



## Studies on graft copolymerization of 3-acrylamidopropyl trimethylammonium chloride on pullulan

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### ABSTRACT

Graft-polymerization of (3-acrylamidopropyl)-trimethylammonium chloride onto pullulan using potassium persulfate as an initiator was carried out in an aqueous solution. Evidence of grafting was obtained by comparing <sup>1</sup>H NMR, FT-IR spectra, SEM and TGA analysis of pullulan and the grafted copolymer. The effects of reaction conditions on the grafting parameters (such as initiator, monomer, and pullulan concentrations, reaction time and temperature) were investigated, and the optimal conditions for the grafting reaction were established. A plausible mechanism for the free-radical grafting was suggested. The obtained graft copolymer was designed to be used in waste water treatment processes and drug delivery.

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### 1. Introduction

Chemical modification of natural polymers is a promising method for production of new biomaterials with specific properties (solubility, biodegradability, chemical or thermal stability, and mechanical behavior). Cationic polysaccharides such as cationic cellulose (Burke & Palepu, 2001), guar (Rodriguez, Alvalez-Lorenzo, & Concheiro, 2003), starch (Granö, Yli-Kauhaluoma, Suortti, Käkki, & Numi, 2000), chitosan (Paulino, Simionato, Garcia, & Nozaki, 2006), chitosan derivatives (Babak, Desbrières, & Tikhonov, 2005; Lee, Jo, Kwon, Kim, & Jeong, 1998; Wu, Seo, Sasaki, Irie, & Sakurai, 2006) and dextran (Wang, Xu, Zhou, & Tan, 2007) are large-scale commercial products with hydrophilicity, biodegradability and antibacterial properties.

Pullulan, a linear, non-ionic polysaccharide with a repeated unit of maltotriose condensed meanly through a (1 → 6)- $\alpha$ -D linkage, prepared by culturing of *Aureobasidium pullulans* with starch and sugar (Wallenfels, Bender, Keilich, & Bechtler, 1961) has been used extensively in the food and pharmaceutical industries. Notably, pullulan accumulates in the liver in a significantly higher amount than other water-soluble polymers (Yamaoka, Tabata, & Ikada, 1993;

Yamaoka, Tabata, & Ikada, 1995). Chemically modified pullulans with improved properties are gaining interests mainly because the polysaccharide portion of the product is flexible in structure, water soluble and biodegradable. Their applications may relate to agriculture, industry, medical treatment and sanitation, and so on (Leathers, 2003; Singh, Saini, & Kennedy, 2008).

Grafting of synthetic polymers on natural polysaccharides has been widely used as one of the most convenient ways to combine the advantages of natural and synthetic macromolecules. A number of papers have been published on the grafting polymerization of N-isopropylacrylamide (Masci, Bontempo, & Crescenzi, 2002), ethylenic compound (Seizo, Kozo, Nobuhiro, & Fumio, 1975), lactide (Ohya, Maruhashi, & Ouchi, 1998), ethylene glycol (Jiao, Fu, & Jiang, 2004), butyl acrylate (Tian, Gao, Yu, & Duan, 1992), p-hydroxystyrene (Chen, Oshima, & Kumanotani, 1985), methyl methacrylate (Wu, Jin, Kim, Tong, & Chen, 2009) onto pullulan.

In order to find an inexpensive and efficient initiator, in this study we used an initiator system based on potassium persulfate. This system was found to be an efficient redox initiator in this specific system in aqueous medium. This approach is one of the most interesting methods of grafting vinyl monomers on polymer possessing oxidizable functional groups, in which free radicals are formed on backbone of polymer.

This paper deals the synthesis of pullulan grafted with (3-acrylamidopropyl)-trimethylammonium chloride using peroxydisulfate as initiator with the aim to develop a hybrid product which could be used in waste water treatment or as a matrix for drug delivery. The influence of initiator, monomer and polymer

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concentration, reaction time and temperature on grafting parameters was studied.

## 2. Experimental and methods

### 2.1. Materials

Pullulan (Pul),  $M_w = 200,000$  g/mol, was purchased from Hayashibara Lab. Ltd. (Okoyama, Japan). (3-acrylamidopropyl)-trimethylammonium chloride (APTAC) (75 wt. % solution in water) (Aldrich, Chemical Corp., Milwaukee, WI, USA) and potassium peroxydisulfate (KPS) (Fluka, Buchs, Germany) have been used as such.

### 2.2. Methods

#### 2.2.1. Graft copolymerization

The grafting reaction was carried out under nitrogen atmosphere in a three-necked flask equipped with a nitrogen inlet and a reflux condenser immersed in a thermostated oil bath.

In a typical reaction, pullulan (1 g) dissolved in 30 mL distilled water was purged for 30 min with nitrogen. A required amount of initiator (KPS) was added. After 15 min supposed to be enough to induce free radicals onto pullulan chains, a predetermined amount of monomer (APTAC) was charged to the flask under nitrogen atmosphere and the reaction was continued for a predetermined temperature and time. The grafting homogenous mixture was precipitated with vigorous stirring in a large excess of acetone and the grafted copolymer separated through filtration. Thereafter, the homopolymer was extracted from the crude material with methanol for 72 h using a soxhlet apparatus. Finally, the grafted pullulan was solubilized in distilled water, dialysed for 5 days at 20 °C for removal of water soluble species, and recovered by freeze-drying.

The synthesis of homopolymer (pAPTAC) was carried out using the same conditions as those of the graft reaction without the addition of the pullulan. The concentration of monomer was fixed at 0.16 M.

#### 2.2.2. Grafting parameters

The grafting polymerization process was followed gravimetrically. The increase in weight of the grafted pullulan over that of the pullulan, indicated the grafting of APTAC onto pullulan. The graft yields were characterized by the following parameters (Gao, Yu, Wang, Chang, & Tian, 1998):

$$\text{Grafting ratio } \% G = \frac{\text{Weight of grafted chains}}{\text{Weight of pullulan}} \times 100$$

$$\text{Grafting efficiency } \% E = \frac{\text{Weight of grafted chains}}{\text{Weight of polymer formed}} \times 100$$

$$\text{Conversion } \% C = \frac{\text{Weight of polymer formed}}{\text{Weight of monomer charged}} \times 100$$

$$\text{Homopolymer } \% H = 100 - \% E$$

All data were averaged from three measurements.

#### 2.2.3. Grafted copolymer composition

The copolymer composition was determined by nitrogen analysis and  $^1\text{H}$  NMR spectroscopy.  $^1\text{H}$  NMR spectra were recorded on a Bruker Avance DRX 400 NMR, using deuterated water as the solvent.

#### 2.2.4. Infrared (IR) spectral analysis

The grafted and un-grafted pullulan samples were dried under vacuum at 50 °C for 24 h, then were prepared accordingly to the

KBr technique and analysed with a Fourier transform infrared spectrophotometer (VERTEX 70, Bruker, Austria) in the frequency ranges of 400–4000  $\text{cm}^{-1}$ .

#### 2.2.5. Scanning electron microscopy (SEM)

The morphology of un-grafted and grafted pullulan, in powdered form, was examined using an environmental scanning electron microscope (ESEM) type Quanta 200, operating with secondary electrons in low vacuum, at 25 kV.

#### 2.2.6. TGA analysis

Thermogravimetric analysis (TGA) was performed under nitrogen flow (20  $\text{cm}^3 \text{min}^{-1}$ ) at heating rate 10 °C  $\text{min}^{-1}$  until 700 °C, with a Mettler Toledo model TGA/SDTA 851 (Mettler Toledo Corporation, Switzerland).

## 3. Results and discussion

### 3.1. Determination of optimum reactions conditions

The effect of variation of potassium persulfate, (3-acrylamidopropyl)-trimethylammonium chloride and pullulan concentration, along with time and temperature on grafting parameters has been studied.

#### 3.1.1. Effect of temperature

The effect of reaction temperature on graft copolymerization of APTAC onto pullulan was investigated by changing the temperature from 30 to 90 °C, while keeping other reaction variables constant. The results given in Fig. 1a show that by increasing the temperature up to 80 °C, the graft yield, grafting efficiency and monomer conversion increase continuously, then levels off. The positive effect of temperature on grafting is due to the fact that both the production rate of free radicals and access of APTAC molecules to pullulan reaction sites increases. However, above this temperature, it was noticed a decrease of all grafting parameters, probably due to a greater probability of chain termination and chain transfer reactions (Abdel Razik, 1997; Li, Li, Li, Ding, & Zong, 2004).

The rate of graft copolymerization ( $k$ ) was evaluated by measuring the rate of monomer disappearance, using the following equation (Pourjavadi & Zohuriaan-Mehr, 2002):

$$k(\text{mols/Ls}) = \frac{1000 \times W_{\text{polymer formed}}}{M \times t \times V}$$

where  $M$  is the molar mass of the monomer (g/mol),  $t$  and  $V$  are the total reaction time (s) and total volume (mL) of the reaction mixture, respectively.

The apparent first-order APTAC disappearance rate constants were then used to determine the apparent activation energy as shown in Fig. 1b. Based on the slopes of the Arrhenius plot, the activation energy for the graft copolymerization of APTAC onto pullulan backbone was found to be 42 kJ/mol. Similar values for the overall activation energy for the grafting of 4-vinylpyridine onto carboxymethylated cotton (Leza, Casinos, & Guzman, 1989), 2-(dimethylamino)ethyl methacrylate onto starch (Zhang & Chen, 2001) were obtained.

#### 3.1.2. Effect of monomer concentration

The increase in monomer concentration would be expected to increase both the percentage of grafting and the molecular weight of grafting copolymer (Abdel Razik, 1997; Aggour, 2001). Indeed, the results presented in Fig. 2 indicate that as the APTAC concentration increases from 0.075 to 0.25 mol/L both %  $G$  and %  $H$  diminishes. However, the grafting efficiency %  $E$ , and monomer conversion %  $C$ , decreases. When the monomer concentration increases over 0.25 mol/L, the grafting ratio, the grafting efficiency and the

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