

Modified Carrageenan. 4. Synthesis and Swelling Behavior of Crosslinked κ C-g-AMPS Superabsorbent Hydrogel with Antisalt and pH-Responsiveness Properties

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ABSTRACT: To synthesize a novel biopolymer-based superabsorbent hydrogel, 2-acrylamido-2-methylpropanesulfonic acid (AMPS) was grafted onto kappa-carrageenan (κ C) backbones. The graft copolymerization reaction was carried out in a homogeneous medium and in the presence of ammonium persulfate (APS) as an initiator, *N,N,N',N'*-tetramethyl ethylenediamine (TMEDA) as an accelerator, and *N,N'*-methylene bisacrylamide (MBA) as a crosslinker. A proposed mechanism for κ C-g-AMPS formation was suggested and the hydrogel structure was confirmed using FTIR spectroscopy. The affecting variables on swelling capacity, i.e., the initiator, the crosslinker, and the monomer concentration, as well as reaction temperature, were systematically optimized. The swelling measurements of the hydrogels were conducted in aqueous solutions of LiCl, NaCl, KCl,

MgCl₂, CaCl₂, SrCl₂, BaCl₂, and AlCl₃. Due to the high swelling capacity in salt solutions, the hydrogels may be referred to as antisalt superabsorbents. The swelling of superabsorbing hydrogels was measured in solutions with pH ranging 1 to 13. The κ C-g-AMPS hydrogel exhibited a pH-responsiveness character so that a swelling-deswelling pulsatile behavior was recorded at pH 2 and 8. The overall activation energy for the graft copolymerization reaction was found to be 14.6 kJ/mol. The swelling kinetics of the hydrogels was preliminarily investigated as well. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 255–263, 2005

Key words: carrageenan; hydrogels; swelling; pH sensitivity; crosslinking

INTRODUCTION

Vinyl graft copolymerization onto polysaccharide backbones is a well-known method for synthesis of natural-based superabsorbent hydrogels.^{1–4} The first industrial superabsorbent hydrogel, hydrolyzed starch-graft-polyacrylonitrile, was synthesized using this method.⁵ These biopolymer materials are crosslinked hydrophilic polymers, capable of absorbing large quantities of water, saline, or physiological solutions.⁶ They are widely used in many fields such as hygiene, cosmetics, and agriculture.^{7–9}

Hydrogels responding to external stimuli such as heat, pH, electric field, chemical environments, etc, are often referred to as “intelligent” or “smart” hydrogels. These responsive hydrogels have become an important area of research and development in the field of medicine, pharmacy, and biotechnology.^{10, 11}

Because of their exceptional properties, i.e., biocompatibility, biodegradability, renewability, and nontoxicity, polysaccharides are the main part of the natural-based superabsorbent hydrogels.

Carrageenans are commercially important hydrophilic polysaccharides that occur in numerous species of seaweeds.¹² These linear sulfated polymers are composed of D-galactose and 3,6-anhydrogalactose units. The types of carrageenans differ only in the position and number of ester sulfate groups. Schematic diagram of the most important type of the carrageenan family, i.e., kappa-carrageenan (κ C), is presented in Figure 1.

Following continuous research on modification of carrageenans,^{13–15} in this article, we attempted the synthesis of a novel superabsorbent hydrogel by crosslinking graft copolymerization of 2-acrylamido-2-methylpropanesulfonic acid onto kappa-carrageenan with pH-responsiveness and low salt-sensitivity properties. The presence of hydrophilic sulfate groups with high ionization tendency and less sensitivity to salt solution was our main idea for synthesis of carrageenan-based superabsorbent hydrogels.

EXPERIMENTAL

Materials

Kappa-carrageenan (Condinson Co., Denmark), *N,N'*-methylene bisacrylamide (MBA, Fluka), ammonium persulfate (APS, Fluka, Switzerland), 2-acryl-

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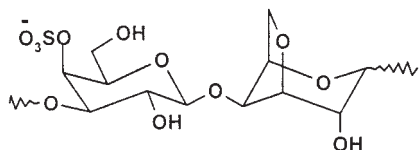


Figure 1 Repeating disaccharide units of kappa-carrageenan (κ C).

amido-2-methylpropanesulfonic acid (AMPS, from Merck), and *N,N,N',N'*-tetramethyl ethylenediamine (TMEDA, Merck, Germany) were of analytical grade and used without further purification. All other chemicals were also analytical grade. Double-distilled water was used for the hydrogel preparation and swelling measurements.

Preparation of hydrogel

Synthesis of the hydrogel, κ C-*g*-AMPS, was carried out using APS as an initiator, TMEDA as an accelerator, and MBA as a crosslinker in an aqueous medium. A general procedure for chemically crosslinking graft copolymerization of AMPS onto κ C was conducted as follows. κ C (1.0 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three-blade propeller type, 350 rpm), including 30 mL deoxygenated doubly distilled water. The reactor was immersed in a thermostated water bath preset at the desired temperature (50–90°C). After complete dissolution of κ C to form a homogeneous solution, certain amounts of completely neutralized AMPS (1.0–5.0 g in 5 mL H₂O) and MBA (0.3–0.7 g in 5 mL H₂O) were simultaneously added to the reaction mixture. After stirring for 15 min, the initiator solution (0.05–0.30 g APS in 5 mL H₂O) with 0.2 mol % of TMEDA, based on monomer content, was added to the mixture. After 60 min, the produced hydrogel was poured into excess nonsolvent methanol (200 mL) and remained for 3 h to dewater. Methanol was then decanted and the product was cut to small pieces (diameter \approx 5 mm). Again, 100-mL fresh methanol was added and the hydrogel was left for 24 h. Finally, the filtered hydrogel was dried in an oven at 50°C for 5 h. After grinding, the powdered superabsorbent was stored away from moisture, heat, and light.

Swelling measurements using tea bag method

The tea bag (i.e., a 100-mesh nylon screen) containing an accurately weighed powdered sample (0.5 ± 0.001 g) was immersed entirely in 200 mL distilled water and allowed to soak for 3 h at room temperature. The sample particle sizes were 40 to 60 mesh (250–350 μ m). The tea bag was hung up for 15 min to remove

the excess solution. The equilibrium swelling (*ES*) was calculated according to following equation:

$$ES(\text{g/g}) = \frac{\text{Weight of swollen gel} - \text{Weight of dried gel}}{\text{Weight of dried gel}} \quad (1)$$

Swelling in various salt solutions

Absorbency of the κ C-*g*-AMPS hydrogel was evaluated in 0.15M solutions of LiCl, NaCl, KCl, MgCl₂, CaCl₂, SrCl₂, BaCl₂, and AlCl₃ according to the above method described for swelling measurement in distilled water. In addition, swelling capacity of the hydrogel was measured in different concentrations (0.001–1.5M) of LiCl, CaCl₂, and AlCl₃ salt solutions.

Absorbency at various pHs

Individual solutions with acidic and basic pHs were prepared by dilution of NaOH (pH 10.0) and HCl (pH 1.0) solutions to achieve pH greater than and equal to 6.0 and pH less than 6.0, respectively. The pH values were precisely checked by a pH meter (Metrohm/620, accuracy ± 0.1). 0.5 g (± 0.001 g) of the dried hydrogel was used for the swelling measurements according to eq. (1).

pH sensitivity

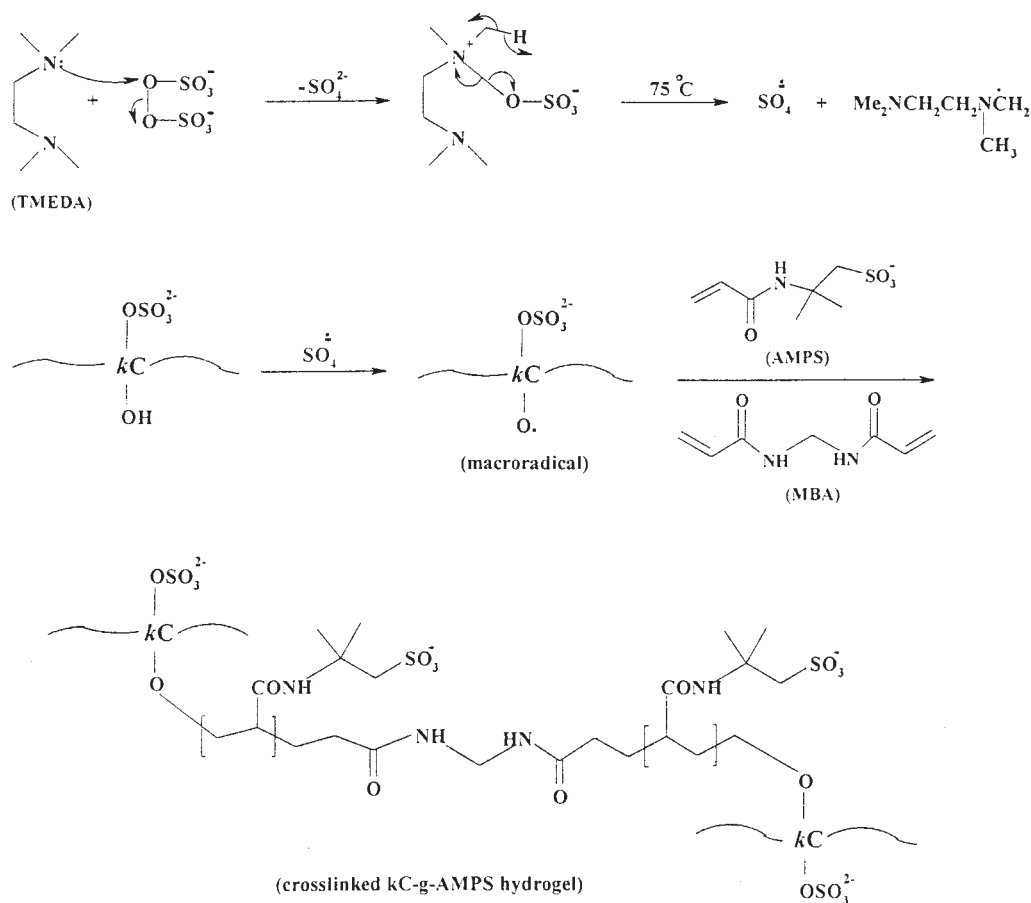
pH sensitivity of the hydrogel was investigated in terms of swelling and deswelling of the final product at two basic (pH 8.0) and acidic (pH 2.0) solutions, respectively. Swelling capacity of the hydrogels at each pH was measured according to eq. (1) at consecutive time intervals (30 min).

Swelling kinetics

For studying the rate of absorbency of the hydrogels, certain amount of samples (0.5 ± 0.001 g) were poured into numbers of weighed tea bags and immersed in 200 mL distilled water. At consecutive time intervals, the water absorbency of the hydrogels was measured according to the above-mentioned method.

Infrared spectroscopy

FTIR spectra of samples were taken in KBr pellets using an ABB Bomem MB-100 FTIR spectrophotometer.



Scheme 1 Proposed mechanistic pathway for synthesis of κ C-g-AMPS hydrogel.

RESULTS AND DISCUSSION

Synthesis and spectral characterization

The mechanism for crosslinking graft copolymerization of AMPS onto κ C backbones in the presence of APS, TMEDA, and MBA is shown in Scheme 1. As shown in the scheme, at the first step, the accelerator, TMEDA, causes easier dissociation of persulfate initiator to sulfate radical-anions. The resulted sulfate anion-radical then abstracts hydrogen from the hydroxyl groups of the κ C. So, this persulfate-saccharide redox system results in active centers on the substrate to radically initiate AMPS grafting onto κ C backbones. Since a crosslinking agent, i.e., MBA, is presented in the reaction mixture, the three-dimensional network results.

FTIR spectroscopy was used for identification of the hydrogel, κ C-g-AMPS. Figure 2 shows the IR spectra of the polysaccharide, κ C, and the resulting hydrogel. The bands observed at 842, 913, 1016, and 1222 cm^{-1} can be attributed to D-galactose-4-sulfate, 3,6-anhydro-D-galactose, glycosidic linkage, and ester sulfate stretching of κ C backbone, respectively [Figure 2(a)]. The broad band at 3200–3600 cm^{-1} is due to stretching of –OH groups of κ C. The κ C-g-AMPS hydrogel com-

prises a κ C backbone with side chains that carry carboxamide functional groups that are evidenced by a new characteristic absorption band at 1660 cm^{-1} [Figure 2(b)]. This peak is attributed to carbonyl stretching in carboxamide groups of AMPS. The stretching band of –NH overlapped with the OH stretching band of the κ C portion of the copolymer.

To obtain additional evidence of grafting, a similar graft copolymerization was conducted in the absence of the crosslinker. After extracting the homopolymer (PAMPS), appreciable amounts of synthetic polymer percentage of the graft copolymer (75%) were concluded. The graft copolymer spectrum was very similar to Figure 2(b). Also according to preliminary measurements, the sol (soluble) content of the hydrogel networks was as little as 1.5%. This fact practically proves that all AMPS are involved in the polymer network. So, the monomer percent in the network will be very similar to that of the initial feed of reaction.

Optimization of the grafting conditions

The factors affecting the graft copolymerization of AMPS onto κ C, i.e., MBA, AMPS, and APS concentration as well as reaction temperature, were systemati-

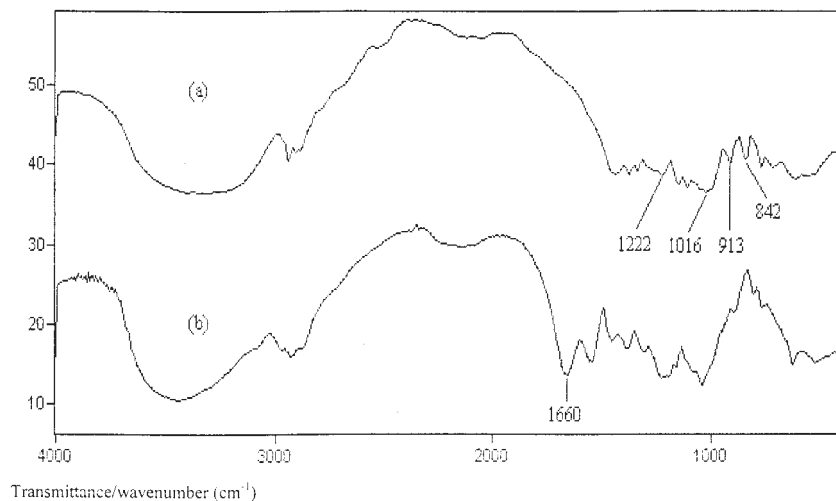


Figure 2 FTIR spectra of κC (a) and crosslinked $\kappa\text{C-g-AMPS}$ (b).

cally optimized to achieve superabsorbent with maximum water absorbency.

Effect of MBA concentration

The effect of crosslinker concentration (C_c) on swelling capacity of crosslinked $\kappa\text{C-g-AMPS}$ was investigated. As shown in Figure 3, more values of absorbency are obtained by lower C_c . Such a well-known behavior has been reported by pioneering scientists.^{7,11,16} In fact, higher C_c decreases the free space between the copolymer chains and consequently the resulting highly crosslinked rigid structure cannot be expanded and hold a large quantity of water. This power law behav-

ior between swelling capacity and MBA concentration [eq. (2)] was conducted from Figure 3.

$$\text{Swelling capacity} \approx K[\text{MBA}]^{-n} \quad (2)$$

The K and n in eq. (2) are constant values for an individual superabsorbent. The n value represents the extent of the sensitivity of the hydrogel to the crosslinker content, while the K value gives an amount useful for comparing the extent of swelling versus fixed crosslinker content. The $K = 0.59$ and $n = 1.67$ is obtained from the curve fitted with eq. (2).

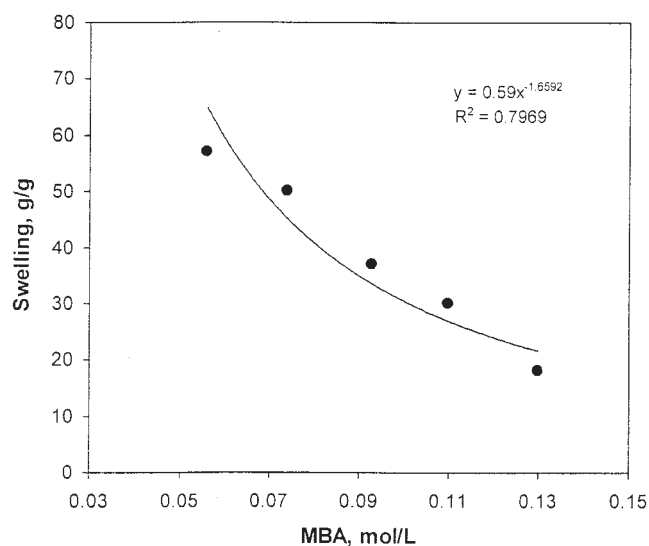


Figure 3 Effect of crosslinker concentration on swelling capacity. Reaction conditions: κC , 1.0 g; AMPS, 0.41 mol/L; APS, 0.025 mol/L; H_2O , 50 mL; 75°C , 60 min.

Effect of AMPS concentration

The swelling capacity as a function of monomer concentration was investigated and results shown in Figure 4. According to this figure, the absorbency is increased with increasing the AMPS concentration from 0.14 up to 0.41 mol/L and, then, it is decreased considerably with a further increase in the amount of monomer. The maximum absorbency (142 g/g) is obtained at 0.41 mol/L of the monomer, AMPS. The initial increase in swelling capacity can be attributed to (a) greater availability of monomer molecules in the vicinity of the chain propagating sites of κC macroradicals and (b) increase in the hydrophilicity of the hydrogel originated from higher AMPS content that, in turn, causes a stronger affinity for more absorption of water. The swelling loss after the maximum may be attributed to (a) preferential homopolymerization over graft copolymerization, (b) increase in viscosity of the medium, which restricts the movement of free radicals and monomer molecules, and (c) the enhanced chance of chain transfer to monomer mole-

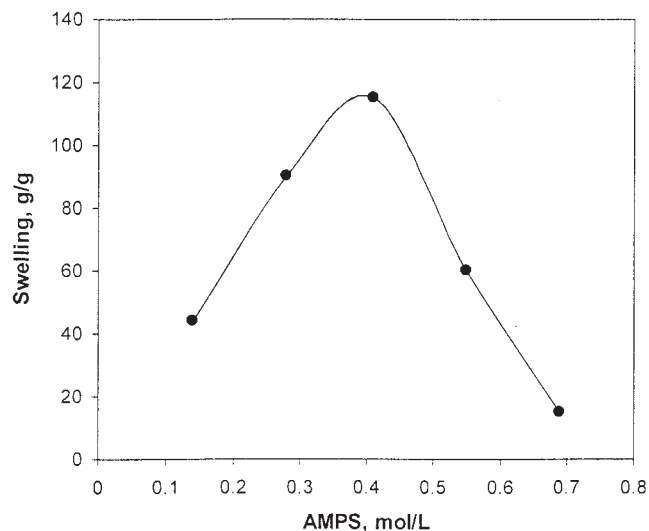


Figure 4 Effect of monomer concentration on swelling capacity. Reaction conditions: κ C, 1.0 g; MBA, 0.056 mol/L; APS, 0.025 mol/L; H₂O, 50 mL; 75°C, 60 min.

cules. Such behaviors have been reported by other investigators.¹⁷⁻¹⁹

Effect of APS concentration

The relationship between the initiator concentration and water absorbency values was studied by varying the APS concentration from 0.006 to 0.037 mol/L (Figure 5). It is observed that the absorbency is substantially increased with an increase in the APS concentration and then it is decreased. Initial increment in water absorbency may be attributed to an increased number of active free radicals on the κ C backbone.

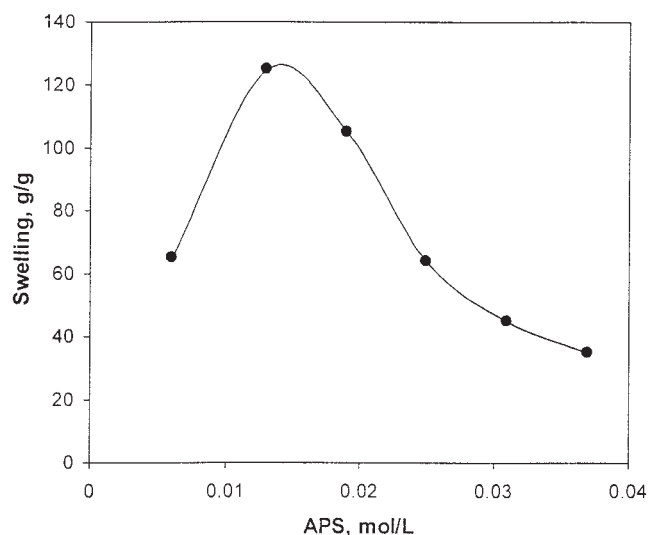


Figure 5 Effect of initiator concentration on swelling capacity. Reaction conditions: κ C, 1.0 g; MBA, 0.056 mol/L; AMPS, 0.41 mol/L; H₂O, 50 mL; 75°C, 60 min.

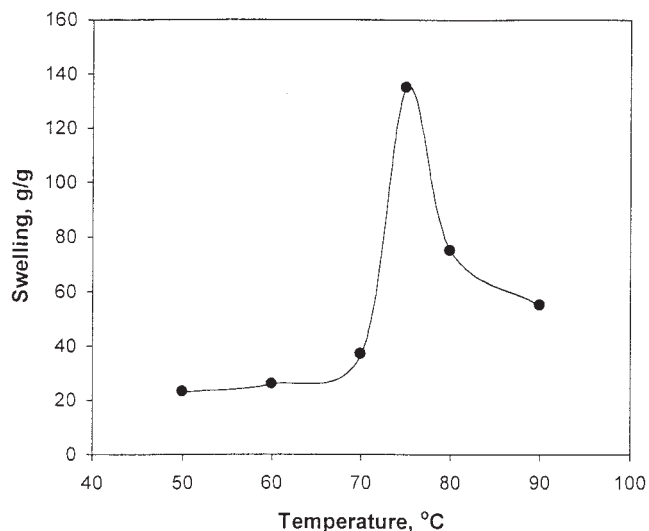


Figure 6 Effect of reaction temperature on swelling capacity. Reaction conditions: κ C, 1.0 g; MBA, 0.056 mol/L; AMPS, 0.41 mol/L; H₂O, 50 mL; 60 min.

The subsequent decrease in swelling is originated from an increase in the terminating step reaction via bimolecular collision, which, in turn, causes the enhancement of crosslinking density. This possible phenomenon is referred to as "self crosslinking" by Chen and Zhao.²⁰ In addition, the free radical degradation of κ C backbones by sulfate radical-anions is an additional reason for swelling loss at higher APS concentration. The proposed mechanism for this possibility was reported in the previous work.¹⁵ A similar observation was recently reported by Hsu et al.²¹ in the case of degradation of chitosan with potassium persulfate.

Effect of reaction temperature

The swelling capacity of the hydrogels prepared with various reaction temperatures is shown in Figure 6. Higher temperatures favor the rate of diffusion of AMPS to the κ C macroradicals as well as increase the kinetic energy of radical centers. In addition, higher temperatures increase the rate of decomposition of the thermally dissociating initiator, APS.²² The temperatures higher than the optimum value (75°C), however, lead to low-swelling superabsorbents. This swelling loss may be attributed to (a) oxidative degradation of κ C chains by sulfate radical-anions, (b) increasing the rate of termination and chain transfer reactions, and (c) decomposition of APS to give O₂ (a radical scavenger), which reacts with primary free radicals [eqs. (3) and (4)],²³ resulting in decreased molecular weight and decreased swelling (the sulfate radical anions may react with water to produce hydroxyl radicals [eq. (3)] and finally oxygen [eq. (4)].



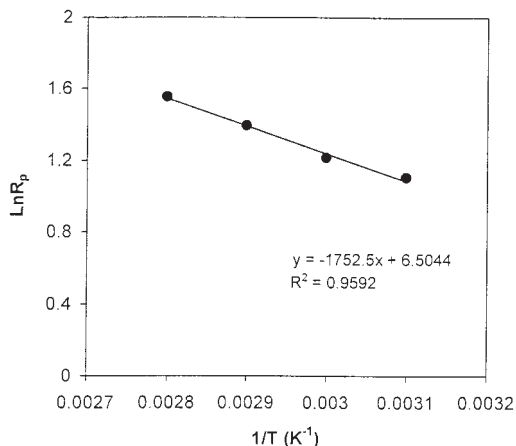
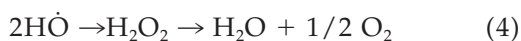


Figure 7 Plot of $\text{Ln}R_p$ versus $1/T$.



The rate of graft copolymerization (R_p) was calculated simply using the following empirical formula,²⁴ for four initial points of Figure 6:

$$R_p(\text{molL}^{-1}\text{s}^{-1}) = \frac{m_H}{MTV} \quad (5)$$

where m_H (g) stands for the weight of produced dry hydrogel, M (g mol^{-1}) denotes the molecular weight of AMPS, T and V are the reaction time (s) and total volume (L) of the reaction mixture, respectively. The overall activation energy (E_a) for the graft polymerization reaction was calculated via the slope of the plot $\text{Ln}R_p$ versus $1/T$ (Figure 7) based on the Arrhenius relationship [$k_p = A \exp(-E_a/RT)$]. Therefore, E_a for the graft copolymerization of AMPS onto polysaccharide backbones was found to be 14.6 kJ/mol.

Swelling in salt solutions

The swelling capacity of "ionic" absorbents is significantly affected by various factors of the external solution. For instance, swelling ability of "anionic" hydrogels in various salt solutions is appreciably decreased compared to the swelling values in distilled water. This well-known undesired swelling loss is often attributed to a "charge screening effect" of the additional cations causing a nonperfect anion-anion electrostatic repulsion.¹⁶ Therefore, the osmotic pressure resulting from the mobile ion concentration difference between the gel and aqueous phases decreased and consequently the absorbency amounts decreased. In addition, in the case of salt solutions with multivalent cations, "ionic crosslinking" at the surface of particles caused an appreciable decrease in swelling capacity. It is obvious that swelling decrease strongly depends on

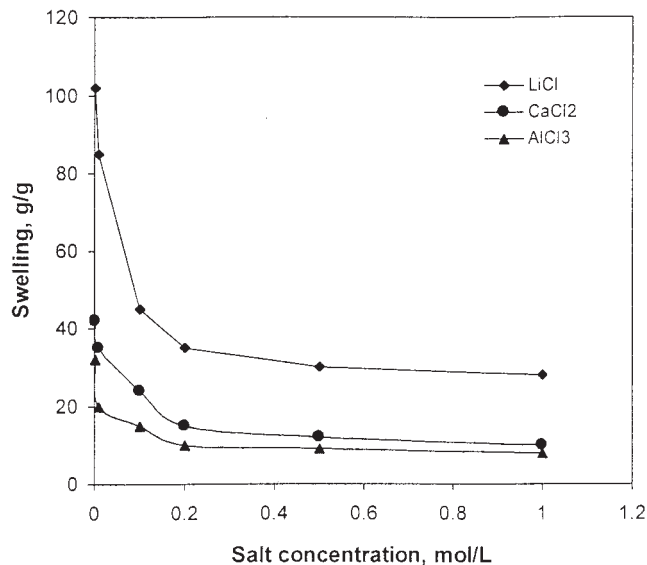


Figure 8 Swelling dependency on saline concentration for the $\kappa\text{C-g-AMPS}$ superabsorbent hydrogel.

the "type" and "concentration" of salt added to the swelling medium. Figure 8 illustrates a reverse and power law relationship between concentration of salt solutions (LiCl, CaCl_2 , and AlCl_3) and swelling capacity of the hydrogel, $\kappa\text{C-g-AMPS}$. In addition, as shown in the figure, with the increased charge of the cation, the degree of crosslinking increased and swelling capacity consequently decreased ($\text{LiCl} > \text{CaCl}_2 > \text{AlCl}_3$).

To study the effect of cation radius on swelling behaviors, the equilibrium swelling absorbency was measured in two series of 0.15M chloride salt solutions of Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} (Table I). Tako et al.²⁵ reported that the κC molecules formed intermolecular cation bridges between the sulfate group of an adjacent anhydro-D-galactose residue with large cations, such as K^+ , Rb^+ , and Cs^+ , but not with small cations, e.g., Li^+ and Na^+ . In fact, aqueous solutions of κC with specific cations, especially K^+ , form physically crosslinked thermoreversible polyelectrolyte gels. The stronger interaction between sul-

TABLE I
Swelling and Salt-Sensitivity (f) of $\kappa\text{C-g-AMPS}$ Hydrogel in Distilled Water and Different Salt Solutions (0.15M).

Swelling medium	Swelling ratio (g/g)	f
H ₂ O	95	—
LiCl	85	0.11
NaCl	83	0.13
KCl	65	0.32
MgCl ₂	49	0.48
CaCl ₂	40	0.59
SrCl ₂	35	0.63
BaCl ₂	31	0.67

fate groups of κ C molecules and large cations have been observed by Pass et al.²⁶ using measurement of activating coefficients of various cations in several salt solutions. Thus, κ C has the highest affinity for crosslinking with K^+ among monovalent cations of the studied salt solutions. As a result, swelling of the synthesized hydrogels in KCl solution is lower than in LiCl and in NaCl solutions (swelling capacity in LiCl and NaCl solutions is almost equal, but in KCl solution a decrease in absorbency is observed). Similar results are also observed in the case of chloride solutions of Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} (Table I). However, the synthesized hydrogels in this work comprise lots of "nonionic" amide groups and "antisalt" sulfate anions. Therefore, the swelling capacity of these hydrogels in salt solutions was not significantly decreased in comparison with water absorbency values. To achieve a comparative measure of salt sensitivity of the hydrogels, we defined a dimensionless salt sensitivity factor (f) as follows:²⁷

$$f = 1 - \frac{[(\text{swelling in salt solution}) / (\text{swelling in distilled water})]}{\quad} \quad (6)$$

The f values are also given in Table I. The low values of f factor (0.11–0.67) show clearly that the synthesized hydrogels comprise low salt sensitivity. This antisalt behavior is due to the presence of many sulfate groups in κ C and AMPS parts with high ionization tendency and low salt-sensitivity characteristics. Since the sulfate ions do not keep cations in their vicinity, the "charge screening effect" is not so effective. Similar results were obtained in previous work.¹³ In addition, Lim et al.²⁸ and Barbucci et al.²⁹ achieved such conclusions in the case of synthesis of sodium starch sulfate-*g*-polyacrylonitrile superabsorbent and sulfated carboxymethylcellulose hydrogel, respectively. They attributed the enhanced absorbency to increased charge density and ionization tendency brought about by the introduction of sulfate anions. The effect of charge and radius of cations on swelling ratio, which was described earlier, can also be concluded from Table I.

Effect of pH on equilibrium swelling

In this series of experiments, swelling ratio for the synthesized hydrogels was measured in different pH solutions ranged from 1.0 to 13.0 (Figure 9). Since the swelling capacity of all "anionic" hydrogels is appreciably decreased by the addition of counter ions (cations) to the swelling medium, no buffer solutions were used. Therefore, stock NaOH (pH 10.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Maximum swelling (35 g/g) was obtained at pH 8. In

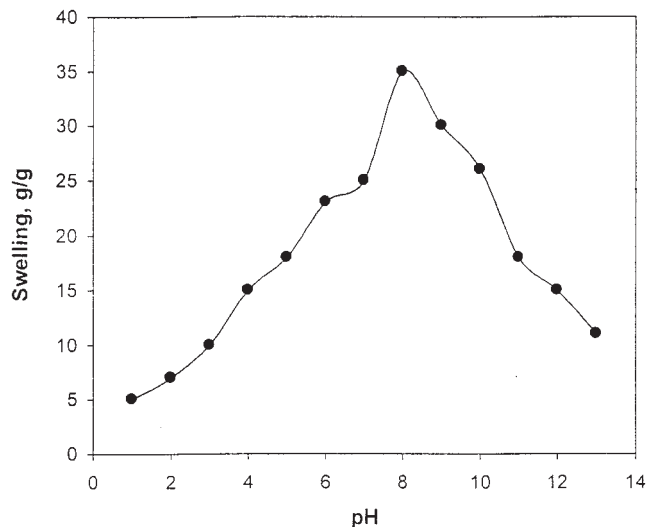


Figure 9 Effect of pH on the swelling capacity of κ C-*g*-AMPS superabsorbent hydrogel.

acidic media, most sulfonate groups are protonated, so decreased repulsion of anionic groups leads to a decreased swelling ratio. At higher pHs (5–8), some sulfonate groups are ionized and the electrostatic repulsion between COO^- groups causes an enhancement of the swelling capacity. The reason of the swelling loss for the highly basic solutions is the charge screening effect of excess Na^+ in the swelling media, which shield the sulfonate anions and prevent effective anion–anion repulsion.

pH reversibility of κ C-*g*-AMPS hydrogel

The synthesized hydrogel, κ C-*g*-AMPS, shows different swelling behaviors in acidic and basic pH solutions. Therefore, we investigated the reversible swelling–deswelling behavior of this hydrogel in solutions with pH 2.0 and 8.0 (Figure 10). At pH 8.0, the hydrogel swells up to 32 g/g due to anion–anion repulsive electrostatic forces, while, at pH 2.0, it shrinks within a few minutes due to protonation of sulfonate groups. This sharp swelling–deswelling behavior of the hydrogels makes them suitable candidates for controlled drug delivery systems. Such on–off switching behavior as reversible swelling and deswelling has been reported for other ionic hydrogels.^{30–33}

Swelling kinetics

Figure 11 represents the rate of water uptake of the hydrogel, κ C-*g*-AMPS, with a certain particle size (40–60 mesh). According to the figure, the rate of water absorbency sharply increases and then begins to level off. For preliminary study of swelling kinetics, a

“Voigt-based model” may be used for fitting the swelling data [eq. (7)].³⁴

$$S_t = S_e(1 - e^{-t/\tau}) \quad (7)$$

where S_t is the swelling at time t , S_e is the equilibrium swelling (power parameter), and τ is the rate parameter. The rate and power parameters were determined to be 21 min and 97 g/g, respectively. It means that the synthesized carrageenan-based hydrogel takes 21 min to absorb 0.63 of its equilibrium capacity of water absorbency. Since the τ value is a measure of swelling rate (i.e., the lower the τ value, the higher the rate of swelling), it can be used for comparative evaluation of the rate of water absorbency of superabsorbent polymers on the condition that the particle size of the comparison samples are the same or, at least, in the same range.

CONCLUSIONS

In the present study, κ C-g-AMPS superabsorbent hydrogel was synthesized in an aqueous solution using a persulfate initiator and a hydrophilic crosslinker. The optimum reaction conditions to obtain maximum water absorbency (135 g/g) were found to be MBA 0.056 mol/L, AMPS 0.41 mol/L, APS 0.013 mol/L, and reaction temperature 75°C. Swelling measurements in various salt solutions showed that the synthesized hydrogels are low salt sensitive due to the presence of antisalt sulfate groups in the κ C and AMPS parts of the network. However, swelling loss in salt solutions, in comparison with distilled water, can be attributed to a charge screening effect and ionic crosslinking for

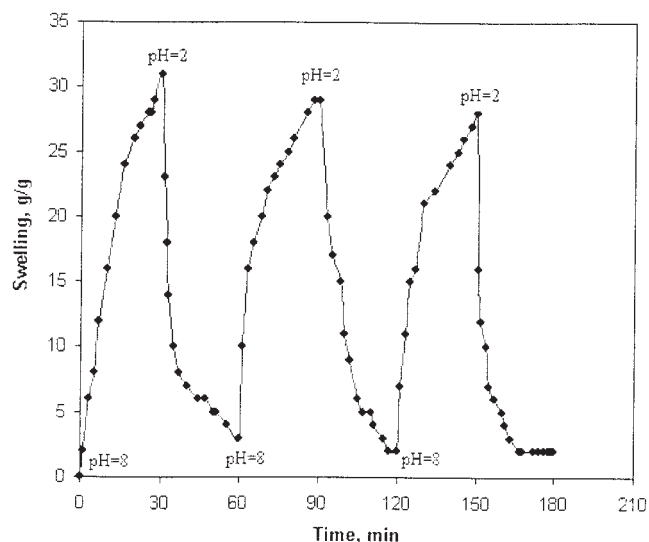


Figure 10 The pH responsiveness (on–off switching) behavior of κ C-g-AMPS superabsorbent hydrogel in solutions with pH 2.0 and 8.0.

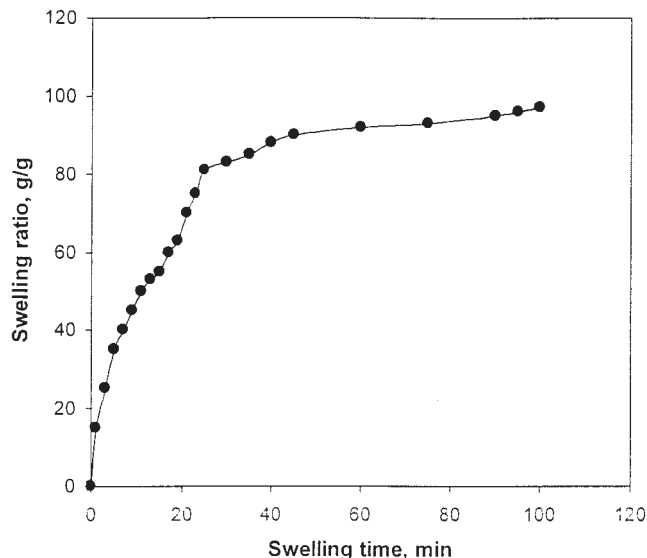


Figure 11 Swelling kinetics of κ C-g-AMPS hydrogel in water. Particle size of the dried gel was 250–350 μ m.

mono- and multivalent cations, respectively. Swelling capacity of κ C-g-AMPS hydrogel in various pH solutions (1–13) as well as swelling–deswelling behavior of the product exhibited high absorbency at basic pHs and reversible pH-responsiveness properties. Therefore, the synthesized hydrogels in this work, with antisalt and high pH sensitivity may be considered as excellent candidates for various applications, such as designing novel drug delivery systems.

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