



Cationization of kappa- and iota-carrageenan – Characterization and properties of amphoteric polysaccharides



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ARTICLE INFO

Article history:

Received 11 June 2014

Received in revised form 10 February 2015

Accepted 16 February 2015

Available online 5 March 2015

Keywords:

Kappa-carrageenan

Iota-carrageenan

Cationization

Amphoteric polysaccharides

3-Chloro-2-

hydroxypropyltrimethylammonium

chloride

ABSTRACT

Commercial kappa- and iota carrageenans were cationized with 3-chloro-2-hydroxypropyltrimethylammonium chloride in aqueous sodium hydroxide solution. For kappa-carrageenan three derivatives with different degrees of substitution were obtained. Native and amphoteric kappa-carrageenans were characterized by NMR and infrared spectroscopy, scanning electron and atomic force microscopy; methanolysis products were studied by electrospray ionization mass spectrometry. Young moduli and the strain at break of films, differential scanning calorimetry, rheological and flocculation behavior were also evaluated; the native and the amphoteric derivatives showed different and interesting properties. Cationization of iota-carrageenan was more difficult, indicating as it was previously observed for agarose, that substitution starts preferentially on the 2-position of 3,6-anhydrogalactose residues; in iota-carrageenan this latter unit is sulfated.

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1. Introduction

Cationic polysaccharides, mainly starch and cellulose derivatives, have found very wide applications. Among others, they are employed as effective flocculants over a wide range of pH being very useful for sustained organic and inorganic matter in wastewater carrying negative charges. They are also used as wet-end additives in paper making, controlling flocculation, retention and paper strength. Introducing a cationic group in starch gives good mineral binding properties; this is required for anchoring the mineral to the fibers. Cellulose derivatives are employed in industries concerned with oilfield treatments, medical products, cosmetics, etc. (Kavaliuskaite, Klimaviciute, & Zemaitaitis, 2008; Radosta et al., 2004; Song, Sun, Zhang, Zou, & Zhang, 2008). In these investigations several cationic groups have been linked to a polysaccharide

backbone (amino, imino, ammonium, sulfonium, or phosphonium groups) (Auzély-Velty & Rinaudo, 2003; Rinaudo, 2008).

One of the most common reactions used for modification involves the etherification with 2-hydroxy-3-(*N,N,N*-trimethylammonium)propyl groups (Prado & Matulewicz, 2014). This reaction can be carried out with 2,3-epoxy-trimethylammonium chloride (EPTAC). As EPTAC is unstable, usually this reagent is prepared *in situ* from 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC). Even though the latter reagent has been widely used for the cationization of starches and celluloses, there are only a few reports on its utilization with seaweed polysaccharides.

In a previous paper we reported the cationization of commercial agarose with CHPTAC and the influence of experimental parameters on different properties of the obtained derivatives (Prado, Matulewicz, Bonelli, & Cukierman, 2011a). Flocculation performances of two derivatives of different degree of substitution (*DS*) were evaluated showing a comparable behavior to that of commercial polyacrylamides used for water treatment (Prado, Matulewicz, Bonelli, & Cukierman, 2011b).

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In recent years, there has been an increase in interest in the preparation of cellulose and starch derivatives containing both acidic and basic groups of different strengths in the chain. Thus amphoteric polysaccharides were obtained by etherification of anionic carboxymethylcellulose (CMC) with CHPTAC (Hebeish, Higazy, Shafei, & Sharaf, 2010; Zhang, 2001) or by reaction of starch with EPTAC and then with succinic anhydride (Lekniute, Peciulyte, Klimaviciute, Bendoraitiene, & Zemaitaitis, 2013) or with CHPTAC/EPTAC and sodium phosphates (Lin et al., 2012; Zhang, Zhang, Ju, & Yang, 2005). Recently, the cationization of heparin with CHPTAC has been reported (Šimkovic, Mendichi, Kelnar, Filip, & Hricovíni, 2015). The grafting of cationic monomers onto CMC with various initiation systems has been also investigated. For example CMC was used to graft with 2-(dimethylamino)ethyl methacrylate in aqueous medium using ammonium persulfate and *N,N,N,N'*-tetramethylethylenediamine as the initiating system (Zhang & Tan, 2000). Amphoteric polysaccharides have found various and different applications in: papermaking, flocculation, wastewater and oilfield drilling treatments, adsorption of dyes and heavy metal ions, cosmetics, etc. (Zhang, 2001; Zhang et al., 2005).

Herein, we report the cationization of native sulfated polysaccharides (kappa- and iota-carrageenan) with CHPTAC and characterization of the amphoteric derivatives.

2. Materials and methods

2.1. Materials

Kappa-carrageenan (Gelcarin PC-911, batch No. 30824049, water viscosity at 1.5%, 75 °C and 30 rpm on a Brookfield Viscosimeter 29 mPa s) and iota-carrageenan (Gelcarin GP-379, batch No. 30522040, water viscosity in the same conditions 26 mPa s) were provided by Productos Destilados S.A.I.C/FMC Biopolymer Corp. Number-average molecular weight of both polysaccharides was determined using the colorimetric method of Park and Johnson (1949): molecular weight of kappa-carrageenan 124,100 Da, molecular weight of iota-carrageenan 270,900 Da. The concentration of counterions in both carrageenans was determined by flame atomic absorption spectrometry using a Shimadzu AA 6800 equipment (Tokyo, Japan). Kappa-carrageenan: (%) Na⁺ 0.41, K⁺ 2.40, Ca²⁺ 3.40, Mg²⁺ 0.21; iota-carrageenan: (%) Na⁺ 0.93, K⁺ 2.50, Ca²⁺ 2.40, Mg²⁺ 0.20.

The cationizing reagent was (3-chloro-2-hydroxypropyl)trimethylammonium chloride 60% w/w aqueous solution (Sigma–Aldrich, Inc., USA). For the flocculation tests, USP type kaolin from Sigma–Aldrich Inc. was employed. All the other reagents were of analytical grade.

2.2. Methods

2.2.1. Synthesis of cationized carrageenans

The cationization of the polysaccharides was performed according to the method described by Prado, Matulewicz, Bonelli, and Cukierman (2011a). In brief, 1.333 g of kappa-carrageenan (molecular weight of the average unit, 204 Da) and 1.667 g of iota-carrageenan (molecular weight of the average unit, 255 Da), corresponding to 6.53 mmol of the average unit were dissolved in water and the final volume of reaction was 100 mL. The reaction time was 2 h at 60 °C. The concentrations of CHPTAC and NaOH were varied (Table 1). After the solution was neutralized with 1 M HCl, the mixture was dialyzed (molecular weight cutoff of 6000–8000 Da) against 0.5% NaCl and then distilled water, and freeze dried.

Table 1

Molar concentrations of reagents added and degree of substitution determined by elemental analysis.

Samples	NaOH (M)	CHPTAC (M)	DS
K1	0.30	0.15	0.21
K2	0.60	0.30	0.31
K3	0.90	0.60	0.41
I1	0.60	0.30	0.11

2.2.2. Elemental analysis

Elemental analyses were performed on an EAI Exeter Analytical, Inc. CE-440 apparatus (USA). These were carried out by triplicate and the mean values are reported.

Sulfate content was also analyzed by the turbidimetric method of Dodgson and Price (1962).

The degree of substitution was determined from the nitrogen content (%N). The formula used adapted to kappa-carrageenan, molecular weight of the average unit 204 Da, was:

$$DS = \frac{204 \times \%N}{1400 - (152 \times \%N)}$$

For iota-carrageenan, the molecular weight of its average unit (255 Da) was employed.

2.2.3. FT-IR infrared spectroscopy

FT-IR spectroscopy was performed in a PerkinElmer Spectrum BX II FT-IR Spectrophotometer (PerkinElmer Inc., USA) employing the KBr disc method; the range measured was 4000–650 cm⁻¹, and 32–64 scans were taken with a resolution of 2–4 cm⁻¹.

2.2.4. NMR spectroscopy

The spectra of the polysaccharides (20 mg) were recorded in D₂O (0.7 mL), after isotopic exchange (3 × 0.5 mL). Spectra were recorded at room temperature on a Bruker Avance II 500 MHz spectrometer (Karlsruhe, Germany). For 500 MHz ¹H NMR experiments, the parameters were: a spectral width of 7.5 kHz, a 30° pulse, and acquisition time of 4.37 s; for 8 scans. For 125 MHz ¹³C NMR experiments, the parameters were: a spectral width 30.9 kHz, a 45° pulse for K1 and 60° for K2, an acquisition time of 0.55 s, and a relaxation delay of 0.30 s; for 64,000 scans. In all cases, signals were referenced to internal acetone at 2.21 ppm for ¹H NMR and 31.1 ppm for ¹³C NMR experiments, respectively.

The degree of substitution was also determined by means of ¹H NMR (*DS*_{NMR}). *A* is the area at the indicated chemical shift:

$$DS_{NMR} = \frac{A_{3.21}}{(A_{5.08} + A_{5.11}) \times 18}$$

2.2.5. ESI mass spectrometry

Derivatization of the analyte prior to its analysis by electrospray ionization (ESI) mass spectrometry was performed by methanolysis: samples (20 mg) were treated with 3 mL of methanol–HCl (1.5 M) at 100 °C for 3 h. The solvent was removed with dry air and the products were left in a vacuum desiccator overnight in order to assure its dryness.

ESI mass spectra were obtained in the positive-ion mode using a Bruker Daltonics microTOF-Q II ESI-Qq-TOF mass spectrometer (Bremen, Germany). N₂ was used as both drying and nebulizing gas and the electrospray capillary was set at 4.5 kV. The mass scan was in the range of *m/z* 50–950.

2.2.6. Scanning electron microscopy

Samples were previously platinum sputtered under argon atmosphere. Scanning electronic microscopy (SEM) was performed in a Zeiss DSM 982 Gemini microscope (Carl Zeiss, Munich, Germany) equipped with a field emission gun (FEG) and an in-lens secondary

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