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Synthesis and properties of biodegradable hydrogels of κ-carrageenan grafted acrylic acid-co-2-acrylamido-2-methylpropanesulfonic acid as candidates for drug delivery systems

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Abstract

Novel types of highly swelling hydrogels were prepared by grafting crosslinked polyacrylic acid-co-poly-2-acrylamido-2-methylpropanesulfonic acid (PAA-co-PAMPS) chains onto κ-carrageenan through a free radical polymerization method. Here, we propose a mechanism for κ-carrageenan-g-PAA-co-PAMPS formation and confirm the hydrogel structure using FTIR spectroscopy. The effect of grafting variables (i.e. concentration of methylenebisacrylamide (MBA), acrylic acid/-2-acrylamido-2-methylpropanesulfonic acid (AA/AMPS) weight ratio, ammonium persulfate (APS), κ-carrageenan, neutralization percent and reaction temperature) were systematically optimized to achieve a hydrogel with a maximum swelling capacity. The maximum water absorbency of the optimized final product was 1238 g/g, while poly-2-acrylamido-2-methylpropanesulfonic acid-g-κ-carrageenan and polyacrylic acid-g-κ-carrageenan hydrogels swelled to a range of 135–800 g/g. The swelling of superabsorbent hydrogels was measured in various solutions with pH values ranging from 1 to 13. In addition, the pH reversibility, on–off switching behavior and swelling kinetics in distilled water were preliminarily investigated.

Keywords: Superabsorbent; κ-Carrageenan; Acrylic acid; 2-Acrylamido-2-methylpropanesulfonic acid

1. Introduction

In the past two decades, the delivery of oral drug systems to the colon for the local treatment of a variety of bowel diseases and for improving systemic absorption of drugs susceptible to enzymatic digestion in the upper gastrointestinal tract has been extensively investigated. Targeting drugs to the colon can be achieved in several ways [1]. The pH-sensitive delivery systems, such as hydrogel-based polymers, can be a simple and practical means for colon-specific drug delivery.

Hydrogels are a unique class of polymeric materials that absorb enormous amounts of water when allowed to remain in a water reservoir for a long

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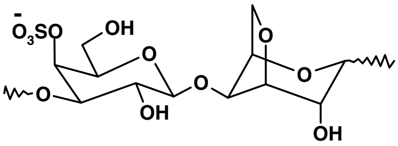
time. The underlying property accounting for this unusual behavior of hydrogels is their transition from a glassy to a rubbery state when contacted with thermodynamically compatible solvents [2].

A polyelectrolyte gel is formed after flexible polymer chains are crosslinked and ionizable groups are attached. These ionizable groups completely dissociate in solution, form strong electrolyte groups and produce an electrostatic repulsion force among themselves, thus influencing the expansion of the network. Due to their excellent properties of hydrophilicity, high swelling capacity, lack of toxicity and biocompatibility, these superabsorbent polymeric materials are used for many applications such as drug carriers, artificial organs, soil conditioners for agriculture and horticulture, disposable diapers, water blocking tapes, absorbent pads, gel actuators, drilling fluid additives, polymer cracks blocking materials, feminine napkins, firefighting, extraction of precious metals, extraction of solvents, release of agrochemicals, etc. [3,4]. One of the best methods for the synthesis of these polymers is chemical grafting of vinylic monomers such as acryl amide and acrylic acid onto low cost and biodegradable polysaccharides such as starch, chitosan, and cellulose by using various initiating systems followed by crosslinking with hydrophilic crosslinkers [5,6]. These superabsorbent polymeric materials are abundant, inexpensive and available and their biodegradability and ability to be easily modified suggest their applications in colon-targeted drug delivery systems.

κ-Carrageenan is a collective term for linear sulfated polysaccharides that are obtained commercially by alkaline extraction of certain species of red seaweeds [7]. A schematic diagram of the idealized structure of the repeated units for the most well-known and most important type of κ-carrageenan is shown in Scheme 1.

We selected AMPS and AA as ionic vinyl monomers. AMPS has received attention in the last few years due to its strongly ionizable sulfonate groups; AMPS and AA dissociate completely throughout the pH range. Thus, hydrogels derived from AMPS and AA exhibit pH-dependent swelling behavior.



Scheme 1. Repeating disaccharide units of κ-carrageenan.

The present article represents the optimized synthesis of a novel biopolymer-based superabsorbent hydrogel through crosslinking graft copolymerization of AA-co-AMPS onto κ-carrageenan under normal atmospheric conditions. We studied the dependence of swelling behavior of the hydrogels on the reaction conditions and pH of the external environment. A novel hydrogel was designed to take advantages of the biodegradability of κ-carrageenan and pH dependence of PAA-co-PAMPS. The obtained gels are expected to have colon-specific drug delivery properties.

Furthermore, high viscosity of κ-carrageenan solutions decreased diffusion of molecular oxygen in the reaction mixture, consequently decreased the inhibiting effect of the oxygen in the free radical polymerization process. This fact has previously been observed in other polysaccharides [8,9]. Therefore, we were able to apply a crosslinking graft copolymerization reaction under atmospheric conditions to shorten and simplify the industrial process.

2. Experimental

2.1. Materials

The polysaccharide, κ-carrageenan was purchased from Condinson Co. (κ-C, Denmark); *N*,*N*-methylenebisacrylamide (MBA, from Merk) as a crosslinker, ammonium persulfate (APS, from Fluka) as a water soluble initiator, acrylic acid and 2-acrylamido-2-methylpropane sulfonic acid (AA, AMPS from Merck) as ionic monomers, were of analytical grade and used without further purification.

3. Graft copolymerization

Water (25 mL) and κ-C (1.0 g) were added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021) while stirring (200 rpm). The reactor was placed in a thermostat water bath preset at the desired temperature (65–90 °C) for 20 min. After dissolving κ-carrageenan and homogenizing the mixture, the monomers and crosslinker solutions (AA, AMPS and MBA) were simultaneously added and the reaction mixture was stirred for an additional 15 min. To initiate polymerization, APS was added and gelation was observed within 10–15 min (final volume of solution = 35 mL). The reaction product was allowed to cool to ambient