

Synthesis of Novel Polysaccharide-Based Superabsorbent Hydro Gels Via Graft Copolymerization of Vinylic Monomers onto Kappa-Carrageenan

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Abstract—Highly water-absorbing polymers of neutralized poly(acrylic acid-co-MAA) onto Kappa-carrageenan were synthesized in an effort to investigate the influences of environment parameters (pH, salinity) on water absorption. The polymerization reaction was carried out in an aqueous medium and in the presence of ammonium persulfate (APS) as an initiator. The structure of hydrogels were confirmed by FTIR spectroscopy Kappa-carrageenan and the hydrogels as well as solubility characteristics of the products. In addition, the extent of water absorption and the absorption rate were studied to determine their relationship with the environment parameters.

Index Terms—Kappa-Carrageenan Meth Acrylic Acid, Acrylic Acid, Water Absorption.

I. INTRODUCTION

Superabsorbent hydrogels are hydrophilic networks which capable to absorb and retain considerable amounts of water or physiological fluids [1]. Because of their excellent characteristics, they are used in many applications such as in disposable diapers, feminine napkins, agriculture, and medicine [2]. After the first reported superabsorbent polymer by the U.S. Department of Agriculture [3], significant attention was paid to synthesis of these materials with high absorbency, gel strength, and absorption rate. Due to their biocompatibility, biodegradability and non-toxicity, polysaccharides are the main part of the natural-based superabsorbent hydrogels. One of the best methods for the synthesis of these polymers is graft copolymerization of vinylic monomers onto polysaccharides [4-6]. This article represents an optimized synthesis of novel superabsorbent hydrogels based on kappa-carrageenan (κ C, Fig. 1) through graft copolymerization of acrylamide (AAM), acrylic acid (AA), or methacrylic acid (MAA) in the presence of a crosslinking agent and an initiator, to form hydrogels with super-swelling capacity, pH-responsiveness and low salt-sensitivity properties.

II. EXPERIMENTAL

A. Synthesis of hydrogen

A general procedure was conducted as follows. In order to remove of oxygen, doubly-distilled water was boiled for

30 min and after cooling to room temperature, pure argon gas was bubbled in water for 15 min. Then certain amounts of water (30 mL) and κ C (1.0 g) were added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, 600 rpm). The reactor was immersed in a thermostated water bath preset at 80 °C. The reaction was protected from air by a very mild purging of argon during the reaction. After complete dissolution of κ C, the initiator, ammonium persulfate (APS, 0.10 g) was added to this solution and allowed to stirring for 30 min. Then the monomer, AAm (2.5 g), AA (3.5 g), or MAA (3.0 g) and the crosslinker, methylene bisacrylamide (MBA, 0.05 g), were simultaneously added to the mixture. After 60 min, the produced gel was poured into methanol (200 mL) and was remained for 24 h to dewater. The hardened gel particles were filtered and dried at 50 °C for 5 h. After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat and light.

III. RESULTS AND DISCUSSION

A. Reaction Mechanism

Crosslinking graft copolymerization of vinyl monomers (AAM, AA, and MAA) onto κ C was shown in Scheme 1. The persulfate initiator is decomposed under heating to generate sulfate anion-radical. The radical abstracts hydrogen from the hydroxyl group of the polysaccharide substrate to form alkoxy radicals on the substrate. So, this persulfate-saccharide redox system is resulted in active centers on the substrate to radically initiate polymerization of monomers led to a graft copolymer. Since a crosslinking agent, e.g. MBA, is presented in the system, the copolymer comprises a crosslinked structure. In the case of AAM, the hydrophilic network may be hydrolyzed under alkaline conditions for converting the non-ionic carboxamide groups to anionic carboxylate groups and yield another hydrogel network. On the other hand, in the case of AA and MAA, partially neutralization converts some carboxylic acid groups to carboxylate anions[5].

B. Spectral Characterization.

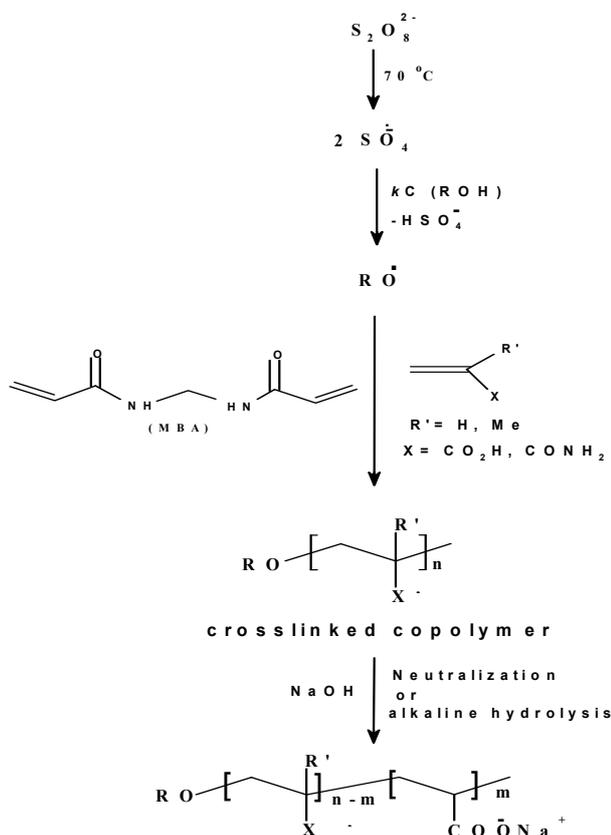
For identification of hydrogels, infrared spectroscopy was used. The products comprise a κ C backbone with side chains that carry carboxamide and/or carboxylate functional groups that are evidenced by peaks at 1660, 1407, 1557 cm^{-1} . These peaks attributed to C=O stretching in carboxamide functional groups of PAAM and symmetric and asymmetric stretching modes of carboxylate groups, respectively.

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C. PH-sensitivity and Pulsatile Behavior

Swelling of the synthesized hydrogels was measured in buffer solutions with pHs varied from 1.0 to 13.0. Maximum swelling was obtained at pH 8. At pHs < 8, the carboxylate anions are protonated, so the main anion-anion repulsive forces are eliminated and consequently swelling decreased. The reason of the swelling-loss for the highly basic solutions is "charge screening effect" of excess cations in the swelling media which shield the carboxylate anions and prevent effective anion-anion repulsion.



Scheme 1 A proposed mechanism for synthesis of κ C-based superabsorbent hydrogels.

The hydrogels were also showed reproducible swelling-deswelling cycles. This behavior is shown for hydrolyzed κ C-g-PAAm product (Fig. 1). At pH 8.0, the hydrogel swells up to 140 g/g due to anion-anion repulsive electrostatic forces, while at pH 2.0, it shrinks within a few minutes due to the protonation of carboxylate groups.

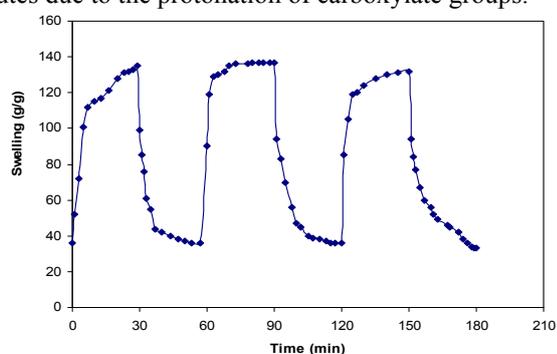


Fig. 1 The pH-responsiveness behavior of hydrolyzed κ C-g-PAAm hydrogel in buffer solutions (pH 2.0 and 8.0).

D. Effect of Salinity on Swelling.

To study various saline effects on the swelling behavior of the hydrogels, equilibrium swelling was measured in 0.15

M solutions of LiCl, NaCl, KCl, CaCl₂, and AlCl₃ (Table 1). A dimensionless salt sensitivity factor, f , was calculated according to Eq. (2):

$$f = 1 - [(\text{swelling in a given fluid}) / (\text{swelling in water})] \quad (2)$$

TABLE 1 EFFECT OF SALINITY ON EQUILIBRIUM SWELLING (ES) OF THE SUPERABSORBENT HYDROGELS PRODUCED.

Swelling medium	κ C-g-PAAm		Partially hydrolyzed κ C-g-PAAm		Partially neutralized κ C-g-PAA		Partially neutralized κ C-g-PMAA	
	ES (g/g)	f	ES (g/g)	f	ES (g/g)	f	ES (g/g)	f
H ₂ O	51	-	1560	-	789	-	234	-
LiCl	45	0.12	98	0.94	72	0.91	37	0.84
NaCl	40	0.22	127	0.92	81	0.9	46	0.8
KCl	24	0.53	135	0.91	75	0.9	51	0.78
CaCl ₂	21	0.59	18	0.98	30	0.96	17	0.93
AlCl ₃	14	0.79	6	0.99	9	0.99	7	0.97

Generally, all swelling values in saline media for all networks are expectedly decreased. The reason is usually attributed to the "charge screening effect". An additional reason in the case of CaCl₂ and AlCl₃ is "ionic crosslinking" between anionic sites of chains and multi-valent cations. However, the swelling capacity of the synthesized hydrogels in LiCl, NaCl and KCl is yet considerable. Since the sulfate ions do not keep cations in their vicinity, the "charge screening effect" is not so effective. For confirming this point, we compared salt-sensitivity for κ C-g-PAAm with other hydrogels (Table 1). In the case of κ C-g-PAAm, sulfate groups are the only anions assisted the hydrogel to swell, so the low salt-sensitivity of the superabsorbents (f 0.12-0.79) is certainly due to the presence of these anionic species. In other hydrogels, lots of carboxylate anions are introduced to the hydrogel systems. Therefore, very high salt-sensitivity (f 0.9-0.99) is due to charge screening effect and enhancement of ionic crosslink density.

IV. CONCLUSION

Novel high pH-responsive and low salt-sensitive superabsorbent hydrogels were synthesized by crosslinking graft copolymerization of AAm, AA, and MAA onto κ C backbone. Swelling capacity of the hydrogels in various buffers was appreciable. It was also showed that pH-responsiveness and swelling-deswelling behavior of the hydrogels make them suitable biomaterials to design new systems for controlled drug delivery. Swelling measurement of the synthesized hydrogels in different salt solutions showed appreciable swelling capacity, especially in LiCl, NaCl, and KCl solutions, due to anti-salt characteristics of the carrageenan part sulfate groups of the superabsorbing hydrogels.

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Synthesis and super-swelling behavior of a novel low salt-sensitive protein-based superabsorbent hydrogel: collagen-g-poly(AMPS), Turk J Chem, 2010, 34, 739-752

Studies on graft copolymerization of 2-hydroxyethylmethacrylate onto kappa-carrageenan initiated by ceric ammonium nitrate, Journal of The Chilean Chemical Society, 55N^o 4(2010)

Swelling Behaviour of a Novel Protein-Based Super Absorbent Hydrogel Composed of Poly(methacrylic Acid) and Collagen, Asian Journal of Chemistry, 2010, 22, 6734-6746

His Major Research Interests are:

Hydrogel Synthesis and Properties. Hydrophilic polymer networks especially superabsorbent polymers (SAPs) are of his main interests. SAPs

are hydrogels having ability to absorb huge amounts of water or aqueous fluids, as high as 10-1000 times their own weight. Their application includes mainly healthcare products (baby napkins, female pads) as well as the resins using in agriculture. They have revolutionized the arid-area agriculture and soil conditioning. These glutinous hydrogels have been one of his main research interests. Interpenetrating polymer network (IPN) hydrogels are also interested.

Modification of Natural Polymers. Natural polymers from renewable resources such as carbohydrate polymers (starch, cellulose, carrageenans, chitin, natural gums) are interested to be chemically modified (e.g., monomer grafting, or IPN formation) to achieve water soluble/swellable materials. The products may be used in a wide range of applications, e.g., medicine, pharmacy (biocompatible devices, drug delivery systems), water treatment (flocculants), water-borne surface coatings, cosmetics and food industries (thickeners), enhanced oil recovery (shear stabilized drilling mud), and drug reducing agents.

And His Current Research Interests are:

Synthesis of novel superabsorbent hydrogels with high pH and low salt sensitivity

Synthesis of intelligent hydrogels as excellent candidate in controlled release drug delivery systems.

Synthesis of composite hydrogels for preparing of new superabsorbents with high mechanical stability.

Modification of natural polymers via free radical graft copolymerization of vinylic monomers.

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