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Graft copolymerization of 2-hydroxyethylmethacrylate onto carboxymethyl chitosan using CAN as an initiator

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Abstract

O-Carboxymethyl chitosan (CMCH) was prepared and characterized by FTIR spectroscopy. Graft copolymerization of 2-hydroxyethylmethacrylate (HEMA) onto CMCH using ceric ammonium nitrate (CAN) as an initiator was carried out in an aqueous solution. Evidence of grafting was confirmed by comparison of FTIR spectra of CMCH and the grafted copolymer as well as scanning electron micrograph (SEM) of the products. The effects of concentration of CAN, HEMA, reaction time and temperature on graft copolymerization were studied by determining the grafting percentage, grafting efficiency. With keeping other condition constant, the optimum grafting conditions was obtained as following: CMCH, 2 g; CAN, 0.2 M; and HEMA, 0.384 mol/l; reaction temperature, 40 °C; and reaction time, 4.5 h.

Keywords: Carboxymethyl chitosan; 2-Hydroxyethylmethacrylate; Ceric ammonium nitrate

1. Introduction

Cellulose and chitin as biopolymers is the most abundant organic compound in nature and estimated to be at levels approaching 10^{11} ton annually [1]. Chitin has been a major structural exoskeleton since the Cambrian Period, more than 550 million years ago. The total amount of chitin harvestable without unbalancing the marine ecosystem is estimated to be 1.5×10^{8} kg/year [2], mostly from the shells of crustaceans such as crab, shrimp and krill. Chitosan is the *N*-deacetylated derivative of chitin, though this *N*-deacetylation almost never complete [3,4]. Actually, the names 'chitin' and 'chitosan' corresponds to a family of polymers varying in acetyl content. Therefore the degree of acetylation determines whether the biopolymer is chitin or chitosan. Chitosan [(1→4)-2-amino-2-deoxy-β-D-Glucan] is a biocompatible polymer and have found a number of applications as biomaterials in tissue engineering and in a controlled drug release system for various route of delivery [5–9]. Chemical modification of chitosan is an important topic for production of bifunctional material.

Considerable interest has been focused on chemical modification by grafting synthetic polymers onto chitin and chitosan [10–17]. Graft copolymerization of vinyl monomers onto chitosan and other natural polymers can introduce desired properties and enlarge the field of potential application of them by choosing various types of side chains. In recent years number of initiator systems has been developed to initiate graft copolymerization. Initiators, such as ceric ammonium nitrate (CAN), potassium persulfate (KPS) and ammonium persulfate (APS) usually produce free radical sites on polymer. However, the properties of grafted chitosan have been improved but not so much because of its regular structure and the strong intermolecular hydrogen bonds. Recent researchers showed that grafting onto pre-modified chitosan is quite significant in view of preparing polysaccharide-based advanced materials with multi functions [18]. But there are very limited reports about the graft copolymerization of pre-modified chitosan derivatives [19–21].

In this paper, multiple-derivated chitosan (CMCH-*g*-HEMA) was prepared by etherification of chitosan with mono chloroaceticacid followed by the graft polymerization of 2-hydroxyethylmethacrylate, and the effects of reaction conditions like reaction time, reaction temperature, concentration of HEMA and concentration of CAN on graft copolymerization were investigated.

2. Experimental

2.1. Materials

Chitosan (molecular weight 8.4×10^{4}; the degree of deacetylation 85%) provided by Central Institute of Fisheries

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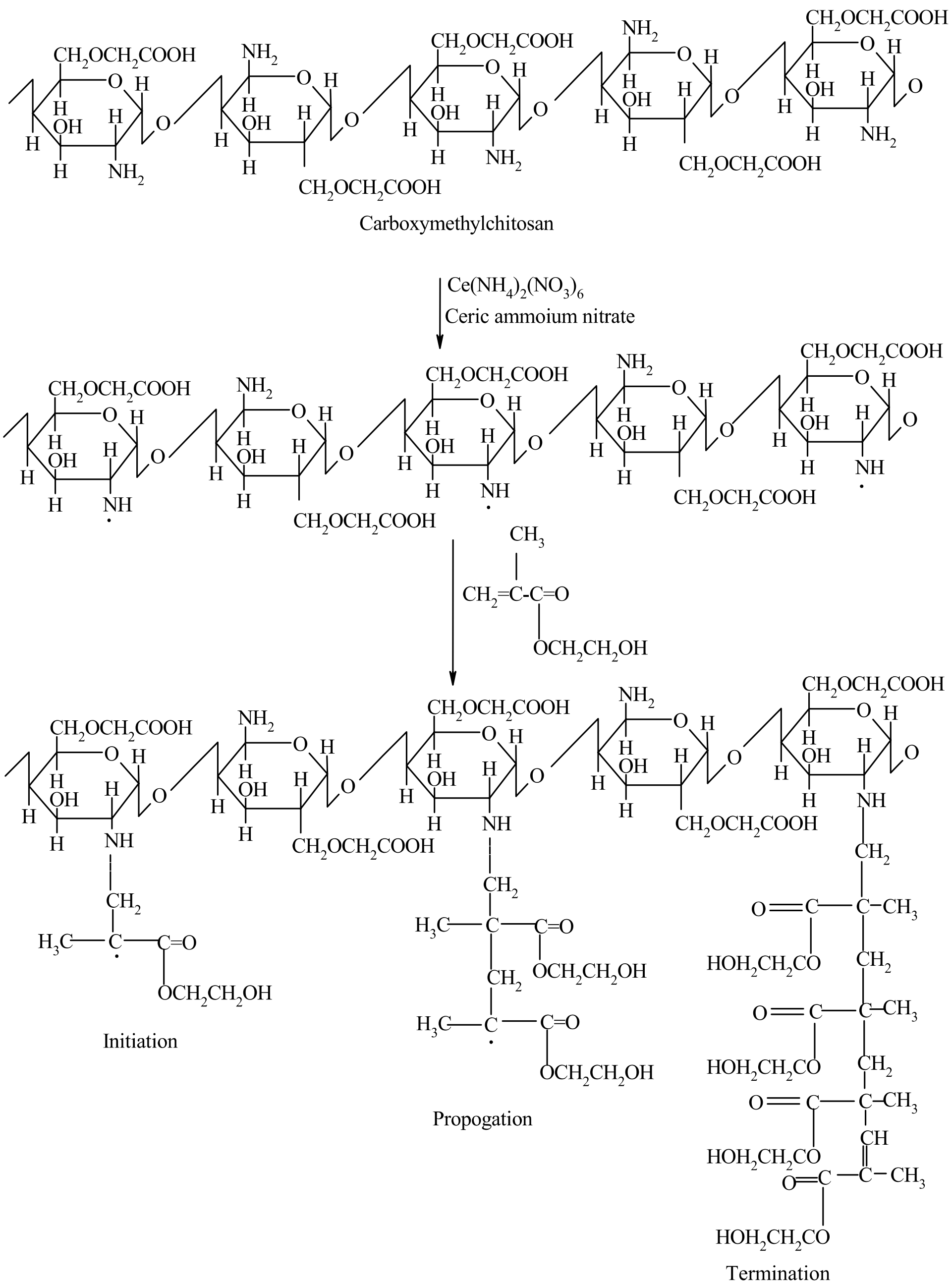

Fig. 1. Reaction scheme of CMCH-*g*-HEMA.

Technologies, India. Ceric ammonium nitrate (CAN) of analytical grade reagent was supplied from S.D. Fine Chemical, India. HEMA was obtained from National Chemical, India. All the other reagents are analytical grade and used without further purification.

2.2. Preparation of O-carboxymethylchitosan

To synthesize O-carboxymethylchitosan, chitosan (10 g), sodium hydroxide (13.5 g) and solvent isopropenol (100 ml) were suspended into a flask to swell and alkalize at room temperature for 1 h. The temperature was maintained in a water bath. The mono chloroaceticacid (15 g) was dissolved in isopropenol, and added into the reaction mixture drop wise within 30 min and reacted for 4 h at 55 °C. Then the reaction was stopped and isopropenol was discarded. Ethyl alcohol (80%) wad added and solid product was filtered and rinsed with 80–90% ethyl alcohol to desalt and dewater, and vacuum dried at 50 °C. The degree of substitution (DS) of CMCH was determined by pH-metry and found to be 0.31 [22].

2.3. Graft copolymerization

A small amount of CMCH (2 g), a predetermined amount of HEMA, and 100 ml double distilled water were charged into a three necked round bottom flask in a constant temperature water bath maintained at a 40 °C. Nitrogen gas was bubbled for 30 min to remove the dissolved oxygen under stirring. 0.20 M