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Hydroxypropylcellulose-*graft*-poly(*N*-isopropylacrylamide) — novel water-soluble copolymer with double thermoresponsivity

Summary — A copolymer showing two cloud points was obtained by grafting poly(*N*-isopropylacrylamide) (PNIPAM) onto hydroxypropylcellulose (HPC). The structure of the polymer was verified using ^{1}H NMR, FT-IR, GPC, and elemental analysis. The values of cloud points could be changed by increasing ionic strength and as a result of the interactions with surfactants.

Keywords: hydroxypropylcellulose, poly(*N*-isopropylacrylamide), thermosensitive polymer, cloud point, polymer-surfactant interactions, fluorescence probe.

HYDROKSYPROPYLOCELULOZA-*graft*-POLI(*N*-IZOPROPYLOAKRYLOAMID) — NOWY ROZPUSZCZALNY W WODZIE KOPOLIMER WYKAZUJĄCY PODWÓJNĄ TERMOCZUŁOŚĆ

Streszczenie — Metodą naszczepienia poli(*N*-izopropyloakryloamidu) (PNIPAM) na hydroksypropylocelulozie (HPC) otrzymano kopolimer wykazujący dwa punkty zmętnienia. Strukturę polimeru potwierdzono wykorzystując badania metodami ^{1}H NMR, FT-IR, GPC oraz analizy elementarnej. Wartości temperatury w punktach zmętnienia ulegały zmianie w wyniku siły jonowej oraz w wyniku oddziaływań z surfaktantami.

Słowa kluczowe: hydroksypropyloceluloza, poli(*N*-izopropyloakryloamid), polimer termoczuły, punkt zmętnienia, oddziaływania polimer-surfaktant, sonda fluorescencyjna.

INTRODUCTION

Stimuli-responsive polymers have been intensely studied because of their numerous potential uses, *e.g.* in medicine [1, 2], pharmacy [3, 4], biotechnology [5, 6] and environmental protection [7]. Temperature-responsive materials have been of particular interest because temperature can be easily controlled and it is a strong stimulus in many applications. Poly(*N*-isopropylacrylamide) (PNIPAM) is perhaps the best known member of the class of thermo-responsive polymers. Specifically, PNIPAM was extensively exploited in the area of biological applications (*e.g.* in the controlled drug delivery) due to the fact that its low critical solution temperature (LCST) of 32—34 °C corresponds well with the range of physiological temperatures [8, 9]. PNIPAM precipitates from water upon heating above LCST due to the coil-to-globule transition [10]. Studies on the synthesis and characterization of PNIPAM-based polymers presenting several functionalities, which make them interesting materials in drug delivery, nanotechnology or microfluidics, have been reported and broadly reviewed elsewhere [11].

Recently, there were obtained more complex thermo-responsive polymers, displaying two cloud points [12—16], however, none of them was based on natural polymers.

In the current paper we present the results of our studies on novel thermosensitive polymer obtained by grafting PNIPAM on a hydroxypropylcellulose (HPC) chain. To the best of our knowledge the synthesis of the copolymer of HPC and PNIPAM has not yet been reported. Employing natural polymer, such as cellulose is particularly attractive due to its favorable properties such as biocompatibility, accessibility (cellulose is one of the most abundant natural polymers) and low price. HPC is a thermo-sensitive derivative of cellulose which in dilute aqueous solutions exhibits LCST of about 41 °C [17]. This value is only slightly higher than typical physiological temperatures. Combining PNIPAM and HPC by grafting yielded a novel thermosensitive material with interesting properties that might find applications in the biomedical field. Both components of the copolymer are widely used in this area, a fact which stems from their safety, availability and good performance. The properties of the proposed copolymer can be fine-tuned in the range of biologically relevant temperatures, namely from 32 to 41 °C.

The changes in the ionic strength influence the size of the polymeric micelles and polymer solubility [18]. As

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both components of the synthesized copolymer have the polar groups able to interact with low molecular weight electrolytes, we found it important to widen our research by testing the influence of increased ionic strength on the solution properties of the new polymer. That seems crucial, taking into account its potential biological applications, where high ionic strengths are often encountered.

Finally, as far as the possible environmental applications are considered, we have found the studies on the interactions between HPC-*g*-PNIPAM and surfactants, both ionic and nonionic, of great significance. Polymer-surfactant interactions have attracted both scientific and industrial interest [19, 20]. In particular, using smart polymers, which can strongly interact 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 from water. Moreover, the reversibility of the response of smart polymers to stimuli may allow recovery of the surfactant.

EXPERIMENTAL

Materials

The following materials were used:

— hydroxypropylcellulose (HPC, $\overline{M}_n$ = 10 000, $\overline{M}_w$ = 80 000, Aldrich),

— *N*-isopropylacrylamide (NIPAM, Aldrich),

— dodecyltrimethylammonium chloride (DTAC, Fluka, 99 %),

— potassium permanganate (POCh Gliwice, analytical grade),

— sodium hydroxide (POCh Gliwice, analytical grade),

— sodium chloride (POCh Gliwice),

— sulfuric acid (POCh Gliwice, analytical grade),

— sodium dodecylsulfate (SDS, Fluka, 99 %),

— polyethylene (4) lauryl ether trade name Brij® 30 (Fluka).

Water was distilled twice. Pyrene was recrystallized twice from methanol.

Synthesis of HPC-*g*-PNIPAM

6 g of HPC was dissolved in 100 cm^3 of water. The solution was degassed by bubbling nitrogen for 30 min and 0.0158 g (0.10 mmol) of $KMnO_4$ in 1 cm^3 of water was added. After 5 min the resulting solution became colorless. Next, 1.2 cm^3 (22.48 mmol) of concentrated H_2SO_4 and 3.42 g (30.22 mmol) of NIPAM dissolved in 5 cm^3 of water was added. The reaction mixture was heated up to 60 °C and kept at this temperature for 4 h under constant mixing with a magnetic stirrer and bubbling with nitrogen. The reaction mixture was cooled down and neutralized with NaOH solution. The precipitate was removed by decantation. Polymer solution was dialyzed for 1 week against distilled water in a 12 000 cutoff dialysis tube and the precipitate was removed by decantation, followed by dialysis for another week against NaCl solution with concentration of 1.5 mol/dm^3. Also during this procedure the precipitate was removed by decantation. The polymer solution was dialyzed for one more week against distilled water and finally freeze-dried to obtain 2.2 g of the polymer.

Apparatus

The elementary analysis (C, H, and N) was performed with a Euroea 3000 analyzer.

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.

FT-IR spectra were obtained on a Bruker IFS 48 spectrometer.

NMR spectra were measured in DMSO-d$_6$ using a Bruker AMX 500 spectrometer.

Gel permeation chromatography (GPC) analyses were performed using a Waters GPC system equipped with a bank of three columns (PL Aquagel-OH 30, 40, and 60) and tandem PDA/RI detectors.

The size of the aggregates was measured using a Malvern Instruments Nano-ZS Zetasizer.

Cloud point measurements

The cloud point 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 [8]. Shortly, the solution was gradually heated using Peltier accessory within the range from 15 to 77 °C at the rate of 0.5 °C/min, while continuously stirred. Cloud point values were then determined based on the changes of the solution optical density with temperature at 400 nm.

Fluorescence studies

Saturated aqueous solution of pyrene (c = 6.4·10^{-7} mol/dm^3) was obtained as follows [9]. A few milligrams of pyrene were dissolved in 1 cm^3 of methanol and the solution was placed in a 1 dm^3 flask. Methanol was then evaporated to form a film of pyrene on the walls of the flask. 900 cm^3 of water were added and sonicated for 30 min. Dry samples (a few milligrams) of the studied polymers were dissolved in the obtained solution of pyrene. Fluorescence emission spectra of the resulting solutions were measured in the range from 360 nm to 500 nm using excitation wavelength of 320 nm. For hydrophobicity studies 0.5 g/dm^3 and 1 g/dm^3 samples of HPC-*g*-PNIPAM were prepared. These concentrations were low enough to prevent the sample turbidity to interfere with the fluorescence measurements at temperatures above the cloud point.

GPC measurements

As the eluent was used 0.1 M solution of NaCl with flow rate of 0.6 cm^3/min. Sample volume was 150 mm^3 and concentration of the HPC-*g*-PNIPAM sample was 10 g/dm^3.

Dynamic light scattering (DLS) measurements

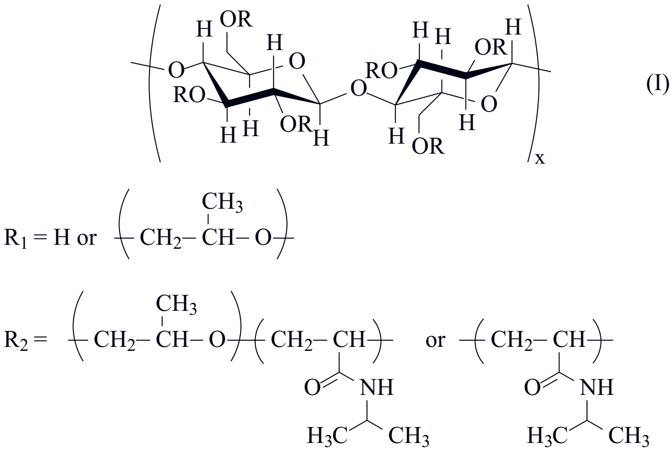
A sample of HPC-*g*-PNIPAM in the form of a solution in distilled water with concentration of 2 g/dm^3 was equilibrated at a given temperature for 3 min before the measurement. Each measurement was repeated 30 times and an average of the statistically relevant results was calculated.

RESULTS AND DISCUSSION

HPC-*g*-PNIPAM synthesis and characterization

The aim of the present study was to obtain a new thermoresponsive polymer showing two different phase transitions and corresponding two cloud point values. The idea was to combine two polymers which are known to exhibit thermo-sensitivity and to respond to temperature changes within the range relatively close to the physiological temperatures. For that purpose hydroxypropylcellulose (HPC) was selected and further modified by grafting with poly(*N*-isopropylacrylamide) (PNIPAM) chains.

The grafting reaction was carried out according to the procedure developed by Hebeish *et al.* [21] for grafting of acrylonitrile onto starch, where potassium permanganate was used as an initiator. This method was further studied by Zhang *et al.* [22]. It was proposed, that the graft copolymerization of acrylonitrile onto starch initiated by $KMnO_4$ in the presence of an acid occurs through the reduction of Mn^{7+} ions to Mn^{4+} and then to Mn^{3+} and/or Mn^{2+} and the radicals are formed along the polymer chain. Since radicals are formed only along the polysaccharide chain, the formation of the homopolymer may be minimized when using dilute $KMnO_4$ solutions to avoid chain transfer. Analogical processes take place during grafting onto HPC [23]. The structure of the resulting polymer is proposed in Formula (I).



(I)

$R_1 = H \text{ or } -\!\left(CH_2-\overset{CH_3}{CH}-O\right)\!-$

$R_2 = -\!\left(CH_2-\overset{CH_3}{CH}-O\right)\!-\!\left(CH_2-\underset{\underset{H_3C-CH-CH_3}{O=C-NH}}{CH}\right)\!- \text{ or } -\!\left(CH_2-\underset{\underset{H_3C-CH-CH_3}{O=C-NH}}{CH}\right)\!-$

HPC: $R = R_1$
HPC-*g*-PNIPAM: $R = R_1$ or R_2

The degree of grafting, defined as n_{NIPAM}/n_{Glu}, calculated based on the elemental analysis, was found to be 0.28, which is rather low. It is difficult to determine the dispersity of the polymer, because each glucose unit of HPC contains three hydroxyl groups, two secondary and one primary, which may give rise to radicals and start side chain growth with different yields.

The structure of HPC-*g*-PNIPAM was confirmed using ^1H NMR. A new signal at 4.0 ppm was found in the spectrum of the grafted polymer, which was ascribed to the protons bound directly to the carbon closest to the nitrogen atom of the NIPAM unit (data not shown here). The FT-IR spectrum of HPC-*g*-PNIPAM shows an additional weak band at 1648 cm^{-1}, which can be attributed to the deformation vibrations of the secondary amine of the attached NIPAM group (data not shown here).

To exclude the formation of the PNIPAM homopolymer the GPC analysis was performed. Chromatograms of the polymer aqueous solution were obtained using UV-Vis and refractive index detectors (data not shown here). For both detectors only one signal at the same retention time was found, confirming that no homopolymerization occurred.

Thermoresponsive character of HPC-*g*-NIPAM

Changes in the transmission with temperature of the aqueous solution of HPC-*g*-PNIPAM copolymer were measured and results are presented in Figure 1. Based on the obtained dependence two different cloud point values were found at 35 °C and 45 °C.

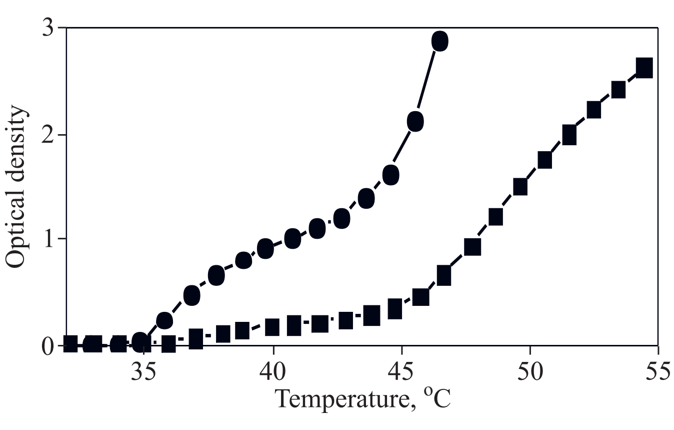


Fig. 1. Temperature induced changes in the optical density of HPC-g-PNIPAM aqueous solution at the concentration of 2 (■) and 5 g/dm³ (●)

The first cloud point value can be ascribed to the phase transition of the PNIPAM chains whereas the second one is due to the HPC chain transition. Both values are higher than those for relative homopolymers. This fact can be explained by the interaction between HPC and PNIPAM units resulting in the conformations of the polymer chains which differ significantly from those of the homopolymers.

Below 35 °C the solvent (water) molecules form hydrogen bonds with the amide groups of PNIPAM chains. Also the hydroxypropyl groups present in the HPC main chain are well solvated. When the temperature rises the polymer hydrophobicity increases due to the disruption of the hydrogen bonds between PNIPAM chains and water molecules. As a result, the intramolecular interactions within HPC-*g*-PNIPAM macromolecules become stronger, leading to the change of PNIPAM chains conformation from the stretched one to the more compact globular form. Hydrophobic isopropyl groups are buried inside the random coil and water is excluded from the interior of the microdomains formed. This process manifests itself in the increased turbidity of the HPC-*g*-PNIPAM solution. Further heating of the solution leads to the rupture of hydrogen bonds between HPC chains and water molecules and, as a consequence, the interactions between HPC segments in the HPC-*g*-PNIPAM chain become stronger. This leads to further increase in hydrophobicity of the polymer and results in the folding of the random coil into the compressed globular form. It can be seen as the second rise of the transmission at *ca.* 45 °C. At that temperature the phase separation occurs and polymer precipitates from the solution in the form of larger aggregates.

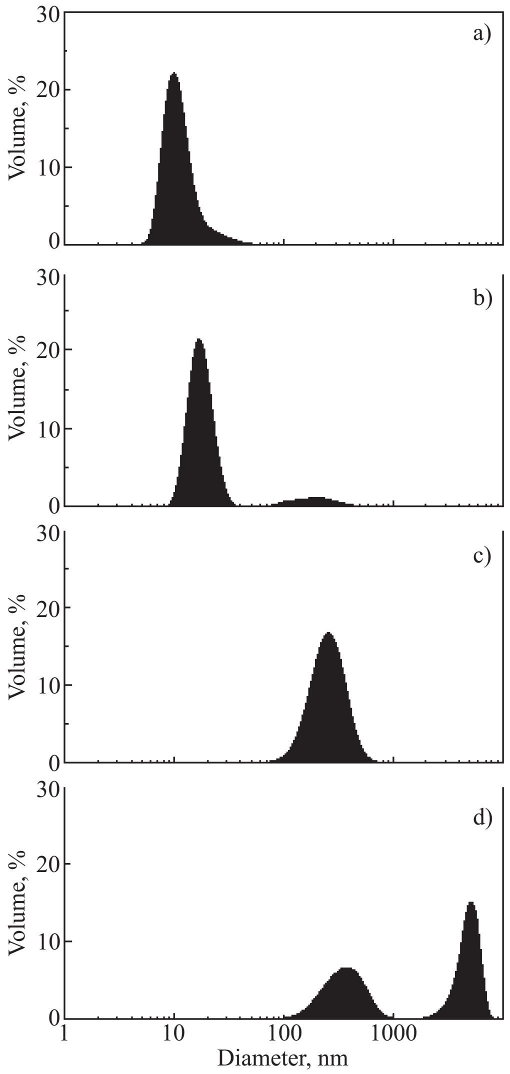


Fig. 2. DLS results for HPC-g-PNIPAM solutions (c_p = 2.0 g/dm^3) measured at: a) 30 °C, b) 35 °C, c) 37 °C, d) 40 °C

To better illustrate the temperature-induced changes in the polymer particle size measurements were performed using the dynamic light scattering (DLS) method. As it can be seen in Figure 2, at temperatures below the first cloud point the particle size was about 10 nm. When the temperature reached 35 °C the particles started to grow and larger aggregates about 300 nm in size appeared (Fig. 2b). When the temperature approached the second cloud point, characteristic of HPC, the third mode appeared at even greater diameters, while the mode corresponding to single chains disappeared (Fig. 2c and 2d). This may be interpreted as a confirmation of the existence of two different components responsible for the phase transition phenomena in the HPC-*g*-PNIPAM polymer.

To further study the formation process of the hydrophobic domains in aqueous solution of HPC-*g*-PNIPAM at elevated temperatures, pyrene was used as a fluorescent molecular probe. Pyrene, being a hydrophobic molecule, preferably locates itself in the hydrophobic regions formed by the polymeric chains. The relative intensities of the first and third vibrational bands in the fluorescence emission spectrum of pyrene depend strongly on the polarity of the microenvironment surrounding its molecules [24]. To determine the hydrophobicity of the microdomains formed by the polymeric chain in different conditions (*e.g.* temperatures) the ratio of the intensities of the third and the first vibrational bands in the fluorescence spectrum of solubilized pyrene (I_3/I_1) is calculated,

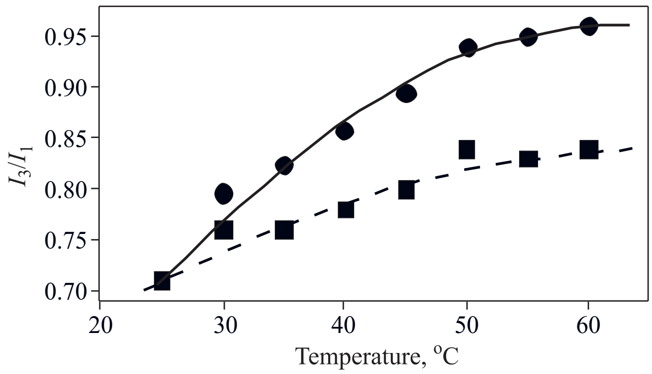


Fig. 3. Temperature dependence of the I_3/I_1 ratio for HPC-g-PNIPAM aqueous solutions with concentration 0.5 g/dm^3 (■) and 1.0 g/dm^3 (●)

which is proportional to the hydrophobicity of the pyrene environment.

Figure 3 illustrates the dependence of I_3/I_1 ratio for pyrene solubilized in the HPC-*g*-PNIPAM aqueous solution on the temperature range from 25 to 65 °C at two different concentrations. As expected, with growing temperature pyrene molecules experience more and more hydrophobic microenvironment, created by the microdomains formed by the polymer chains. However, the phase transitions are not reflected in the plot of the I_3/I_1 ratio which increases at a roughly constant rate in the temperature range covering both cloud points.

Influence of ionic strength on the HPC-*g*-PNIPAM cloud points

The effect of the ionic strength on the values of both cloud points of the aqueous solution of HPC-*g*-PNIPAM was studied using sodium chloride as a model low molecular weight electrolyte. As it is presented in Figure 4, the 2 g/dm^3 solutions of HPC-*g*-NIPAM show two cloud points for NaCl concentrations up to 1 mol/dm^3. In Fig. 5 the effect of NaCl concentration on cloud points is shown.

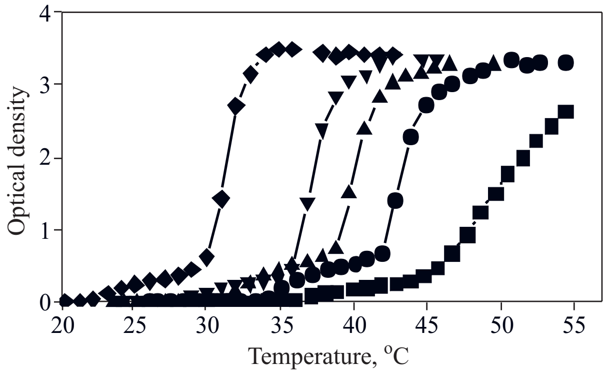


Fig. 4. Temperature induced changes in the optical density of HPC-g-PNIPAM aqueous solutions (c_p = 2.0 g/dm^3) for c_{NaCl} of 0 (■), 0.1 (●), 0.3 (▲), 0.5 (▼), and 1.0 mol/dm^3 (♦)

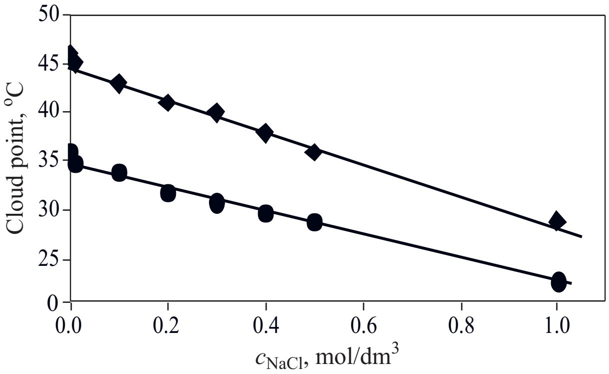


Fig. 5. Dependence of the first (♦) and the second (●) cloud point values of HPC-g-PNIPAM solutions on the NaCl concentration

Both cloud points decrease with increasing concentration of NaCl. These changes are clearly linear, with the decrease rate slightly higher for the second cloud point.

Thus, by increasing the ionic strength up to 1 mol/dm^3 the first and the second cloud points can be decreased from about 35 to 23 °C and from 46 to 29 °C, respectively.

Interactions of HPC-*g*-PNIPAM with an anionic, cationic and nonionic surfactant

Anionic surfactant — SDS

The temperature dependence of the optical density for different SDS concentration is shown in Figure 6. The cloud points of the aqueous solutions of HPC-*g*-PNIPAM were determined. SDS at concentrations up to 10^{-4} mol/dm^3 does not induce visible changes in the cloud point values of HPC-*g*-PNIPAM.

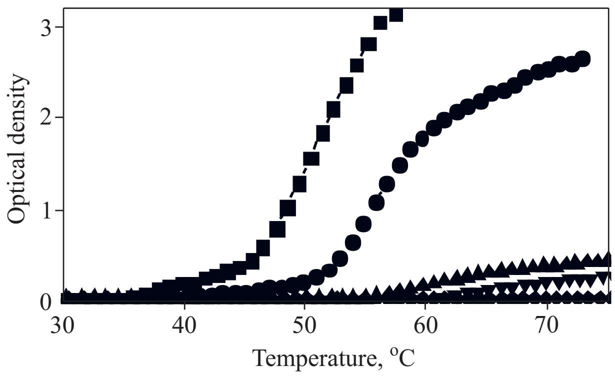


Fig. 6. Dependence of the optical density of HPC-g-PNIPAM aqueous solutions (c_p = 2.0 g/dm^3) on temperature for c_{SDS} of 0 (■), 1 · 10^{-3} (●), 2 · 10^{-3} (▲), 3 · 10^{-3} (▼), and 1 · 10^{-2} mol/dm^3 (♦)

However, when the concentration of SDS reached 10^{-3} mol/dm^3 there was a substantial increase in both cloud point values. As the critical micellization concentration (*cmc*) of SDS is known to be 3.5 · 10^{-2} mol/dm^3, the SDS concentration of 1 · 10^{-3} mol/dm^3 can be identified as the critical aggregation concentration (*cac*) for this polymer-surfactant system, *i.e.* the concentration at which the formation of the polymer-surfactant aggregates begins. The interactions between HPC-*g*-PNIPAM and SDS, as well as these between ionic parts of SDS molecules, affect the hydrophilic-hydrophobic equilibrium and lead to the shift of the polymer cloud point towards higher values. Moreover, heating of the polymer solutions at SDS concentrations of 2 · 10^{-3} mol/dm^3 and higher to temperatures above the cloud point results in only slight increase of the solution turbidity. It suggests that the polymer-surfactant aggregates are much smaller than the purely polymeric aggregates forming in the absence of SDS at the same temperature. Also, at the SDS concentration between

$2 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$ mol/dm^3 only one phase transition can be distinguished in the plots in Figure 6. At SDS concentration higher than $1 \cdot 10^{-2}$ mol/dm^3 the system does not display any cloud points.

Cationic surfactant — DTAC

The influence of DTAC on the temperature response of HPC-*g*-PNIPAM was studied and is shown in Figure 7. The presence of DTAC at the concentration of $1 \cdot 10^{-4}$ mol/dm^3 does not change the value of the lower cloud point and only slightly changes the higher cloud point. At the DTAC concentration of $1 \cdot 10^{-3}$ mol/dm^3 a noticeable decrease in both the first and the second cloud point values was observed, more pronounced for the second one. Taking into account the value of *cmc* for DTAC in water ($1.5 \cdot 10^{-2}$ mol/dm^3), it can be assumed that in that concentration region the formation of the polymer-surfactant complexes can be expected. Indeed, the further decrease of the cloud points occurring at DTAC at the concentration of $1 \cdot 10^{-2}$ mol/dm^3 was observed. Again, the cloud point value assigned to the HPC component of the polymer is shifted much stronger than the cloud point associated with the PNIPAM component. It may be speculated that DTAC interacts more efficiently with the HPC part of the macromolecule due to the hydroxyl groups present in the HPC structure. They exhibit weakly acidic character, which may attract the cationic surfactant electrostatically. Such interaction affects the hydrophilic-hydrophobic equilibrium and shifts the cloud point toward lower temperatures. The opposite direction of the cloud point shift in the case of the anionic SDS and cationic DTAC may be explained by the fact that the negatively charged molecules of SDS should be repelled by hydroxyl groups of HPC, preventing formation of the polymer-surfactant complexes, while the opposite is true for DTAC.

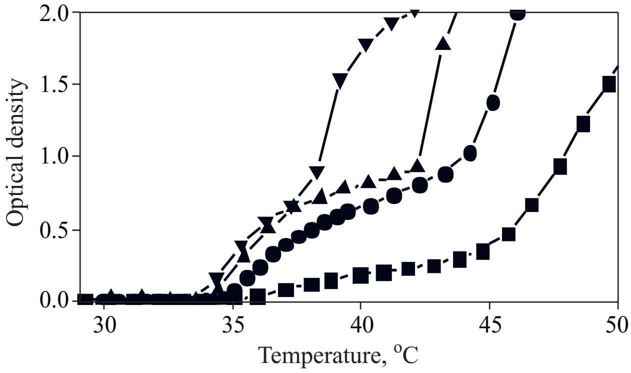


Fig. 7. Temperature dependence of the optical density HPC-g-PNIPAM solutions (c_p = 2.0 g/dm^3) for SDS concentrations of 0 (■), 1·10^{-4} (●), 1·10^{-3} (▲), and 1·10^{-2} mol/dm^3 (▼)

Nonionic surfactant — BRIJ® 30

The temperature dependence of the optical density for various BRIJ® 30 concentrations is presented in Figure 8. The turbidity measurements revealed that BRIJ® 30, a nonionic surfactant, does not cause any noticeable changes in any cloud point values of HPC-*g*-PNIPAM up to the concentration of $1 \cdot 10^{-3}$ mol/dm^3. For BRIJ® 30 concentration of $1 \cdot 10^{-3}$ mol/dm^3 a slight decrease in the first cloud point was observed whereas the second one was not shifted. That can be explained taking into account stronger interaction of BRIJ® 30 with PNIPAM than with HPC chains. At the concentrations of the surfactant being of the order of 10^{-2} mol/dm^3 the hydroxyl groups of BRIJ® 30 are close enough to form hydrogen bonds with HPC component of the polymer, resulting in strong shift of the HPC cloud point to lower values.

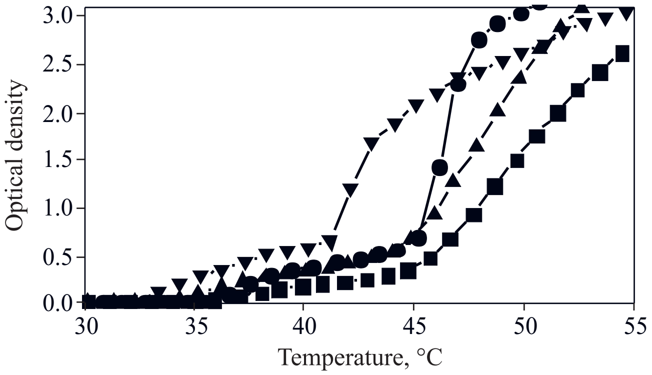


Fig. 8. Temperature dependence of the optical density of HPC-g-PNIPAM solutions (c_p = 2.0 g/dm^3) for BRIJ® 30 concentrations of 0 (■), 1·10^{-4} (●), 1·10^{-3} (▲), and 1·10^{-2} mol/dm^3 (▼)

CONCLUSIONS

A new thermosensitive polymer, HPC-*g*-PNIPAM, characterized by two temperature phase transitions, was obtained *via* grafting of PNIPAM side chains along the HPC main chain. Its structure was confirmed by NMR, FT-IR, GPC, and elemental analyses. Turbidity measurements revealed two cloud points in the aqueous solution of HPC-*g*-PNIPAM — at 35 and 45 °C. Further studies have shown the significant influence of the ionic strength on both cloud point values. The presence of increasing concentrations of NaCl led to the linear decrease of both transition temperatures. The interactions of HPC-*g*-PNIPAM with ionic and nonionic surfactants were analyzed and confirmed by significant changes in the cloud point values. While in presence of anionic SDS both cloud point values shifted to higher temperatures with increasing concentration of the surfactant, in the presence of cationic DTAC and nonionic BRIJ® 30 the opposite effects were observed. That can be explained considering both electrostatic as well as specific interactions of these surfactants with weakly acidic hydroxyl groups of HPC and with grafted PNIPAM chains.

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