

Novel polyelectrolyte complexes between *N*-carboxyethylchitosan and synthetic polyelectrolytes

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Abstract

Novel polyelectrolyte complexes (PEC) between the polyampholyte *N*-carboxyethylchitosan (CECh) and polyacid or polybase have been prepared. The complex formation between CECh and poly(2-acryloylamido-2-methylpropanesulfonic acid) (PAMPS), poly(acrylic acid) (PAA) or poly(ethylene imine) (PEI) has been studied. The complex CECh/PAMPS is formed in the pH range from 1.2 to 6.0. The complex CECh/PAA is formed in the range 4.8–6.0 and CECh/PEI—from pH 5.4 to 7.0. The stoichiometry of the complexes depends on the pH value of the medium. In case of CECh/PAMPS and CECh/PAA the maximum quantity of complex is formed in excess of CECh and in the case of CECh/PEI—in excess of PEI. It has been shown that PEC formation between CECh and PAMPS improves the haemocompatibility of CECh. © 2005 Elsevier Ltd. All rights reserved.

Keywords: *N*-carboxyethylchitosan; Polyelectrolyte complexes; Haemocompatibility

1. Introduction

Polyelectrolyte complexes (PEC) are formed by interactions between macromolecules that carry oppositely charged ionisable groups [1]. During the last years PECs on the base of natural and synthetic polymers evoke a particular interest. Chitosan is a natural polyaminosaccharide and a weak base. Its PECs with different natural and synthetic polyacids: carboxymethylcellulose [1], alginic acid [2], poly(acrylic acid) [3–5] are known. Previously we have shown that water-insoluble PEC is formed from

chitosan and poly(2-acryloylamido-2-methylpropanesulfonic acid) (PAMPS) by mixing their aqueous solutions [6] or by template polymerization of 2-acryloylamido-2-methylpropanesulfonic acid (AMPS) onto chitosan matrix [7]. Complex formation is due to ionic interactions between the protonated amino groups of chitosan and ionized sulfo groups of AMPS-units. The stoichiometry of the complex chitosan/PAMPS does not depend on the pH value of the medium—at pH values from 1.5 to 5.6 maximum quantity of complex is formed at equimolar ratio [aminoglucoside units]:[AMPS-units]. The complex chitosan/PAMPS is stable up to pH 8. The formation of PECs between chitosan and copolymers of AMPS and acrylic acid (AA) was also shown [8]. The composition and stoichiometry of

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PECs between chitosan and the copolymers depend on the degree of ionization of chitosan and of the copolymers and on the pH of the medium. The formation of a complex chitosan/PAMPS or chitosan/copolymers of AMPS and AA leads to improvement of the haemocompatibility of chitosan [9]. Chitosan dissolves in water only at pH values lower than 6.0. This is often considered as a limitation of its applications as a biomaterial. This is one of the reasons why the preparation and study of water-soluble chitosan derivatives is of interest.

In the present study PECs have been obtained from *N*-carboxyethylchitosan by mixing its aqueous solutions with polyacid or polybase solutions. The effects of pH of the medium and the nature of the polymer partner—PAMPS, poly(acrylic acid) (PAA), or poly(ethylene imine) (PEI) on the PECs stoichiometry have been investigated. The haemocompatibility of CECh and its complexes with PAMPS has been evaluated.

2. Experimental methods

2.1. Materials

Chitosan (molecular weight 3.8×10^5 , Aldrich, degree of deacetylation 80%), acrylic acid (AA) and 2-acryloylamido-2-methylpropanesulfonic acid (AMPS) (Fluka), and poly(ethylene imine) (molecular weight 25,000, Aldrich) were used. Acrylic acid was distilled under reduced pressure prior to use. All other chemicals as well as the salts used for preparation of the buffer solutions were of analytical grade of purity and used as received. The following buffer solutions were used: pH 1.2 (HCl/KCl); pH 4.8, 5.4 and 5.8 ($\text{CH}_3\text{COOH}/\text{NaOH}$); pH 6.0 and 6.5 (citric acid/sodium citrate); and pH 7.0 ($\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$).

2.2. Preparation and characterization of the polymers and complexes

PAA was prepared by free radical polymerization in 25% solution of the monomer in toluene at 25 °C under nitrogen initiated with 2,2'-azobisisobutyronitrile ($[M] = 2.3 \text{ mol/l}$, $[I] = 0.001 \text{ mol/l}$). The \bar{M}_v of PAA was 25×10^4 , as determined in 2N NaOH using the Mark–Houwink equation: $[\eta] = 42.2 \times 10^{-3} \times \bar{M}_v^{0.64}$ [10]. PAMPS was prepared as described previously [6]. \bar{M}_v of PAMPS (9.8×10^5) was determined in 5 N NaCl using the equation: $[\eta] = 2.11 \times 10^{-3} \times \bar{M}_v^{0.80}$ [11].

Carboxyethylchitosan (CECh) was prepared according to a procedure described by Sashiwa et al. [12]. Briefly: 5 g (0.03 mol with respect to base unit) chitosan were dissolved in 250 ml aqueous solution of acrylic acid, consisting of 4.26 g monomer (0.06 mol), molar ratio $[\text{NH}_2]:[\text{COOH}] = 1:2$. The obtained homogenous solution was heated for 24 h at 90 °C under continuous stirring. After cooling 1.25 N NaOH was added to the solution to attain pH 10. The obtained sodium salt was then dialyzed against distilled water.

\bar{M}_w of CECh was determined by the static light scattering method. Solutions of CECh in bidistilled water in concentration range 0.0001–0.002 g/L were used. The intensity of the scattered light between 50° and 126° was measured with LS-DAWN DSP Wyatt Laser Photometer at 632.8 nm and 25 ± 0.1 °C. \bar{M}_w was calculated from the Zimm plot using the programme ASTRA for Windows 4.70. dn/dc value for the polyampholyte solutions was 0.144 ml/g and was determined by using interferometric refractometer Wyatt/Optilab 903, Santa Barbara, CA.

For the potentiometric titration 170 mg of CECh were dissolved either in 100 ml of 0.083 N NaOH or in 100 ml of 0.1 N HCl and titrated at 20 °C with 0.1 N HCl or with 0.083 N NaOH, respectively. A two-point calibration Corning pH-meter 240, equipped with combined electrodes, was used for registration of pH values.

Polyelectrolyte complexes CECh/PAMPS, CECh/PAA and CECh/PEI were prepared by mixing solutions of the polymers in buffers with pH 1.2, 4.8, 5.4, 5.8, 6.0, 6.5, and 7.0 at a constant ionic strength ($I = 0.1$).

For performing gravimetric and viscometric measurements, PECs were prepared by mixing 0.2% solutions and for the turbidimetric measurements 0.01% solutions were mixed. Reactant solutions were mixed and thermostated at 25 °C for 48 h. The obtained white precipitate was isolated by centrifugation (40 min, 4000 rpm) and dried to constant weight. The absorbance at 420 nm was registered on a UV–VIS SPECORD 71 spectrophotometer.

IR spectra of the polymers and the complexes were registered on a spectrophotometer FT-IR Bruker Vector 22 on a KBr pellet or as thin films cast from solution. ^1H NMR spectra were taken on a Bruker DRX 400 NMR spectrometer operating at 400 MHz and 70 °C in D_2O . ^{13}C NMR spectra were taken on a Bruker MSL 300 NMR spectrometer operating at 75.5 MHz and 27 °C in D_2O . Viscosity

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