

# Smart Anionic Polyelectrolytes Based on Natural Polymer for Complexation of Cationic Surfactant

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**ABSTRACT:** The thermosensitive polyelectrolytes were obtained by grafting 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) onto hydroxypropylcellulose (HPC), a biodegradable polysaccharide. The interactions of the polymers with dodecyltrimethylammonium chloride (DTAC), a model cationic surfactant, were studied. It was found by the measurements of the surface tension and the analysis of fluorescence emission of pyrene used as a fluorescent probe, that the HPC-AMPS graft polymers strongly interact with DTAC

with the formation of polymer-surfactant complexes. The critical aggregation concentrations of these polymer-surfactant systems were found to be of the order of  $10^{-5}$  mol/dm<sup>3</sup>. The polymers were found to be potentially useful in the purification of water from cationic surfactants. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2401–2407, 2006

**Key words:** polysaccharides; graft copolymers; surfactants; polyelectrolytes

## INTRODUCTION

The studies on the interactions between water-soluble polymers and surfactants have become more and more intensive since they began in the 60s.<sup>1–3</sup> The studies include nonionic polymers and ionic surfactants,<sup>4–6</sup> nonionic polymers and nonionic surfactants,<sup>7,8</sup> ionic polymers and ionic surfactants,<sup>9–11</sup> and hydrophobically-modified polymers with ionic<sup>12,13</sup> and nonionic<sup>14</sup> surfactants. We are particularly interested in the studies on the interactions of surfactants with stimuli-responsive polymers due to the potential practical applications of these systems.<sup>15</sup> In the previous articles we have described the studies on synthetic thermosensitive polymers obtained by copolymerization of *N*-isopropylacrylamide (NIPAM) with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS)<sup>16,17</sup> and with sodium styrenesulfonate (SSS).<sup>18</sup> These thermosensitive anionic polyelectrolytes interacted very efficiently with cationic surfactants forming polymer-surfactant aggregates and therefore they can be used for purification of water from surfactants. In practical terms, it can be achieved by adding the polyelectrolyte showing a lower critical solution temperature (LCST) to the water contaminated with surfactants bearing the opposite

charges. The polymer-surfactant complexes are formed and they can be easily precipitated by raising the temperature above the LCST of the polyelectrolyte-surfactant system. The surfactant containing precipitate can be then removed, e.g., by filtration. Although the interactions between polymers and surfactants used in these studies were very effective,<sup>16–18</sup> their practical applications were hindered by the concern regarding the possible toxicity of the synthetic polymers applied. Therefore, the current work aims in finding efficient, nontoxic, and easy to use thermosensitive polymers for the purification of water from surfactants using the principle described in our earlier articles.<sup>16–18</sup> Thus, we have decided to test whether the smart natural polymers can be used for that purpose. This article presents the results of our studies on the interactions of a smart anionic polyelectrolyte based on the thermosensitive polysaccharide, hydroxypropylcellulose (HPC), with surfactants. In contrast to other thermosensitive polymers, which are often produced from carcinogenic or teratogenic monomers, HPC is a nontoxic polymer approved by FDA for the use in food, drugs, and cosmetics. However, HPC is a nonionic polymer, therefore, to increase its ability for complexation of ionic surfactants one has to modify it by the introduction of ionic groups of the opposite charge. For the purpose of complexation of cationic surfactants followed by their precipitation above the LCST, grafting of HPC with an anionic monomer seemed to be the optimal synthetic method. Grafting made possible introduction of charged groups into the polymer while preserving the structure of the main HPC chain, which was necessary to retain its thermo-

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sensitivity. The article describes the studies on interactions of nongrafted HPC and HPC grafted with a small amount of AMPS with DTAC (dodecyltrimethylammonium chloride), a model cationic surfactant.

## EXPERIMENTAL

### Materials

Hydroxypropylcellulose (HPC, Aldrich,  $M_w = 60,000$ , the average DP of isopropyl units is about 9), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS, Aldrich, 99%), dodecyltrimethylammonium chloride (DTAC, Fluka, 99%), potassium permanganate (POCH Gliwice, analytical grade), sodium hydroxide (POCH Gliwice, analytical grade), and sulfuric acid (POCH Gliwice, analytical grade) were used as received. Water was distilled twice. Pyrene was recrystallized twice from methanol.

### Polymer synthesis

A typical procedure of synthesis was as follows. In a 250-mL three-necked flask, 6 g of HPC was dissolved in 200 mL of water. The solution was degassed by bubbling nitrogen for 30 min, and 0.0158 g (0.10 mmol) of  $\text{KMnO}_4$  dissolved in 1 mL of water was added. After 5 min the solution became colorless and 2.158 g (22 mmol) of  $\text{H}_2\text{SO}_4$  and 12.47 g (60 mmol) of AMPS was added. Then the reaction mixture was heated in  $60^\circ\text{C}$  for 4 h under constant mixing with a magnetic stirrer while bubbling with nitrogen. The reaction mixture was cooled down and neutralized with NaOH solution. The precipitate was removed by decantation. The polymeric solution was dialyzed for 1 week against distilled water and freeze-dried.

### Apparatus

The elemental analysis (C, H, and N) was performed with a 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 spectra of pyrene were measured using an SLM-AMINCO spectrofluorimeter. The spectra were corrected for the apparatus response using a function supplied by the manufacturer. Surface tension was measured using a K9 Krüss tensiometer.

### 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.<sup>17</sup>

In short, the solution was heated with the Peltier accessory within the range  $15\text{--}70^\circ\text{C}$ . The solution was heated at a rate of about  $0.5^\circ\text{C}/\text{min}$  and stirred at a rate of  $5\text{ s}^{-1}$ . The LCST values were determined from the changes in the turbidity with temperature, expressed as  $1 - T$ , where  $T$  is the apparent transmittance of the polymer solutions at 400 nm.

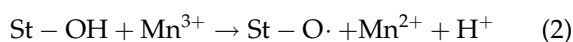
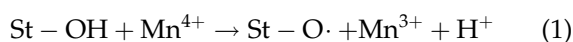
### Fluorescence studies

A saturated solution of pyrene in water ( $6.4 \times 10^{-7}\text{ mol}/\text{dm}^3$ )<sup>19</sup> was obtained as follows. A solution of a few milligrams of pyrene in 1 mL of methanol was placed in a 1 L flask. Methanol was evaporated to form a film of pyrene on the flask walls. The flask was then filled with water and sonicated for 30 min. The dry samples of studied polymers were dissolved in the above saturated aqueous solution of pyrene. The pyrene fluorescence spectra were measured using the excitation wavelength  $\lambda_{\text{ex}} = 320\text{ nm}$ . The widths of the excitation and emission slits were 8 and 2 nm, respectively.

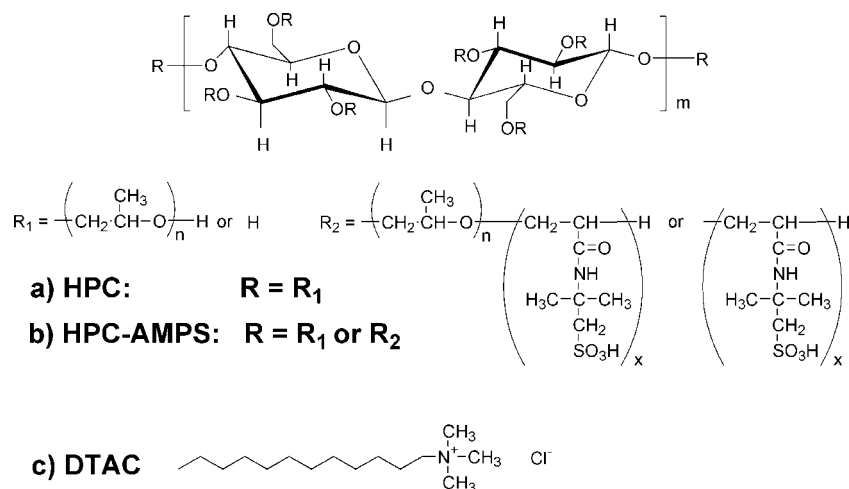
## RESULTS AND DISCUSSION

The aim of the present study was to obtain thermo-responsive polymers, which would be able to form complexes with surfactants, with the view of practically using them to remove surfactants from water upon coprecipitation. For that purpose HPC [Scheme 1(a)] was chosen.

HPC shows the LCST, which for unsubstituted polymer in dilute solution ( $0.1\text{ g}/\text{dm}^3$ ) falls around  $41^\circ\text{C}$ .<sup>20</sup> Therefore, HPC, which is also a nontoxic (approved by United States Food and Drug Administration as a food additive) and biodegradable natural polymer, seems to be a good candidate. However, HPC is a neutral polymer and so to increase its tendency to form complexes with cationic surfactants, we have grafted it with AMPS, an anionic monomer. The reaction was carried out according to the procedure developed by Hebeish et al.<sup>21</sup> for grafting of acrylonitrile onto starch. They have used potassium permanganate to initiate that process. The method was further studied by Zhang et al.<sup>22</sup> It was proposed, that the graft copolymerization of acrylonitrile onto starch initiated by potassium permanganate in the presence of acid occurs through the reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$  and/or  $\text{Mn}^{2+}$  and the radicals are formed along the polymer chain in the following overall processes<sup>22</sup>:



where St-OH represents starch.



**Scheme 1** Structure of HPC (a) nongrafted and (b) grafted with AMPS and (c) structure of DTAC.

In this initiation method, the radicals are formed only along the polysaccharide chain so the formation of the homopolymer may be minimized when using dilute  $\text{KMnO}_4$  solutions to avoid chain transfer, as opposed to initiation using, e.g., peroxides or azo compounds, which inherently result in some degree of homopolymerization of the monomer used for grafting.

We have assumed that analogical processes take place during grafting onto HPC. The resulting structure of the polymer is proposed in Scheme 1(b). We have prepared two polymers with different compositions. The details are given in Table I.

As can be seen from the data given in Table I, the grafting degree is rather low. There is, however, considerable difference between the polymers. The grafting degree is more than seven times higher for HPC-AMPS2 than for HPC-AMPS1. It is difficult to determine the DP of the grafts because each glucose unit contains three hydroxyl groups, two secondary and one primary, which give rise to radicals with probably different yield. Because of lower  $\text{KMnO}_4$  concentration and higher AMPS concentration used in the polymer

**TABLE I**  
Characteristics of the Polymerization Conditions and Studied Polymers

	HPC	HPC-AMPS1	HPC-AMPS2
<sup>a</sup> $c_{\text{KMnO}_4}$ (mol/dm <sup>3</sup> )	–	$2.00 \times 10^{-4}$	$1.00 \times 10^{-4}$
<sup>b</sup> $m_{\text{AMPS}}/m_{\text{HPC}}$	0	1.04	2.08
<sup>c</sup> $n_{\text{AMPS}}/n_{\text{Glu}}$	0	0.78	5.8
LCST	42°C	42°C	45°C

<sup>a</sup>  $c_{\text{KMnO}_4}$  is the concentration of  $\text{KMnO}_4$  used to initiate the polymerization.

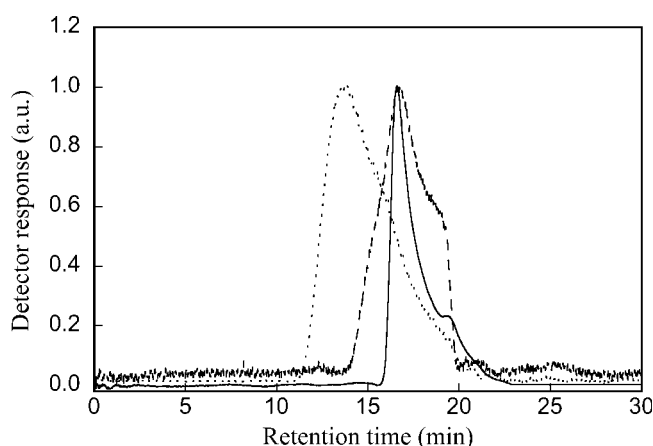
<sup>b</sup>  $m_{\text{AMPS}}/m_{\text{HPC}}$  is the ratio of the weights of AMPS and HPC in the polymers obtained.

<sup>c</sup>  $n_{\text{AMPS}}/n_{\text{Glu}}$  is the average number of AMPS units attached to a glucose unit of HPC found from elemental analysis.

synthesis, it should be expected that the number of grafts is lower and their length greater for HPC-AMPS2 than for HPC-AMPS1. What is also important is that the grafting of AMPS onto HPC chain does not change the LCST value for HPC-AMPS1 and changes it only slightly for HPC-AMPS2, for which the LCST increases only by 3°C. This behavior is similar to that of the thermosensitive copolymers of NIPAM with SSS as studied previously,<sup>18</sup> and it is in strong contrast to that of the copolymers of NIPAM and AMPS,<sup>16,17</sup> for which LCST increased significantly with increasing content of AMPS up to complete disappearance of LCST for AMPS content as little as 10 mol %.

The polymers were further characterized using GPC. Figure 1 shows the GPC traces of unsubstituted HPC and of both graft polymers obtained.

Although the retention time for HPC-AMPS1 did not change compared to that of the native HPC, the trace became significantly wider and begins at the retention time shorter than the one for HPC. We

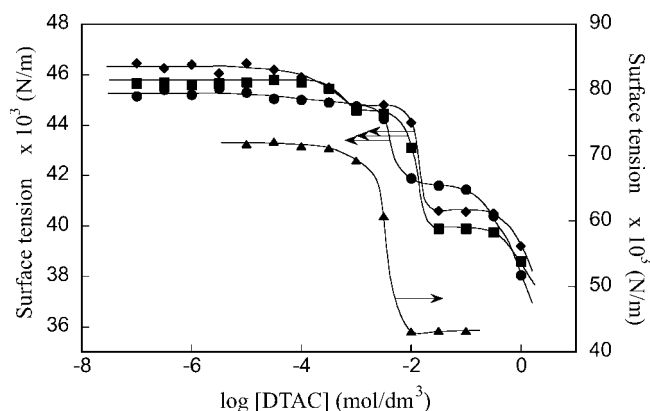


**Figure 1** Normalized GPC traces of HPC (solid line), HPC-AMPS1 (dashed line), and HPC-AMPS2 (dotted line) at  $c_p = 1.0 \text{ g/dm}^3$ .

have confirmed in a control experiment that, under conditions identical to those used in the graft polymerization,  $\text{KMnO}_4$  does not cause scission of the HPC chains. Therefore, the changes in the HPC trace may be ascribed to the grafting reaction.

To achieve higher grafting degree we have decreased  $\text{KMnO}_4$  concentration while increasing AMPS concentration in the polymerization feed. Indeed, the GPC trace for the resulting polymer, HPC-AMPS2, shows a maximum at much shorter retention times than that of the native HPC, which means much more efficient graft polymerization than for HPC-AMPS1, resulting in a substantial increase of the molecular weight.

To study the complexation of DTAC by the graft polymers obtained, we have measured the surface tension of the aqueous solutions of the surfactant used and different polymer-surfactant systems (Fig. 2). The plots indicate that HPC, both nongrafted and grafted, shows significant surface activity decreasing the surface tension of water in  $0.1 \text{ g/dm}^3$  solutions to 45–47 mN/m at  $25^\circ\text{C}$ . The plot of the surface tension of the solution of nongrafted HPC versus DTAC concentration is very similar to that observed for DTAC solution. The rapid change in the slopes of the plot occurs at the same concentration as at the analogous plot obtained for DTAC in the absence of the polymer, i.e., around  $1 \times 10^{-2} \text{ mol/dm}^3$ . Therefore, one may conclude that the cmc (critical micelle concentration) of DTAC did not change in the HPC solution and that HPC does not interact with DTAC, or at least that this interaction is too weak to be detected by surface tension measurement. On the other hand, the respective plots for grafted polymers show two distinctive regions in their plots. That is characteristic of the polymers which form polymer-surfactant complexes. The first jump in the slope occurs at  $[\text{DTAC}]$  about  $10^{-3} \text{ mol/dm}^3$  for both HPC-AMPS1 and HPC-AMPS2 solutions, and can be interpreted as resulting from the formation of polymer-surfactant complexes. Its posi-



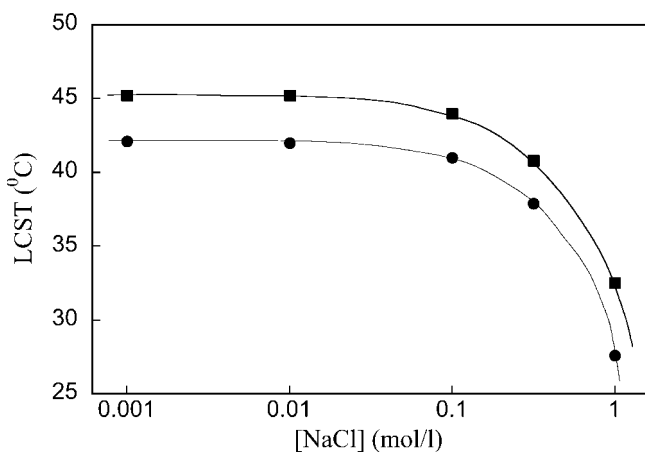
**Figure 2** Surface tension of the DTAC solution in water at  $25^\circ\text{C}$  ( $\blacktriangle$ ) and in  $0.1 \text{ g/dm}^3$  solutions of HPC ( $\bullet$ ), HPC-AMPS1 ( $\blacksquare$ ), and HPC-AMPS2 ( $\blacklozenge$ ).

tion corresponds to the critical aggregation concentration (cac) values for these polymer-surfactant systems. The second jump in the slope is found at about  $3 \times 10^{-2} \text{ mol/dm}^3$  and it can be interpreted as the cmc of DTAC in the polymer-surfactant system. Considerable shift of the cmc value in the grafted polymer-surfactant systems compared to that of the HPC-DTAC system is a manifestation of the complexation of the surfactant by the grafted polymer.

We have investigated the dependence of the LCST values of nongrafted and grafted HPC on DTAC concentration. It was found that the LCST of nongrafted and grafted HPC did not change significantly for DTAC concentrations up to  $1.0 \times 10^{-2} \text{ mol/dm}^3$  (data not shown). This behavior is in contrast to both that of the NIPAM-AMPS<sup>16,17</sup> and NIPAM-SSS copolymers,<sup>18</sup> for which LCST decreased with increasing DTAC concentration at lower DTAC concentration regime and then increased at higher DTAC concentration regime. It was found that when the temperature exceeded the LCST for nongrafted HPC the solutions become milky and, on cooling down below LCST, became clear again, irrespective of DTAC concentration. When DTAC was added to the solutions of HPC-AMPS1 they also became milky when the LCST was exceeded but no precipitate was formed and the turbidity did not disappear when the solutions were cooled down below LCST. On the other hand, adding DTAC to HPC-AMPS2 solutions resulted in the formation of precipitate on exceeding LCST, which did not dissolve on cooling down the solution below LCST, neither. Thus, it may be concluded that for graft copolymers the tendency of the polymer to form complexes with DTAC is stronger for higher AMPS content in the polymer and that complex formation is mainly due to the electrostatic interactions between the surfactant and the polymer. By filtering out the precipitate formed it is possible to remove both the polymer and the surfactant from the solution. Therefore, these polymers may find possible applications in the purification of water from surfactants.

The studies of the effect of the ionic strength on the LCST revealed that LCST decreases with increasing ionic strength, which is also characteristic of the copolymers of NIPAM studied.<sup>16–18</sup> This decrease becomes, however, noticeable only when the ionic strength is higher than 0.1 (Fig. 3) and it is relatively small. The difference in the LCST values between HPC and HPC-AMPS2 is about  $3^\circ\text{C}$  and it does not change with increasing ionic strength. These are important findings in practical terms as they demonstrate that the presence of inorganic salts in water at quite high concentrations, which is often the case, does not effect considerably the LCST value of polymers.

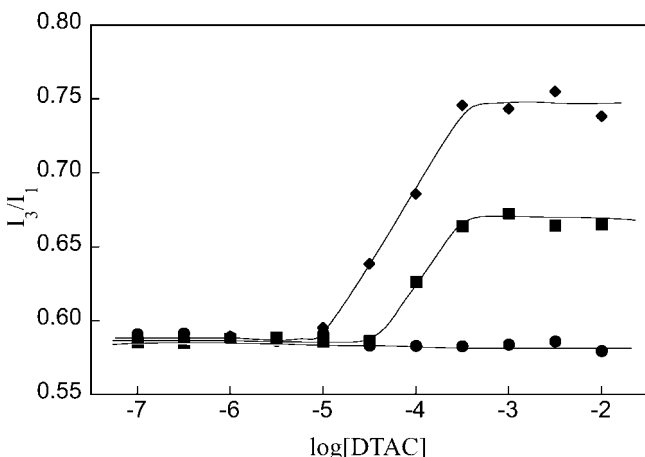
The interactions of the polymers with DTAC were further studied with fluorescence spectroscopy using pyrene as a fluorescent probe. Pyrene is a well-known probe that is used to estimate the hydrophobicity of



**Figure 3** The dependence of LCST for (●) HPC and (■) HPC-AMPS2 on ionic strength at  $c_p = 4 \text{ g/dm}^3$ .

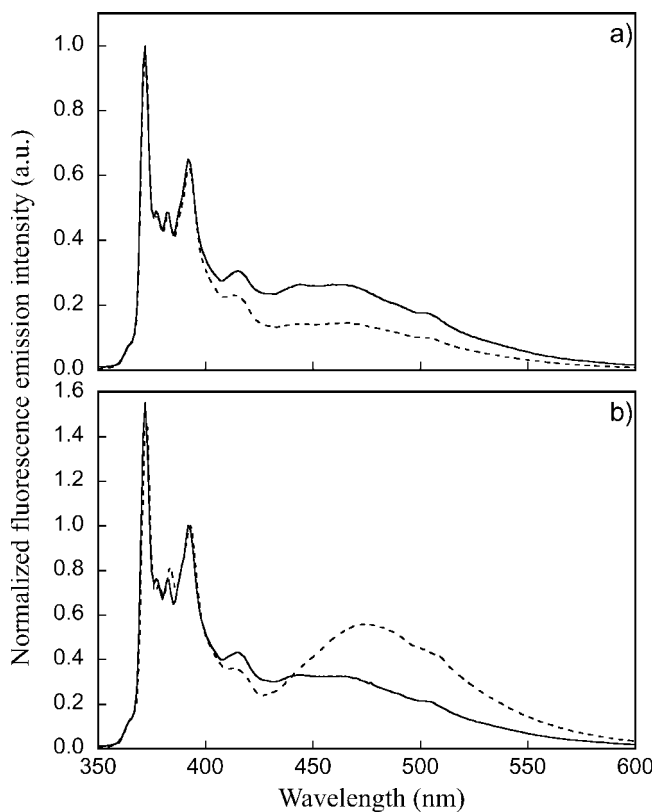
the microenvironment in which it resides. Namely, the ratio of the third and first vibrational bands,  $I_3/I_1$ , in the fluorescence emission spectrum of pyrene is low in polar media and high in the hydrophobic environments. In the case of polymer-surfactant systems when the surfactant concentration exceeds cac the micelles are formed along the polymeric chain which can solubilize pyrene molecules. The environment inside the micelles is hydrophobic, and therefore, the formation of the micelles is accompanied by the increase in  $I_3/I_1$  ratio. The dependence of  $I_3/I_1$  ratio for studied polymer-surfactant systems is shown in Figure 4.

For the HPC-DTAC system the  $I_3/I_1$  ratio does not change with increasing DTAC concentration up to  $1 \times 10^{-2} \text{ mol/dm}^3$  which is slightly below the cmc value of this surfactant, i.e.,  $2.03 \times 10^{-2} \text{ mol/dm}^3$ .<sup>23</sup> The value of the  $I_3/I_1$  ratio in this system, i.e., 0.58–0.59, is characteristic of pyrene in the aqueous



**Figure 4** The dependence of  $I_3/I_1$  ratio of pyrene on DTAC concentration in the solution of HPC (●), HPC-AMPS1 (■), and HPC-AMPS2 (◆) at  $c_p = 0.1 \text{ g/dm}^3$ .

environment and indicates that no polymer-surfactant complexes are formed, as was already indicated by the measurements of the surface tension. The corresponding plots for the grafted HPC are, however, very different. For HPC-AMPS1 polymer, the  $I_3/I_1$  ratio begins to increase at  $[\text{DTAC}] = 3.2 \times 10^{-5} \text{ mol/dm}^3$  and this value can be considered as the cac for that system. For HPC-AMPS2 system the cac is lower, i.e., it occurs at  $[\text{DTAC}] = 1.0 \times 10^{-5} \text{ mol/dm}^3$ . These values are significantly lower than those found in the measurement of the surface tension probably due to the much higher sensitivity of the fluorescence method. The values of the  $I_3/I_1$  ratio for the solutions of HPC-AMPS1 and HPC-AMPS2 are constant at  $[\text{DTAC}] > 3.16 \times 10^{-4} \text{ mol/dm}^3$  and equal to 0.65 and 0.75, respectively. However, at constant DTAC concentration equal or higher than  $1.0 \times 10^{-3} \text{ mol/dm}^3$  the value of  $I_3/I_1$  grows with increasing polymer concentration (data not shown). Thus, it may be concluded that the higher value of  $I_3/I_1$  for HPC-AMPS2 compared to that for HPC-AMPS1 results from larger fraction of solubilized pyrene in the former rather than from higher hydrophobicity of HPC-AMPS2/DTAC complexes.

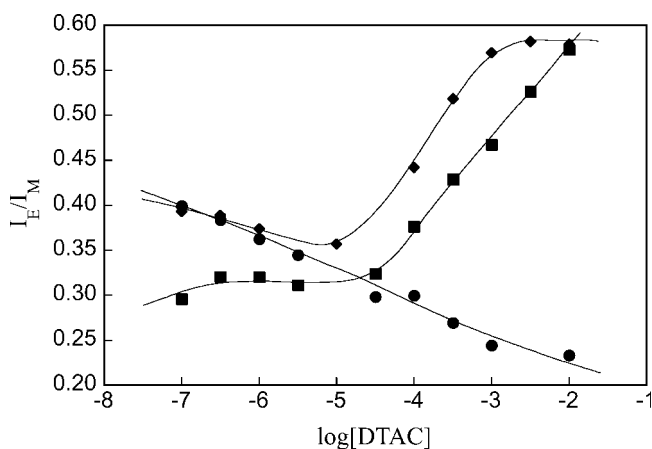


**Figure 5** Fluorescence emission spectra of pyrene ( $c_{\text{Py}} = 1.0 \times 10^{-5} \text{ mol/dm}^3$ ) in the aqueous solution of (a) HPC and (b) HPC-AMPS1 in the absence (solid line) and in the presence of  $1.0 \times 10^{-2} \text{ mol/dm}^3$  of DTAC (dashed line),  $T = 25^\circ\text{C}$ .

The above conclusions are confirmed by the analysis of another feature of the pyrene fluorescence emission spectrum, i.e., the excimer emission. The emission of pyrene excimers appears in the systems where the pyrene concentration, or at least its local concentration, is high and in which pyrene molecules have enough rotational freedom to assume parallel arrangement necessary to form excimers. The excimer emission was found around 475 nm in the solution of HPC in which pyrene was present [Fig. 5(a)]. It may be concluded that due to the hydrophobic interactions pyrene is organized along HPC polymeric chains although, as could be found in Figure 4, the polarity of that environment around the pyrene molecules is as high as that of water. The addition of DTAC results in the decrease of excimer emission most likely because in that system pyrene molecules interact not only with polymer chain but also with hydrophobic part of surfactant molecules that lowers its local concentration around the polymer chains and decreases the probability of excimer formation.

On the other hand, when DTAC is dissolved in the solutions of grafted HPC at the concentration above the  $c_{ac}$  of these systems, the pyrene molecules are solubilized within the surfactant micelles formed along the polymeric chains, which results in high local concentration of pyrene inside them and is therefore accompanied with the increased excimer emission [Fig. 5(b)].

The changes of the excimer emission relative to the monomer emission with increased DTAC concentration were measured as the changes of the  $I_E/I_M$  ratio, where  $I_E$  is the intensity of the excimer emission measured at 460 nm and  $I_M$  is the intensity of the monomer emission measured at 387 nm (Fig. 6). For the HPC solution, the addition of DTAC results in the monotonous decrease of the  $I_E/I_M$  ratio for the reasons



**Figure 6** The dependence of  $I_E/I_M$  ratio of pyrene ( $c_{Py} = 1.0 \times 10^{-5} \text{ mol/dm}^3$ ) on DTAC concentration in the absence of a polymer ( $\Delta$ ) and in the solution of HPC ( $\bullet$ ), HPC-AMPS1 ( $\blacksquare$ ), and HPC-AMPS2 ( $\blacklozenge$ ) at  $c_p = 0.1 \text{ g/dm}^3$  and  $T = 25^\circ\text{C}$ .

discussed above. On the other hand, for graft polymers the addition of DTAC above certain concentration value result in a significant increase in the  $I_E/I_M$  ratio. The DTAC concentrations at which this occurs are  $3.2 \times 10^{-5}$  and  $1.0 \times 10^{-5}$  for HPC-AMPS1 and HPC-AMPS2, respectively. They are the concentrations at which micelles of DTAC are formed along graft chains of AMPS, and therefore may be interpreted as the respective values of  $c_{ac}$ . They are in a very good agreement with the values obtained from the measurements of the  $I_3/I_1$  ratio. It could be noticed that the value of  $I_E/I_M$  ratio for pyrene solubilized in the solutions of the native HPC and the graft polymers is higher than in the solution of DTAC. This indicates that all the polymers are able to form hydrophobic domains in which pyrene is solubilized at concentration high enough to form excimers. It can also be seen that the  $I_E/I_M$  ratio for HPC-AMPS1 is lower than for HPC-AMPS2. This may be the consequence of the fact that HPC-AMPS1 was obtained using higher  $\text{KMnO}_4$  concentration resulting in denser and more homogeneous distribution of the AMPS grafts along the HPC chain. This should hinder the formation of hydrophobic domains and decrease the ability of the polymer to solubilize pyrene. On the other hand, in the synthesis of HPC-AMPS2 the concentration of  $\text{KMnO}_4$  was lower and the concentration of AMPS was higher than for HPC-AMPS1. This should result in the smaller number of AMPS grafts and their greater length, as mentioned earlier. Therefore, the solubilization ability of HPC-AMPS2 at low DTAC concentration is similar to that of the native HPC.

## CONCLUSIONS

HPC grafted with AMPS interacts strongly with DTAC, a cationic surfactant, as found by the surface tension measurements and fluorescence spectroscopy using pyrene as a fluorescent probe. The  $c_{ac}$  values found for these polymer-surfactant systems are of the order of  $10^{-5} \text{ mol/dm}^3$ . The LCST of the polymers changes only slightly upon grafting compared with the parent HPC. The addition of DTAC to the solutions of the studied polymers does not change their LCST. The addition of DTAC results in the irreversible phase separation of the graft polymer upon exceeding the LCST which was manifested as increased turbidity of HPC-AMPS1 solution and as the precipitation of a polymer-surfactant complex in the HPC-AMPS2 solution. The increase in the ionic strength decreases the LCST of the graft HPC by the same value as that of the parent HPC. The polymer-surfactant interactions, as measured by the  $c_{ac}$  values, are stronger for the polymer with a higher content of AMPS. Strong interactions between these polymers and DTAC make possible their potential practical application in purification of water polluted with the cationic surfactants.

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