

## Studies on graft copolymerization of 2-hydroxyethyl acrylate onto chitosan

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### Abstract

Graft-polymerization of 2-hydroxyethyl acrylate (HEA) onto chitosan (CS) using ammonium persulfate (APS) as an initiator was carried out in an aqueous solution. Evidence of grafting was obtained by comparing <sup>1</sup>H NMR and FT-IR spectra and scanning electron microscopy images of chitosan and the grafted copolymer as well as solubility characteristics of the products. The effects of APS, HEA concentration, reaction temperature and duration of graft-polymerization were studied by determining the grafting parameters, such as grafting percentage and grafting efficiency. The HEA-grafted chitosan product is soluble in a wide pH range, while the original unmodified chitosan is water-soluble only in a narrow pH range. A mechanism for the free-radical grafting was proposed.

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### 1. Introduction

Chitosan is the product obtained at *N*-deacetylation of chitin with strong alkali. Chitin, the naturally occurring polysaccharide [1], is the main substance in carapaces of Crustacea such as shells, crabs, lobsters, and shrimps. It is the second most

abundant polysaccharide on the earth next to cellulose. Although chitosan and its derivatives are widely used in pharmaceutics [2], biomaterials technology [3], and agriculture [4], their poor solubility in water is still quite an obstacle for application in, for instance, a rapidly developing green food and health additives industry.

Chemical modification of natural polymers is a promising method for production of new biomaterials with specific properties. A number of papers have been published on the grafting polymerization of

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acrylonitrile, dimethylaminoethyl methacrylate, acrylamide, and vinylpyrrolidone onto chitosan using ceric ammonium nitrate (CAN) as an initiator [5–9].  $\gamma$ -Ray and photo-induced graft-polymerization of acrylamide, methyl methacrylate, 2-hydroxyethyl methacrylate, styrene and acrylonitrile onto chitosan also have been reported [9–13]. Potassium persulfate has been used as redox initiator for the grafting onto chitosan of methyl methacrylate, methyl acrylate, butyl acrylate, 2-acrylamido-2-methylpropane sulfonic acid, and acrylic acid [7,13–15].

In the present work, chemical modification of chitosan was performed by means of graft-polymerization of 2-hydroxyethyl acrylate. Improved water-solubility of the modified polymer was observed compared to the original chitosan. The effect of the principal reaction variables on the grafting process was investigated.

## 2. Experimental

### 2.1. Materials

Water-soluble chitosan (hydrochloride form) was obtained from Jakwang Co., Korea. The weight-average molecular weight of the sample was 200,000 g/mol. The deacetylation degrees of the chitosan as determined by FT-IR spectroscopy [16] (Satellite 3000 spectrometer, Mattson, USA) and by  $^1\text{H}$  NMR spectroscopy (Bruker 300 NMR spectrometer, USA) were 85% and 88%, respectively. Ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) ( $\geq 98\%$ ) and 2-hydroxyethyl acrylate (96%) were obtained from Aldrich Chemical Co. All the chemicals and reagents were used as received.

### 2.2. Synthesis

In a typical grafting reaction, dry chitosan was first dissolved in distilled water (pH of the resulting solution was 3.6). Then, HEA and APS were added to the chitosan solution and well stirred ( $T = 25^\circ\text{C}$ ). The reaction mixture was transferred in glass ampoules (20 ml) and bubbled with argon for 10 min. Then the ampoules were sealed and placed into a water bath with a magnet stirrer and a digital temperature controller. After the graft-polymerization was accomplished, the reaction mixture was precipitated in acetone, filtered, and rinsed with acetone to remove unreacted monomer. The powder was allowed to dry under vacuum to constant weight. Exhaustive extraction of the product with

ethanol allowed separation of poly(hydroxyethyl acrylate) (PHEA) homopolymer formed during the grafting reaction from chitosan-graft-HEA. The degree of purification was controlled by detection of the PHEA in the alcohol solution using FT-IR spectroscopy. Solubility of polymers in water was controlled by measuring optical density (D) of the solutions at various pH-values on UV-vis spectrometer (UV-2401 PC Shimadzu, Japan) at 400 nm.

### 2.3. Characterisation

FT-IR spectra of the chitosan, PHEA and PHEA-grafted chitosan (CS-g-PHEA) were recorded as KBr pellets on a FT-IR-Satellite 3000 spectrometer (Mattson, USA). The spectra were taken as average over 120 scans from 4000 to  $400\text{ cm}^{-1}$  with resolution  $4\text{ cm}^{-1}$ .  $^1\text{H}$  NMR spectra of the polymers in  $\text{D}_2\text{O}$  solution were obtained on a Bruker 300 NMR spectrometer.

The dynamic viscosities of the polymer solutions were measured with a Rheotest 2.1 (Germany) at the shear rate  $0.123\text{ s}^{-1}$ , rotation rate 0.25 rpm, and at temperature  $60 \pm 0.05^\circ\text{C}$ .

The morphology of the chitosan and CS-g-PHEA samples were observed by SEM. For that, the polymers were precipitated in acetone from 2 wt.% water solutions, and dried in vacuum at room temperature to constant weight. After coating with gold, the samples were analyzed with a JEOL<sup>®</sup> SUPERPROBE 733 electron probe micro analyser. All micrographs were the product of secondary electron imaging used for surface morphology identification with energy dispersion spectrometer INCA ENERGY (Oxford Instruments).

Grafting percentage (%G), grafting efficiency (%E), homopolymer content (%H) were determined as follows [17]:  $\%G = (W_1 - W_0)/W_0 \times 100\%$ ,  $\%E = (W_1 - W_0)/W_2 \times 100\%$  and  $\%H = (W_3 - W_1)/W_2 \times 100\%$ , where  $W_0$ ,  $W_1$ ,  $W_2$ , and  $W_3$  stand for the weight of chitosan in the initial load, weight of HEA-grafted chitosan after purification, monomer load, and weight of grafted chitosan before extraction PHEA, respectively.

## 3. Results and discussion

### 3.1. Synthesis

The grafting reaction of 2-hydroxyethyl acrylate onto chitosan was studied by varying the initial concentrations of the monomer, initiator, and chitosan,

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