



A thermosensitive carrageenan-based polymer: Synthesis, characterization and interactions with a cationic surfactant

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ABSTRACT

Novel polyelectrolytes were obtained by grafting N-isopropylacrylamide (NIPAM) on the ι -carrageenan (CAR) chain. Two polymers with different grafting degrees were synthesized. The polymers were found to show the lower critical solution temperature (LCST) close to that of PNIPAM. The LCST values were dependent on the concentration of salt and cationic surfactant. The interactions of CAR-graft-PNIPAM with a model cationic surfactant–dodecyltrimethyl ammonium chloride (DTAC) in water and 0.15 M NaCl were studied. It was found that both ι -carrageenan and CAR-graft-PNIPAM polymers interact with DTAC. The presence of CAR-graft-PNIPAM in the solution of DTAC induces formation of surfactant aggregates at the critical aggregation concentration much lower than the cmc of the surfactant. c_{ac} increased with ionic strength. The values of c_{ac} for CAR-graft-PNIPAM – DTAC system and standard free enthalpy changes attributed to the complexation process were determined. The results obtained for CAR-graft-PNIPAM were compared with these for the non-modified ι -carrageenan. The surfactant interactions with non-modified and grafted polymers were found to be different in nature.

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Introduction

Recently, there is a growing interest in the studies on interactions between polymers (Dias, Mel'nikov, Lindman, & Miguel, 2000; Hansson, 2006; Kogej, 2010; Pan et al., 2012; Santos et al., 2010), polysaccharides in particular (Desbrieres, Bousquet, & Babak, 2010; Kogej, 2008; Singh et al., 2008), and surfactants. This interest is driven by the fact that these subtle in their nature interactions have profound effect on the solution properties of the individual components. The systems in which stimuli-responsive polymers (smart polymers) are used belong to these, attracting special attention (Ahn, Ahn, & Song, 2008; Chen, Katsuyama, Gong, & Osada, 2003; Chiper, Fournier, Hoogenboom, & Schubert, 2008; Ganji & Abdekhodaie, 2008; Kim, Gong, & Osada, 1999; Kwon, Osada, & Gong, 2006; Shen et al., 2008; Tokuyama & Kato, 2008). They are widely studied because of their potential practical applications as drug delivery systems, and polymer supports for catalysts, chromatography column packing or cell and tissue culture. Poly(N-isopropylacrylamide) (PNIPAM), a thermosensitive polymer, which in aqueous solution displays lower critical solution temperature (LCST), is among the most frequently studied polymers. PNIPAM

homopolymer exhibits thermoreversible phase separation in the aqueous solution in the temperature range of 31–35 °C (Heskins & Guillet, 1968). It was observed that the copolymers of NIPAM with various monomers are also thermosensitive and the value of the LCST is strongly dependent on their composition. This observation is of great importance as it suggests the way for the fabrication of the polymers with a predetermined range of thermosensitivity, which can serve defined purposes. The other method which can be used to tune the thermal sensitivity of these polymers is their interactions with a surfactant (Kogej, 2008; Singh et al., 2008).

Most of the studies on the NIPAM-based polymers are carried out with synthetic systems. However, for many applications, e.g. biomedical, the systems of natural origin would be preferable. In that view, we have previously studied the derivatives of hydroxypropylcellulose, a natural, thermosensitive polymer (Rosół, Szczubiałka, Jachimska, Zapotoczny, & Nowakowska, 2008; Szczubiałka, Rosół, & Nowakowska, 2006).

This paper presents the results of our work on the novel thermosensitive polymer which is based on carrageenan. Carrageenans are a family of linear sulphated polysaccharides–galactose derivatives. They are composed of alternating 3-linked β -D-galactopyranose and 4-linked α -D-galactopyranose or 4-linked 3,6-anhydro- α -D-galactopyranose, forming the disaccharide repeating unit of carrageenans. There are three main classes of carrageenans: kappa, iota and lambda. The sulphated galactans are classified

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according to the presence of the 3,6-anhydro-bridge and the number of sulphate groups. (Campo, Kawano, Brazda Silva, & Carvalho, 2009). For kappa carrageenan charge/dimer ratio is about 1 and anhydrogalactose/dimer ratio is also 1. It has ability to form strong and rigid gels. Iota carrageenan forms soft gels and has charge/dimer ratio about 2.0 and anhydrogalactose/dimer ratio about one. Lambda carrageenan's charge/dimer ratio is about 3.0 and it does not have anhydrogalactose units in its structure. Carrageenans having anhydrogalactose units are able to form helical structures and aggregate forming gels. Lambda carrageenan which does not have anhydrogalactose units does not form gels (Campo et al., 2009). Because of the ability to undergo gelation these polysaccharides are widely used in the food and other industries as thickening and stabilizing agents (Kwon et al., 2006).

We have chosen iota carrageenan for our studies because it is characterized by the relatively high value of charge/dimer ratio and its sulphate groups are oriented toward the external part of the macromolecule, thus making easier the interactions with charged species of other types present in the system. We have modified iota carrageenan (ι -carrageenan) by grafting NIPAM chains on its polysaccharide backbone. This was done to obtain a natural polymer modified as little as possible, however, with the degree of modification with PNIPAM high enough to show thermosensitivity (i.e. LCST). This is of practical importance since such a polymer or a complex of such a polymer with a surfactant may be easily precipitated from the solution just by heating it above LCST allowing removal of a surfactant from water. Thus, such a polymer may be potentially applied in the purification of water from surfactants.

Experimental

Materials

ι -Carrageenan (CAR, Fluka), N-isopropylacrylamide (NIPAM, Aldrich, 99%), dodecyltrimethylammonium chloride (DTAC, Fluka, 99%), potassium permanganate (POCH Gliwice, analytical grade), sodium hydroxide (POCH Gliwice, analytical grade), sulfuric acid (POCH Gliwice, analytical grade) were used as received. Water was distilled twice. Pyrene (Aldrich, 98%) was recrystallized twice from methanol.

Polymer synthesis

The typical polymer synthesis procedure was as follows. In a 250-ml three-necked flask 3 g of ι -carrageenan was dissolved in 200 ml of water. The solution was degassed by bubbling with nitrogen for 30 min and 0.0077 g (0.5 mM) of KMnO_4 dissolved in 2 ml of water was added. After 5 min the solution became colorless and 1.137 g (12 mM) of H_2SO_4 and 1.599 g (14 mM) of N-isopropylacrylamide (NIPAM) was added. Then the reaction mixture was heated and kept at 60 °C for 4 h. The mixture was stirred constantly with a magnetic stirrer and bubbled with nitrogen. The reaction was terminated by rapid cooling of the reaction mixture and neutralizing 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 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 UV-Vis Photodiode Array (PDA) Detector. The 0.1 M NaCl aqueous solution was used as an eluent and the flow rate was 1 ml min⁻¹. ¹H NMR spectra recorded in D₂O, at ambient temperature on a Bruker

500 MHz spectrometer. FT-IR spectra were recorded using a Bruker Equinox 55 spectrophotometer. Fluorescence spectra of pyrene were measured using an SLM-AMINCO spectrofluorimeter. The excitation wavelength was adjusted at $\lambda_{\text{ex}} = 320$ nm. The spectra were corrected for the apparatus response using a function supplied by the manufacturer. Surface tension was measured using a K9 Krüss tensiometer. Isothermal Titration Calorimetry was performed using a VP-ITC isothermal titration calorimeter, MicroCal Inc., Northampton, MA, USA. The amount of heat absorbed or emitted was calculated using an Origin software supplied by the manufacturer. The baseline was generated automatically and at low signal/noise ratio, manually corrected. For all the experiments reference measurements were performed and surfactant solution was added to water. Referential thermal effect was subtracted from thermal effects obtained in the presence of the polymer.

LCST measurements

The LCST values for the polymers were measured using a Hewlett-Packard 8452A spectrophotometer equipped with a Hewlett-Packard 89090A Peltier temperature control accessory, as described earlier (Nowakowska, Szczubiałka, & Grębosz, 2004). 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⁻¹ and stirred at the rate of 5 s⁻¹. The LCST values were determined from the changes in the turbidity with temperature, expressed as $1 - T$, where T was apparent transmittance of the polymer solutions at 400 nm.

DLS measurements

Dynamic light scattering was measured using a Malvern Nano ZS (Malvern Instruments Ltd., Worcestershire, UK) and polymer solutions at 2 g/L. The Nano ZS instrument incorporates non-invasive backscatter (NIBSTM) optics. DLS technique measures the time-dependent fluctuations in the intensity of scattered light which occur because the particles are undergoing Brownian motion. Analysis of these intensity fluctuations enables the determination of the diffusion coefficients of the particles which are converted into a size distribution. The time-dependence autocorrelation function of the photocurrent was acquired every 10 s, with 15 acquisitions for each run. The sample of solutions was illuminated by a 633 nm laser, and the intensity of light scattered at an angle of 173° was measured by an avalanche photodiode. The z-average diameter (d_z) and the polydispersity index (PD) of the samples were automatically provided by the instrument using cumulant analysis. Rh data are apparent values obtained via the Stokes–Einstein equation for spheres.

Solubilization

Pyrene used in the fluorescence spectroscopy studies was solubilized in the systems by slowly injecting microliter volumes of a probe in methanol into the aqueous solutions of the polymers under vigorous shaking. The solutions were shaken for at least 10 min and left in the dark to equilibrate for at least 2 h.

Results and discussion

The grafting of PNIPAM on ι -carrageenan was carried out using KMnO_4 as a redox initiator. Such a procedure was previously used for grafting acrylonitrile onto starch (Hebeish, El-Thalouth, El-Kashouti, & Fattah, 1979). It was suggested that the initiation process occurs through the reduction of Mn^{+4} to Mn^{+3} and/or to Mn^{+2} and that the radicals are formed only along the polysaccharide chain so the formation of the PNIPAM homopolymer is excluded

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