratio of NVF and HPC in the polymer.

[b] n_{NVF}/n_{Glu} is the average number of NVF units attached to a glucose unit of HPC found from elemental analysis.

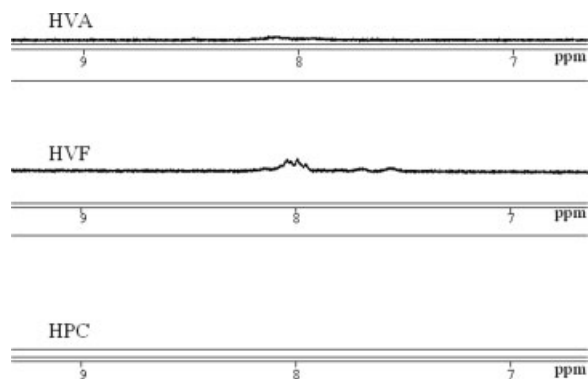[c] Determined for the polymers in 0.1g/L aqueous solution, at pH = 6.5.

Figure 1 ^{1}H NMR spectra of HPC, HVF, and HVA.

HPC was grafted with vinylformamide (VF) using benzoyl peroxide (BPO) as a radical initiator.[19] Grafted polyvinylformamide side chains in the polymer obtained (HVF) were next hydrolyzed in the presence of hydrochloric acid and HPC with polyvinylamine hydrochloride chains (HVA) was obtained.

The structures of the resulting polymers are shown in Scheme 1 and some of their properties are given in Table I.

To find out the extent of hydrolysis the polymers were further studied using ^{1}H NMR spectroscopy. The spectra obtained are shown in Figure 1.

The presence of a signal at 8.1 ppm, characteristic of protons attached to the carbonyl group confirmed grafting of the NVF side chains onto HPC main chain. The signal decreases significantly for HVA because of hydrolysis. The degree of hydrolysis found from the spectra was about 50%.

The results of the elemental analysis (the presence of nitrogen) confirmed successful grafting of NVF onto HPC chains. Grafting resulted in a decrease of the LCST by 3°C compared to the native polymer. As expected, hydrolysis of HVF to HVA raised the
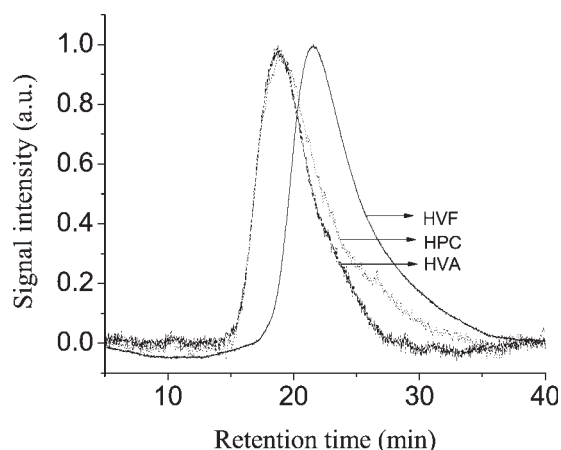

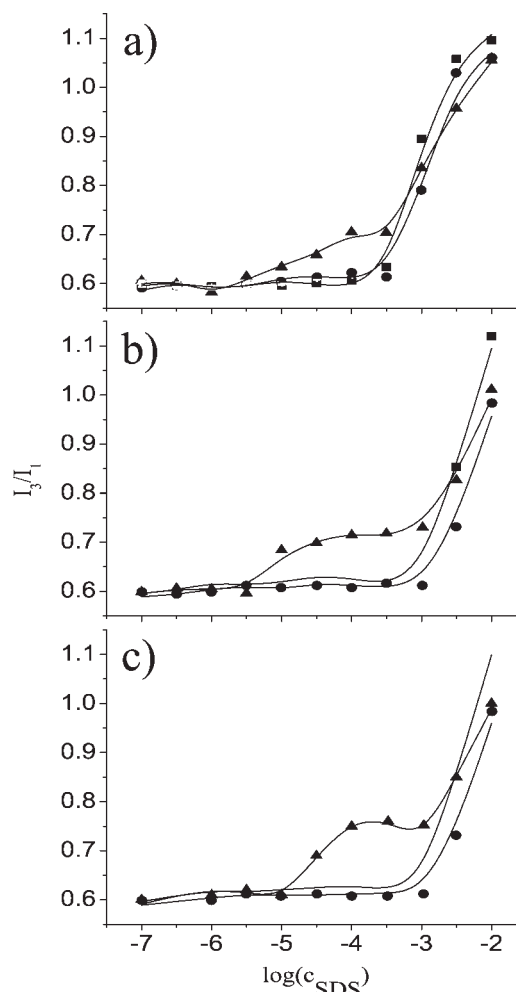**Figure 2** GPC traces for HPC, HVF, and HVA measured at pH = 6.5.

Figure 3 The dependence of I_3/I_1 ratio of pyrene on SDS concentration in the solution of HPC (■), HVF (●), and HVA (▲) at c_p = 0.1 g/dm^3 for (a) pH = 2.5, (b) pH = 6.5, and (c) pH = 9.0.

LCST of the polymer by 5°C. Extending the hydrolysis time from 2–72 h did not influence the LCST value suggesting that the hydrolysis was completed within 2 h. This was confirmed by the fact that GPC traces of the polymers hydrolyzed for 2 h (see later) did not change with increasing hydrolysis time.

The polymers were then analyzed using GPC. Figure 2 shows the GPC traces of HPC, HVF, and HVA polymers. The trace of HVF is shifted towards longer retention times compared to HPC. This could be explained by the fact that grafted NVF chains

TABLE II
Free Enthalpy Values for HVA with SDS Aggregation Process at Three Different pH Values

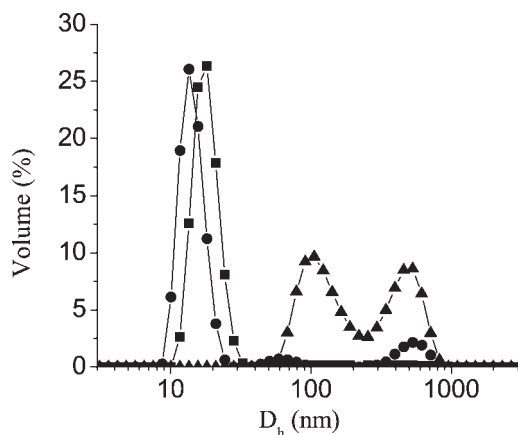|	pH = 2.5	pH = 6.5	pH = 9.0
cac (mol/dm^3)	1.0×10^{-6}	3.2×10^{-6}	1.0×10^{-5}
ΔG_a^0 (kJ/mol)	−34.2	−31.4	−28.5

Figure 4 Particle size distributions for polymer-surfactant systems at c_{SDS} = 1.0 × 10^{-7} (■), 1.0 × 10^{-5} (●), and 1.0 × 10^{-3} (▲) (pH = 2.5 and c_{pol} = 0.1 g/L).

have more hydrophobic character than HPC chains. The behavior of HVF is typical of an amphiphilic polymer which in aqueous solution has a tendency to assume more compact conformation than that of HPC. That corresponds with lower LCST value for HVF than that of HPC, which is characteristic of hydrophobically modified polymers. The retention time of HVA polymer is considerably lower than that of HVF used for hydrolysis. This is due to more hydrophilic character of polyvinylamine side chains than those of HVF. The polymer becomes hydrophilic again which results in more extended conformation and in decrease of its retention time.

The interactions of the polymers with SDS at three different pH values were studied with fluorescence spectroscopy using pyrene as a fluorescent probe. Pyrene is a well-known fluorescence probe used to estimate the hydrophobicity of the microenvironment in which it resides.[20] Namely, the ratio of intensities of the third and first vibrational bands, I_3/I_1, in the fluorescence emission spectrum of pyrene is low in polar media and high in the hydrophobic environments. In the case of polymer-surfactant systems when the surfactant concentration exceeds cac the micelles are formed along the polymeric chain in which pyrene molecules are solubilized. Thus, the presence of the micelles is revealed by increased values of I_3/I_1 ratio. The dependence of

I_3/I_1 ratio on surfactant concentration for polymer-surfactant systems studied at three different pH values is shown in Figure 3.

For HPC-SDS and HVF-SDS systems the I_3/I_1 ratio for the surfactant concentration range of 10^{-7} to 10^{-3} mol/dm^3 is constant and characteristic of that for pyrene residing in the aqueous phase. That indicates that there is no polymer-surfactant complexes formation in the solution under these conditions. The I_3/I_1 ratio increases abruptly when the SDS concentration exceeds 1 × 10^{-3} mol/dm^3 at pH = 6.5 and 3.16 × 10^{-4} mol/dm^3 at pH = 2.5 which is of the order of cmc of SDS (the literature value of cmc of SDS is 8.3 × 10^{-3} mol/dm^3 Ref. 21) and therefore it may be ascribed to the formation of the SDS micelles in a system. The difference from the literature value may result from the fact that the cmc values determined with the fluorescence method are usually lower than those found with other methods due to much higher sensitivity of the former.

The corresponding I_3/I_1 plots for HVA are, however, very different since they show a two-step increase. For HVA polymer the I_3/I_1 ratio increases already at [SDS] = 1.0 × 10^{-5} mol/dm^3 for pH = 9, at [SDS] = 3·10^{-6} mol/dm^3 for pH = 6.5, and at [SDS] = 1 × 10^{-6} mol/dm^3 for pH = 2.5. This is indicative of the formation of polymer-surfactant complexes, i.e., SDS micelles are formed along HVA side chains. These values of surfactant concentrations can be considered as the cac for HVA-SDS system. The cac value for the lower pH occurs at lower surfactant concentration which may be explained considering the protonation of the amine groups. Attraction between positively charged amino groups and negatively charged SDS molecules enhances formation of polymer-surfactant complexes. The amine groups become progressively protonated with decreasing pH which is accompanied with decreasing cac values in HVA-SDS system. At higher SDS concentrations (around 1 × 10^{-3} mol/dm^3) the I_3/I_1 plot for HVA shows also a second increase coinciding with those of HPC and HVF resulting from the formation of free SDS micelles above cmc.

Using the experimental data of cac and based on eq. (1)[22] the free enthalpy of aggregation process

TABLE III
Zeta Potential Values [mV] of 0.1 g/L Polymer Solutions at pH = 2.5 and Various Concentrations of SDS

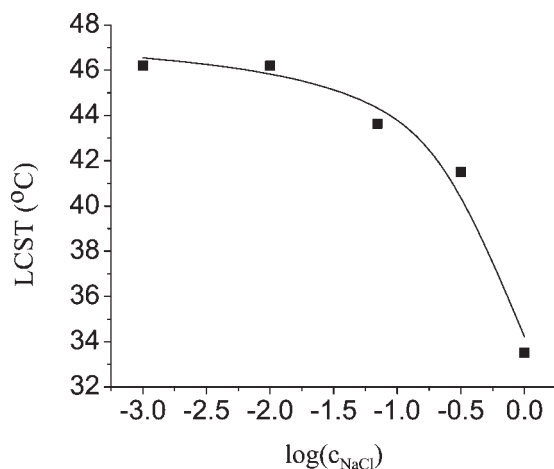| Polymer	Conductivity [mS/cm]	SDS concentration (M)					
		0M	1.0 × 10^{-7}	1.0 × 10^{-6}	1.0 × 10^{-5}	1.0 × 10^{-4}	1.0 × 10^{-3}
HPC	0.0369		4.9 ± 0.8				
HVF	0.0254		1.3 ± 0.7				
HVA	0.1530	13.4 ± 3.1	22.3 ± 1.9	27.3 ± 2.0	17.9 ± 1.7	3.0 ± 0.8	−4.5 ± 0.3

Figure 5 The dependence of LCST for HVA on ionic strength at c_{pol} = 1 g/L and pH = 6.5.

was calculated and the values obtained are collected in Table II.

$$\Delta G_a^0 = RT \ln(\text{cac}) \tag{1}$$

The measurements of dynamic light scattering were carried out for the polymer- surfactant system at constant concentration of polymer (c_{pol} = 0.1 g/L) and pH (pH = 2.5) and various concentrations of surfactant added (see Fig. 4). At c_{SDS} = $10^{-7}M$ the diameter of the particle size is about 20 nm, which could be assigned to the polymer coil. At c_{SDS} = $10^{-5}M$ these particles still exist in solution and a second population of particles about 500 nm in diameter appears. That can be ascribed to polymer-

surfactant complexes. At even higher surfactant concentration of $1 \times 10^{-3}M$ the small objects disappear and two populations of large aggregates of about 100 and 500 nm exist suggesting that all polymeric chains are complexed with surfactant molecules.

Zeta potential measurements answered the question of the kinetic stability of the particles (see Table III).

High positive zeta potential of HVA at low concentrations of SDS reflects the protonation of the amino groups in polymer and negligible interactions between polymer and surfactant. Decrease of the zeta potential of HVA with increasing SDS concentration shows the progressive polymer-surfactant complexes formation, consistent with the fluorescence probe measurements. Initial increase of the zeta potential up to SDS concentration of 1.0×10^{-6} may be due to conformational changes of the polymer induced by the surfactant present in a solution.

We have also studied the response of LCST of HVA to the changes of the ionic strength (Fig. 5). It was found that the LCST begins to decrease for ionic strengths higher than 0.01 and may be lowered down to 33°C in 1M NaCl solutions. Thus, the response of the LCST of HVA is very similar to that of the native HPC.[16]

The AFM height images for HVA deposited on silica surface at temperature below and above LCST are significantly different (see Fig. 6). Average size of objects deposited at room temperature is at least few times higher than that of the objects deposited above LCST. It suggest intramolecular aggregation (intramolecular hydrogen bonds existence) at this polymer in solution (0.1 g/L).
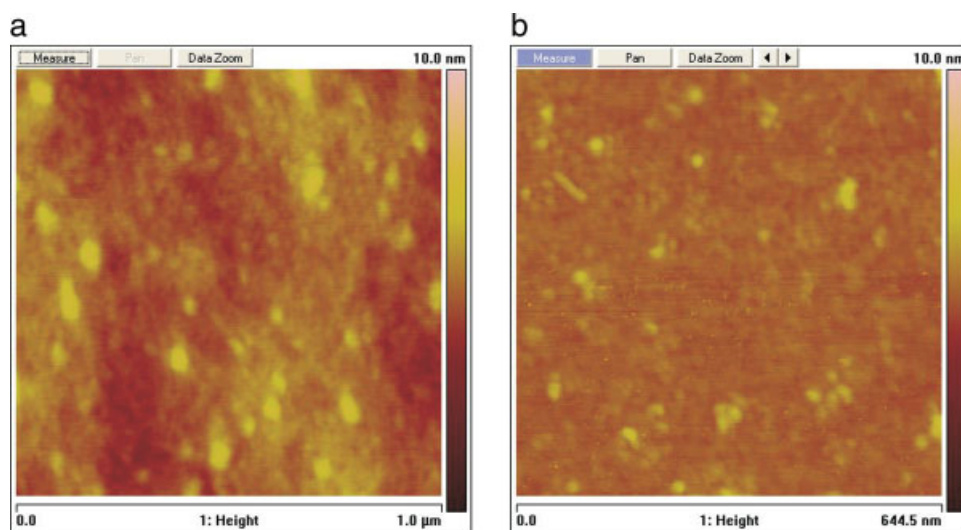

Figure 6 The AFM height image of HVA on silica surface deposited from water solution of polymer (0.1 g/L concentrated) at two different temperatures a) 25°C (below LCST) and b) 60°C (above LCST). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

Novel HPC modified by polyvinylamine grafting polymer was synthesized. The polymer belongs to the class of smart polymers; it is sensitive to the changes in temperature, pH and the ionic strength. The polymer interacts with anionic surfactant, SDS, forming polymer-surfactant complexes. The aggregation process is pH dependent and it starts at very low concentration of surfactant, the cac being of the order of $10^{-6}M$.

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