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Modified Carrageenan. 6. Crosslinked Graft Copolymer of Methacrylic Acid and kappa-Carrageenan as a Novel Superabsorbent Hydrogel with Low Salt- and High pH-Sensitivity

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Abstract: A novel, polysaccharide-based, superabsorbent hydrogel was synthesized through crosslinking graft copolymerization of methacrylic acid (MAA) onto kappa-carrageenan (κC), using ammonium persulfate (APS) as a free radical initiator in the presence of methylenebisacrylamide (MBA) as a crosslinker. A proposed mechanism for κC-*g*-polymethacrylic acid (κC-*g*-PMAA) formation was suggested and the hydrogel structure was confirmed using FTIR spectroscopy. The effect of grafting variables, including MBA, MAA, and APS concentration, was systematically optimized to achieve a hydrogel with the maximum possible swelling capacity. The swelling kinetics in distilled water and various salt solutions were preliminarily investigated. Absorbency in aqueous salt solutions of lithium chloride, sodium chloride, potassium chloride, calcium chloride, and aluminum chloride indicated that the swelling capacity decreased with increased ionic strength of the swelling medium. This behavior can be attributed to the charge screening effect for monovalent cations, as well as ionic crosslinking for multivalent cations. The swelling of superabsorbing hydrogels was measured in solutions with pH ranging from 1 to 13. In addition, the pH reversibility and on-off switching behavior, at pH levels of 3.0 and 8.0, give the synthesized hydrogels great potential as an excellent candidate for the controlled delivery of bioactive agents.

Keywords: carrageenan, methacrylic acid, hydrogels, graft copolymers, swelling.

Introduction

Synthesis and characterization of superabsorbent hydrogels is the main goal of the several research groups in the world.[1-4] These materials are defined as hydrophilic, three-dimensional networks with ability to absorb large values of water, saline solution, or physiological fluids.[5] The absorbed fluids are hardly removable even under some pressure. They are widely used in various applications such as hygienics, foods, cosmetics, and agriculture.[6-8] This accounts for increase in the worldwide production of superabsorbent polymers (SAPs) from 6,000 tons in 1983 to 450,000 tons in 1996.[5] Nowadays, the worldwide production of SAPs is more than one million tons in year. Hence, synthesis and investigation of specific and new superabsorbent hydrogels with high absorbency, mechanical strength and initial absorption rate, is important.

SAPs responding to external stimuli such as heat, pH, electric field, chemical environments, etc, are often referred to as "intelligent" or "smart" polymers. Among these, pH-sensitive hydrogels have been extensively investigated for potential use in site-specific delivery of drugs to specific regions of the gastrointestinal tract and have been prepared for delivery of low molecular weight protein drugs. Therefore, these hydrogels have important applications in the field of medicine, pharmacy, and biotechnology.[9,10]

Natural-based superabsorbent hydrogels have attracted much interest from the viewpoint of improving the tissue tolerance of synthetic polymers and the mechanical properties of natural polymers. The presence of the natural parts guarantees biodegradability of the superabsorbing materials. Because of their biocompatibility, biodegradability and non-toxicity, polysaccharides are the main part of these biopolymers. One of the best methods for the synthesis of these superabsorbent hydrogels is graft copolymerization of vinylic monomers onto polysaccharides. Monomers such as acrylonitrile (AN), acrylic acid (AA), acrylamide (AAm) have been graft copolymerized onto polysaccharides such as starch, cellulose and their derivatives.[11-15] The first industrial superabsorbent hydrogel was synthesized using this method via ceric-induced graft copolymerization of acrylonitrile onto starch followed by alkaline hydrolysis of the

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resulted graft copolymer.[16]

Carrageenans are relatively new polysaccharides to synthesize of natural-based SAPs. These linear sulfated polysaccharides that are obtained from certain species of red seaweeds are composed of D-galactose and 3,6-anhydrogalactose units.[17] 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 (κC), is framed in Scheme I.

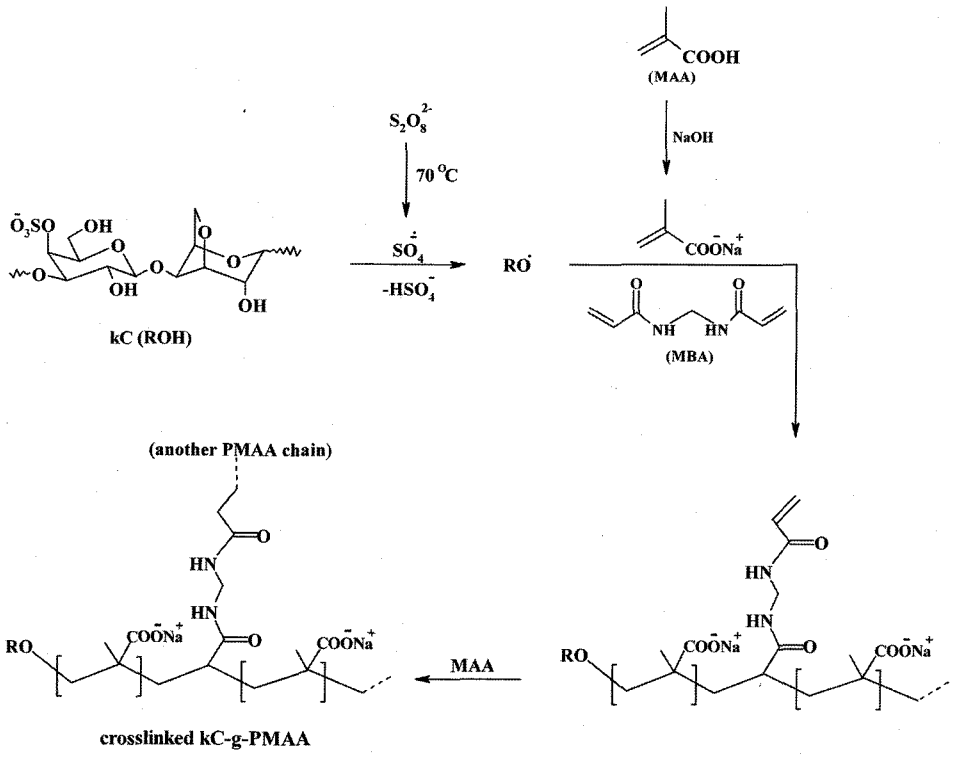
Following a continuous research on modification of carrageenans,[18-22] in this paper, we report synthesis, characterization and swelling behavior of a smart superabsorbing hydrogel, i.e. κC-*g*-PMAA. The presence of hydrophilic sulfate groups with high ionization tendency and less sensitivity to salt solution as well as biodegradability of κC backbones was our main idea for synthesis of carrageenan-based superabsorbent hydrogels. Optimization of the grafting variables affecting on the swelling capacity as well as the salt- and pH-sensitivity of the hydrogels were investigated in detail.

Experimental

Materials. Kappa-carrageenan (κC, from Condinson Co., Denmark), *N*,*N*′-methylene bisacrylamide (MBA, from Fluka), ammonium persulfate (APS, from Fluka), methacrylic acid (MAA, from Merck) 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, κC-*g*-PMAA, was carried out using APS as an initiator and MBA as a crosslinker in an aqueous medium. A general procedure for crosslinking graft copolymerization of MAA onto κC was conducted as follows. κC (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 35 mL deoxygenated doubly distilled water. The reactor was immersed in a thermostated water bath preset at desired temperature (70 °C). After complete dissolution of κC to form a homogeneous solution, certain amounts of completely neutralized MAA (0.5-2.5 g in 5 mL H_2O) and MBA (0.05-1.0 g in 5 mL H_2O) were simultaneously added to the reaction mixture. After stirring for 15 min, the initiator solution (0.02-0.40 g APS in 5 mL H_2O) were added to the mixture. After 60 min, the reaction product was allowed to cool to ambient temperature and was poured to excess non-solvent methanol (200 mL) and remained for 3 h to dewater. Then methanol was decanted and the product scissored to small pieces (diameter ~ 5 mm). Again, 200 mL fresh methanol was added and the hydrogel was remained for 24 h. Finally, the filtered hydrogel is dried in oven at 50 °C for 10 h. After grinding, the powdered superabsorbent hydrogel 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) with average



Scheme I. Proposed mechanistic pathway for synthesis of κC-*g*-PMAA hydrogel.

particle sizes between 40–60 mesh (250-350 μm) was immersed entirely in distilled water (200 mL) or desired salt solution (100 mL) and allowed to soak for 3 h at room temperature. The tea bag was hung up for 15 min in order to remove the excess fluid. The equilibrated swelling (ES) was measured twice using the following equation:

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

The accuracy of the measurements was ±3%.

Absorbency at Various pHs. Individual solutions with acidic and basic pHs were prepared by dilution of NaOH (pH 13.0) and HCl (pH 1.0) solutions (0.1 M) to achieve pH ≥ 6.0 and pH < 6.0, respectively. The pH values were precisely checked by a pH-meter (Metrohm/620, accuracy ±0.1). Then, 0.5 ± 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 3.0) 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 absorbency rate of the hydrogels, certain amount of samples (0.5 ± 0.001 g) was poured into numbers of weighed tea bags and immersed in distilled water (200 mL) or salt solution (100 mL). At consecutive time intervals, the equilibrium swelling capacity 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.

Optimization of the Grafting Variables. In this work, the main factors affecting on the grafting conditions (i.e. concentration of MBA, MAA, and APS) as well as the swelling behavior of the resulted pH-responsive and low salt-sensitive superabsorbent hydrogels were investigated.

Effect of MBA Concentration. The swelling ratio as a function of MBA concentration, for crosslinked κC-*g*-PMAA was investigated (Figure 1). As shown in Figure 1, the absorbency is decreased with increasing the MBA concentration. Maximum swelling (180 g/g) was obtained at 0.006 mol/L of crosslinker concentration. The hydrogels prepared with MBA concentration lower than 0.006 mol/L do not posses good dimensional stability, therefore the swollen gel strength is not sufficient to refer the hydrogels as real "superabsorbents". It is a well-known rule in all of hydrogels that a small increase in degree of crosslinking causes an appreciable decrease in swelling capacity.[6] In fact, more crosslinking concentration causes to the higher crosslinking density and decreases the space between the copolymer chains and consequently, the resulted highly crosslinked rigid

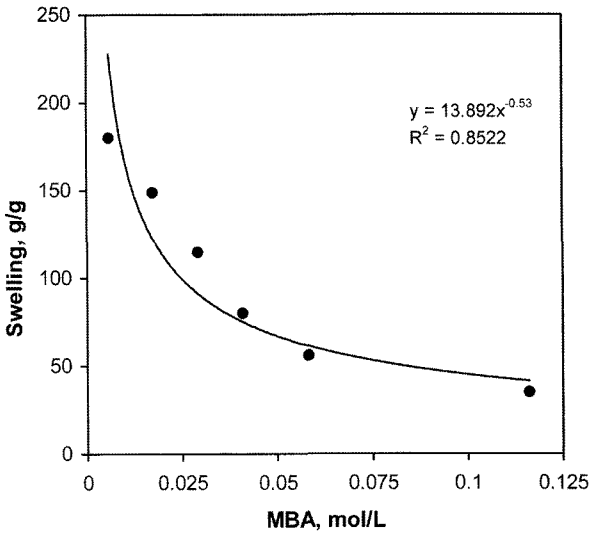


Figure 1. Effect of crosslinker concentration on swelling capacity. Reaction conditions: κC 1.0 g, MAA 0.31 mol/L, APS 0.03 mol/L, H_2O 50 mL, 70 °C, 60 min.

structure cannot be expanded and hold a large quantity of water. Such a well-known behavior reported by pioneering scientists.[6,10,23] This power law behavior between equilibrium swelling and MBA concentration (Eq. (2)) was conducted from Figure 1.

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

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=13.89 and n=0.53 is obtained from the curve fitted with eq. (2).

Effect of MAA Concentration. Figure 2 demonstrates the effect of the monomer concentration on swelling capacity of κC-*g*-PMAA product. The absorbency is increased versus increasing the MAA concentration from 0.12 to 0.47 mol/L and then, it is decreased with a further increase for MAA. The maximum absorbency (201 g/g) is obtained at 0.47 mol/L of the monomer, MAA. The initial increase in swelling values can be attributed to the higher the hydrophilicity of the hydrogel and the greater availability of MAA molecules near the κC macroradicals. 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 molecules. Other investigators[24-26] reported similar conclusions.

To obtain an additional evidence of grafting (or swelling) dependency to the monomer concentration, the percentage of grafting efficiency (%*Ge*) was evaluated with the following

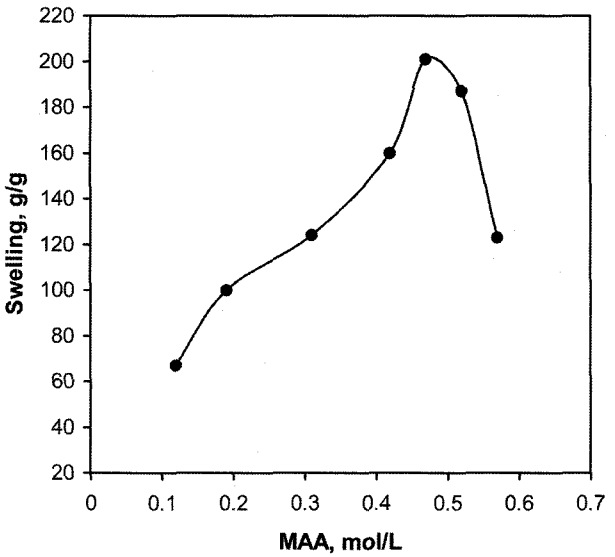


Figure 2. Effect of monomer concentration on swelling capacity. Reaction conditions: κC 1.0 g, MBA 0.006 mol/L, APS 0.03 mol/L, H_2O 50 mL, 70 °C, 60 min.

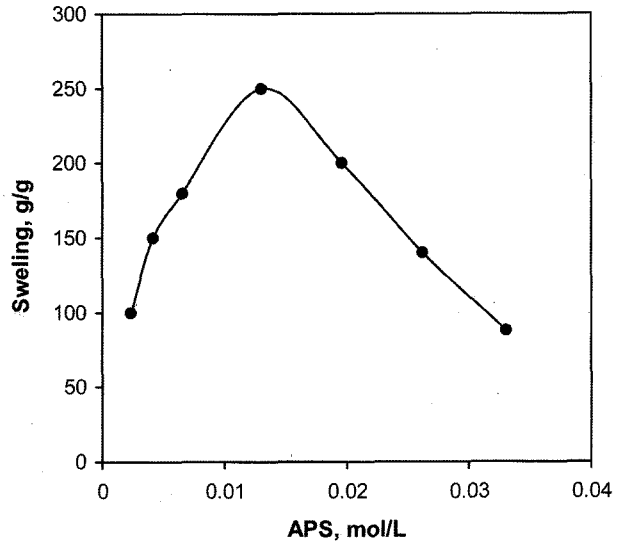


Figure 3. Effect of initiator concentration on swelling capacity. Reaction conditions: κC 1.0 g, MBA 0.006 mol/L, MAA 0.47 mol/L, H_2O 50 mL, 70 °C, 60 min.

weight-basis equation as reported by Fanta:[27]

$$\%Ge = \frac{\text{PMAA Grafted}}{\text{Monomer Charged}} \times 100 \quad (2)$$

The *%Ge* stands for the grafted PMAA formed from initial monomer charged. The *%Ge* parameter was found to be increased (78-85%) by enhancement of methacrylic acid concentration from 0.12 to 0.47 mol/L and then, it is decreased.

Effect of APS Concentration. The effect of initiator content on swelling capacity of crosslinked κC-*g*-PMAA was studied by varying the APS concentration from 0.002 to 0.033 mol/L (Figure 3). As shown in the Figure, swelling capacity is increased with increasing the APS concentration from 0.002 to 0.013 mol/L and then it is considerably decreased with a further increase in the concentration of APS. By increasing the APS concentration up to 0.013 mol/L, the number of active free radicals on the κC backbone is increased which, in turn, resulting in higher graft polymerization extent and consequently higher final water absorbency. The APS concentrations higher than the optimum value, however, lead to low-swelling superabsorbents. This swelling-loss may be attributed to an increase in terminating step reaction via bimolecular collision, which, in turn, causes to enhance crosslinking density. Chen and Zhao[28] refer to this possible phenomenon as "self-crosslinking". In addition, decrease in molecular weight (MW) of grafted PMAA of the hydrogel causes to decrease swelling value. The latter reason is due to the inverse relationship between MW and initiator concentration.[29] Moreover, the free radical degradation of κC backbones by sulfate radical-anions is an additional reason for swelling-loss at higher APS concentration. The proposed mechanism for this possibility is reported in the previous work.[21] Hsu *et al.* recently report a similar observation in the case of degradation of chitosan with potassium persulfate.[30]

Results and Discussion

Mechanism of Hydrogel Formation. A general reaction mechanism for crosslinking graft copolymerization of MAA onto κC backbones in the presence of APS and MBA is shown in Scheme I. The sulfate anion-radical produced from thermally decomposition of APS, abstracts hydrogen from the hydroxyl groups of the κC to form corresponding alkoxy radicals on the substrates. Then the resulted macroradicals radically initiate graft copolymerization of completely neutralized MAA led to a graft copolymer so called κC-*g*-PMAA. Since a crosslinking agent, i.e., MBA, is presented in the reaction mixture, the crosslinked κC-*g*-PMAA network is resulted.

Spectral Characterization. For identification of the hydrogel, infrared spectroscopy was used. Figure 4 shows the IR spectroscopy of κC and κC-*g*-PMAA hydrogel. The bands observed at 841, 918, 1021, and 1222 cm^{-1} can be attributed to D-galactose-4-sulfate, 3,6-anhydro-D-galactose, glycosidic linkage and ester sulfate stretching of κC, respectively (Figure 4(a)). The broad band at 3100-3600 cm^{-1} is due to stretching of –OH groups of κC. The IR spectrum of the hydrogel, κC-*g*-PMAA (Figure 4(b)) shows three new characteristic absorption bands at 1707, 1542, and 1402 cm^{-1} verifying the formation of graft copolymer product. These peaks attributed to carbonyl stretching of the carboxylic acid groups and symmetric and asymmetric stretching modes

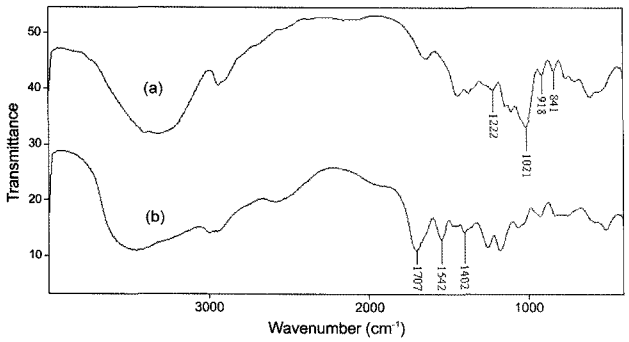


Figure 4. FTIR spectra of κC (a) and κC-*g*-PMAA (b).

of carboxylate anions, respectively.[31] Combination of absorption of the carboxylate and alcoholic O–H stretching bands is appeared in the wide range of 2550-3600 cm^{-1}.

To obtain an additional evidence of grafting, a similar graft copolymerization reaction was conducted in absence of the crosslinker. The resulted product was precipated by pouring the reaction mixture solution into 250 mL of ethanol, and the precipitate was filtered and repeatedly washed with ethanol. Then, 0.5 g of the dried product was poured product in 50 mL of dimethyl formamide solution (a suitable solvent for homopolymer). The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymer, the κC-*g*-PMAA was filtered, washed with ethanol and dried in oven at 50 °C to reach a constant weight. After extracting the homopolymer (PMAA), appreciable amount of synthetic polymer percentage of the graft copolymer (83%) were concluded. Since the FTIR spectrum of the homopolymer and graft copolymer is similar, the homopolymer-free graft copolymer spectrum was compared with that of the hydrogel. The graft copolymer spectrum was very similar to Figure 4(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 MAA are involved in the polymer network. Therefore, the monomer percent in the network will be very similar to that of the initial feed of reaction.

Swelling Kinetics. The rate of absorbency for κC-*g*-PMAA superabsorbent hydrogel was measured in distilled water and in 0.15 molar salt solutions of LiCl, NaCl, KCl, $CaCl_2$, and $AlCl_3$ at room temperature. According to Figure 5, the swelling values versus swelling time follow a power low trend. A "Voigt-based" model may be used for fitting the data.[32]

$$S_t = S_e(1 - e^{-t/\tau}) \quad (4)$$

where S_t is the swelling at time t, S_e is the equilibrium swelling (power parameter) and τ (min) is the "rate parameter". The power parameter (equilibrium swelling capacity) according to Figure 5 is 192 g/g for distilled water. The τ value is a measure of swelling rate (i.e. the lower the τ value, the higher the rate of swelling). Therefore, it can be used for comparative evaluating the rate of absorbency of superabsorbents that the particle size of the comparing samples are the same or, at least, in the same range. It is well known that the swelling kinetics for the superabsorbent polymers is significantly influenced by particle size of the absorbents.[33] The size of the dried hydrogel particles used in our experiment was 250-350 μm. For calculate the rate parameter, by using the above formula and a little rearrangement, one can be plot $\ln(1 - S_t/S_e)$ versus time (t). The slope of the straight line fitted (slope=$-1/\tau$) gives the rate parameter. For example, in the case of distilled water the τ value is 21 min. It means that the κC-*g*-PMAA hydrogel take 21 min to absorb 0.63 of its equilibrium capacity of swelling. The rate parameters for the κC-*g*-PMAA hydrogel in distilled water and LiCl, NaCl, KCl, $CaCl_2$, and $AlCl_3$ salt solutions are found to be 21, 4, 5, 7, 8, and 3 min, respectively. According to the smaller τ value, the swelling in $AlCl_3$ is faster than in other solutions.

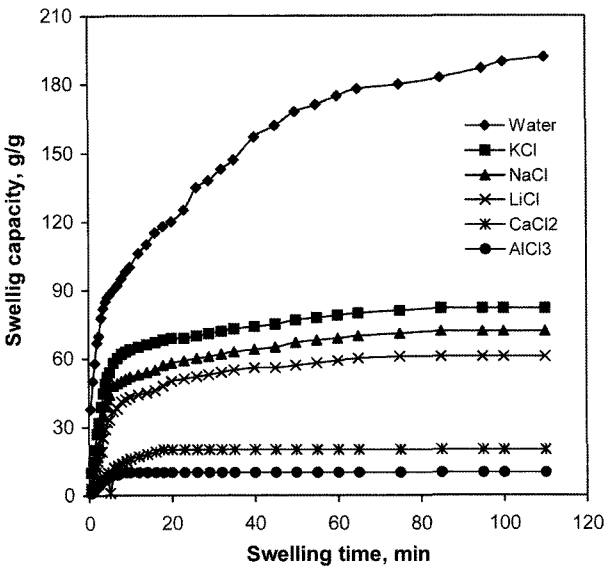


Figure 5. Representative swelling kinetics of the hydrogel, κC-*g*-PMAA, in distilled water and various chloride salt solutions (0.15 M). Particle size of the dried gel was 250-350 μm.

According to Figure 5, the swelling capacities of κC-*g*-PMAA in salt solutions are decreased comparing with the value measured in distilled water (192 g/g). Generally, swelling values for all "anionic" hydrogels in saline media are expectedly decreased.[23] This undesired swelling-loss has been attributed to the "charge screening effect" of the cations led to the reduction of osmotic pressure, the driving force for swelling, between the gel and the aqueous phases. An additional reason is increasing electrostatic attraction between anionic sites of chains and multi-valent cations (Ca^{2+} and Al^{3+}) leading to increased "ionic crosslinking" degree and consequently loss of swelling. The effect of charge of cation

on swelling can be concluded from Figure 5. As shown in the Figure, the absorbency of κC-*g*-PMAA hydrogel in the studied salt solutions is in the order of monovalent > divalent > trivalent cations. With increasing the charge of cation, degree of crosslinking is increased and swelling is consequently decreased. The effect of cation radius on swelling, may also been observed from Figure 5. As reported by Tako *et al.*,[34] 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^+. Thus, κC has the strongest affinity for crosslinking with K^+ among monovalent cations of the studied salt solutions. In the case of our synthesized hydrogel, however, the swelling capacity is in the order of KCl > NaCl > LiCl. The reason is related to the large numbers of carboxylate anions newly added to the structure. The carboxylate anion interacts with small cations (e.g. Li^+) stronger than with large cations, e.g. K^+. The stronger interactions of sulfate-large cation and carboxylate-small cation have been observed by Pass *et al.* using measurement of activating coefficients of various cations in several salt solutions.[35] However, swelling capacity of κC-*g*-PMAA hydrogel in LiCl, NaCl, and KCl is yet considerable. The reason for this anti-salt behavior can be explained as follows: the network, κC-*g*-PMAA, contains κC backbones with sulfate and carboxylate functional groups. The sulfate groups can be dissociated in aqueous media more readily than the carboxylate groups of the synthetic part of κC-*g*-PMAA (in this regard, pK_a of methane sulfonic acid, -2.0, may be compared with that of acetic acid, 4.8). Therefore, the sulfate ions do not keep cations in their vicinity, the charge screening effect is not so effective. In order to verify the major role of sulfate groups of the carrageenan parts of the superabsorbents, the swelling capacity was also calculated in various salt solutions for the full-polysaccharide hydrogel network, i.e. MBA-crosslinked κC without PMAA part, which were prepared under same conditions. Results are summarized in Table I. As shown in the table, the swelling-loss for MBA-crosslinked carrageenan in salt solutions is not appreciable comparing with the value measured in distilled water. Therefore, the reason for high water and saline absorbency in our carrageenan-based hydrogels certainly a result of the presence of sulfate groups in its carrageenan parts. Similar results were obtained in previous work.[20] In addition, Lim *et al.*[36] and Barbucci *et al.*[37] 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.

Table I. Swelling Capacity in Distilled Water and Saline Solutions (0.15 M) for κC-*g*-PMAA and MBA-crosslinked Carrageenan Hydrogels. The Equilibrium Swelling (ES) Capacity was Measured Twice at Room Temperature

Swelling Medium	Crosslinked κC-*g*-PMAA	Crosslinked Carrageenan
	ES (g/g)	ES (g/g)
H_2O	237	29
NaCl	55	24
$CaCl_2$	15	19
$AlCl_3$	6	13

Equilibrium Swelling at Various pH Solutions. Ionic superabsorbent hydrogels exhibit swelling changes at a wide range of pHs. Therefore, in this series of experiments, equilibrium swelling for the synthesized hydrogels was measured in different pH solutions ranged from 1.0 to 13.0 (Figure 6). Since the swelling capacity of all "anionic" hydrogels is appreciably decreased by addition of counter ions (cations) to the swelling medium, no buffer solutions were used. Therefore, stock NaOH (pH 13.0) and HCl (1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively. Maximum swelling (95 g/g) was obtained at pH 8. Under acidic pHs (≤ 4), most of the carboxylate anions are protonated, so the main anion-anion repulsive forces are eliminated and consequently swelling values are decreased. However, some sort of attractive interactions (H-O hydrogen bonding) lead to decreased absorbencies. At higher pHs (5-8), some of carboxylate 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 (pH>8) is "charge screening effect" of excess Na^+ in the swelling media, which shields the solfunate and carboxylate anions and prevents effective anion-anion repulsion. Similar

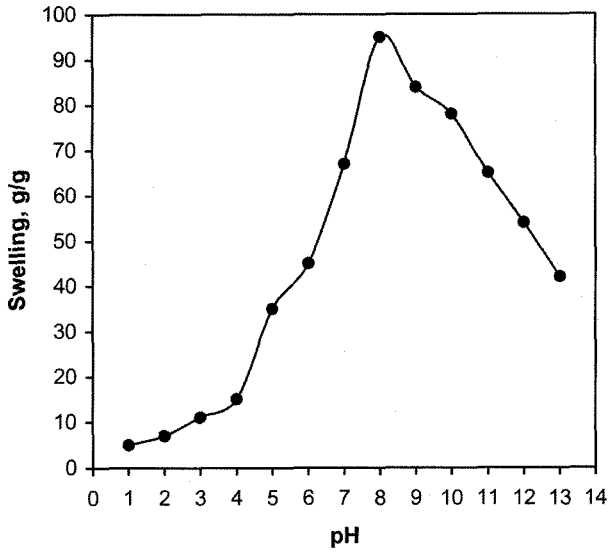


Figure 6. Effect of pH of solution on swelling of κC-*g*-PMAA superabsorbent hydrogel.

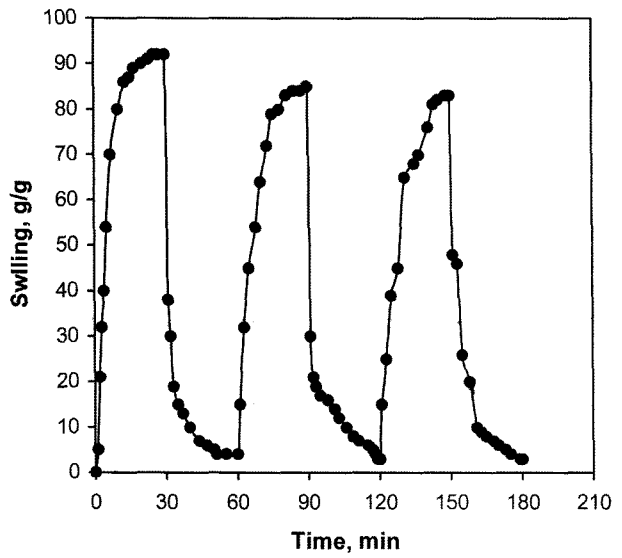


Figure 7. On-off switching behavior as reversible pulsatile swelling (pH 8.0) and deswelling (pH 3.0) of the κC-g-PMAA hydrogel. The time interval between the pH changes was 30 min.

swelling-pH dependencies have been reported in the case of other hydrogel systems.[38-41]

pH-Responsiveness Behavior of κC-*g*-PMAA Hydrogel. Since the synthesized hydrogel, κC-*g*-PMAA, shows different swelling behaviors in acidic and basic pH solutions, we investigated the reversible swelling-deswelling behavior of this hydrogel in solutions with pH 3.0 and 8.0 (Figure 7). At pH 8.0, the hydrogel swells due to anion-anion repulsive electrostatic forces, while at pH 3.0, it shrinks within a few minutes due to protonation of the solfunate and carboxylate anions. This swelling-deswelling behavior of the hydrogels makes them as suitable candidate for designing drug delivery systems. Such on-off switching behavior as reversible swelling and deswelling has been reported for other ionic hydrogels.[42-45]

Conclusions

The superabsorbent hydrogel, κC-g-PMAA, was synthesized by graft copolymerization of methacrylic acid onto kappa-carrageenan, in a homogeneous medium. The maximum water absorbency (250 g/g) was achieved under the optimum conditions that found to be MAA 0.47 mol/L, MBA 0.006 mol/L, and APS 0.013 mol/L. Swelling capacity of κC-g-PMAA hydrogel in various salt solutions, especially in LiCl, NaCl, and KCl solutions is appreciable. This behavior is may be due to anti-salt characteristics of the carrageenan part sulfate groups of the superabsorbing networks. However, swelling-loss in salt solutions, in comparison with distilled water, can be attributed to charge screening effect and ionic crosslinking for mono- and multi-valent cations, respectively. In addition, the swelling of hydrogels exhibited high sensitivity to pH, so that the pH reversibility and on-off switching behavior makes the intelligent hydrogel as a good candidate for considering as potential carriers for bioactive agents, e.g. drugs.

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