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Synthesis, Swelling Behavior, Salt- and Ph- Sensitivity of Cross Linked Carrageenan-Graft-Poly (Acrylamide-Co-Itaconic Acid) Superabsorbent Hydrogel

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Abstract: The polysaccharide, kappa-carrageenan (κC) was chemically modified to achieve a novel superabsorbent hydrogel via graft copolymerization of acrylamide (AAm) and itaconic acid (IA) onto the substrate followed by alkaline hydrolysis. Ammonium persulfate (APS) and N,N'-methylene bisacrylamide (MBA) were used as a free-radical initiator and a crosslinker, respectively. A mechanism for the superabsorbent hydrogel formation was also suggested. Hydrogel formation was confirmed by FTIR spectroscopy. Results from scanning electron microscopy (SEM) observation also showed a porous structure with smooth surface morphology of the hydrogel. The effect of grafting variables (i.e. concentration of MBA, AAm,IA and APS) and were systematically optimized to achieve a hydrogel with swelling capacity as high as possible. Absorbency of superabsorbing hydrogels was examined in buffer solutions with pH ranged 1-13.

Key words: Kappa-Carrageenan · Hydrogel · Ph-Sensitive · Acrylamide · Itaconic Acid

INTRODUCTION

Highly swelling polymers, i.e. superabsorbent hydrogels, are hydrophilic, three dimensional networks that can absorb water in the amount from 10% up to thousands of times their dry weight [1]. They are widely used in various applications such as hygienics, foods, cosmetics and agriculture [2-4]. This accounts for increase in the worldwide production of superabsorbent polymers (SAPs) from 6000 tons in 1983 to 450000 tons in 1996 [1]. Nowadays, the worldwide production of SAPs is more than one million tons in year. Hence, synthesis and characterization of superabsorbent hydrogels is the main goal of the several research groups in the world [5-8].

The properties of the swelling medium (e.g. pH, ionic strength and the counter ion and its valency) affect the swelling characteristics [2-9]. The hydrogels sharply and reproducibly responding to the medium conditions are referred as to "responsive", "smart" or "intelligent". 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 [10, 11]. Although hydrogels made from synthetic polymers, such as polyacrylate, posses excellent water-absorbing properties, their toxicity and non-biodegradability might pose long-time environmental problems and limit their use in drug delivery systems and consumer products. Natural-based SAPs polymers have attracted much attention in medical and pharmaceutical interests because of their non-toxicity, biocompatibility and biodegradability.

Carrageenans are relatively new polysaccharides to synthesize of natural-based superabsorbent polymers. These biopolymers are linear sulfate polysaccharides that are obtained from certain species of red seaweeds [10]. 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. In addition, the presence of the natural parts guarantees biocompatibility, biodegradability and non-toxicity of the superabsorbing materials. Therefore, following a continuous research on modification of kappa-carrageenan, κC, the most well-known type of carrageenan family that its structure is framed in Scheme 1 [11-14], in this paper, we report synthesis and swelling behavior of a novel superabsorbing hydrogel from κC-g-poly (acrylamide-co-itaconic acid). Effect of the grafting and the subsequent reaction variables on the swelling properties as well as the pH-sensitivity of the hydrogels were investigated in detail.

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MATERIAL AND MATHODS

Experimental: The polysaccharide, kappa-carrageenan (κC, from Condinson Co., Denmark); N,N'-methylene bisacrylamide (MBA, from Fluka), acrylamide (AAm, from Merck), were of analytical grade and were used as received. Itaconic acid (IA, Merck) and ammonium persulfate (APS, Merck) was used without purification.

Graft Copolymerization: The graft copolymerization reactions were carried out using APS as an initiator and MBA as a crosslinker in an aqueous solution. A general procedure was conducted as follows. κC (1.00 g) was dissolved in 50 mL degassed distillated water in a three-neck reactor equipped with mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 600 rpm). The reactor was placed in a water bath preset at 80°C. After complete dissolution of the polysaccharide to form a homogeneous solution, a definite amount of APS solution (0.10-0.66 g in 5 mL H_2O) was added into the mixture and was allowed to stir for 15 min. Then certain amounts of AAm (0.40-3.50 g in 5 mL H_2O) and AI (0.40-3.50 g in 5 mL H_2O) and MBA (0.04-0.20 g in 5 mL $H\,O)_2$ were simultaneously added to the reaction mixture. After 60 min, the reaction product was allowed to cool to ambient temperature. The obtained hydrogel was then poured into methanol (500 ml). After complete dewatering for 24 h, the hardened gel particles product were filtered, washed with fresh methanol (2 × 50 mL) and dried at 50°C. 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 particle sizes between 40–60 mesh (250-350μm) was immersed entirely in distilled water (200 mL), desired salt solution (100 mL), or buffer solution (100 mL) and allowed to soak for 3 h at room temperature. The buffer solutions were composed hydrochloric acid and potassium chloride (for acidic pHs), potassium dihydrogen phosphate and di-sodium hydrogen phosphate (for pH 7.0) and borate, boric acid, hydrochloric acid and sodium hydroxide (for basic pHs). The tea bag was hung up for 15 min in order to remove the excess solution. The equilibrated swelling (ES) was measured twice using the following equation:

$$ES(g/g) = \frac{W_2 - W_1}{W_1} \qquad (1)$$

Where W_1 and W_2 are the weights of dry and swollen gel, respectively. The accuracy of the measurements was ±3%.

pH-Sensitivity: pH-sensitivity of the hydrogel was investigated in terms of swelling and deswelling of the final product at two buffered solutions (pHs 3.0 and 8.0). Swelling capacity of the hydrogels at each pH was measured according to Eq. 1 at consecutive time intervals (30 min).

Instrumental Analysis: Fourier transform infrared (FTIR) spectra of samples were taken in KBr pellets, using an ABB Bomem MB-100 FTIR spectrophotometer (Quebec, Canada), at room temperature. The surface morphology of the gel was examined using scanning electron microscopy (SEM). After Soxhlet extraction with methanol for 24 h and drying in an oven, superabsorbent powder was coated with a thin layer of gold and imaged in a SEM instrument (Leo, 1455 VP).

RESULTS AND DISCUSSION

Synthesis and Spectral Characterization: Figure 1 shows a simple mechanism for crosslinking graft copolymerization of Aam and AI onto κC backbones and alkaline hydrolysis of the resulted graft copolymer. At the first step, the thermally dissociating initiator, i.e. APS, is decomposed under heating (80°C) to produce sulfate anion-radical. Then the anion-radical abstracts hydrogen from the hydroxyl group of the κC substrate to form corresponding alkoxy radicals. So, these macroradicals initiate AAm-AI grafting onto κC backbones led to a graft copolymer so called κC-g-PAAm-co-AI. In addition, crosslinking reaction was occurred in the presence of a crosslinker, i.e., MBA.

FTIR Spectroscopy: Infrared spectroscopy was carried out to confirm the chemical structure of the hydrogel. Figure 2 shows the FTIR spectra of κC, H-κC-g-PAAm and H-κCg-PAAm-co-AI. The bands observed at 842, 913, 1016, 1222 and 3200-3400 cm^{-1} can be attributed to D-galactose-4-sulfate, 3,6-anhydro-D-galactose, glycosidic linkage, ester sulfate stretching and stretching of –OH groups of non-modified κC, respectively (Fig. 2a). The hydrogel, H-κC-g-PAAm, comprise a κC backbone with side chains that carry carboxamide functional groups that are evidenced by a new peak at 1660 cm^{-1} (Fig. 2b). This peak attributed to C=O stretching in carboxamide functional groups of PAAm or MBA. The stretching band of –NH overlapped with the -OH stretching band of the κC portion of the copolymer. After addition co-monomer (itaconic acid), the new absorption modes at 1459 and 1557 cm^{-1} can be attributed to symmetric and asymmetric stretching modes of carboxylate groups, respectively (Fig. 2c) [15].

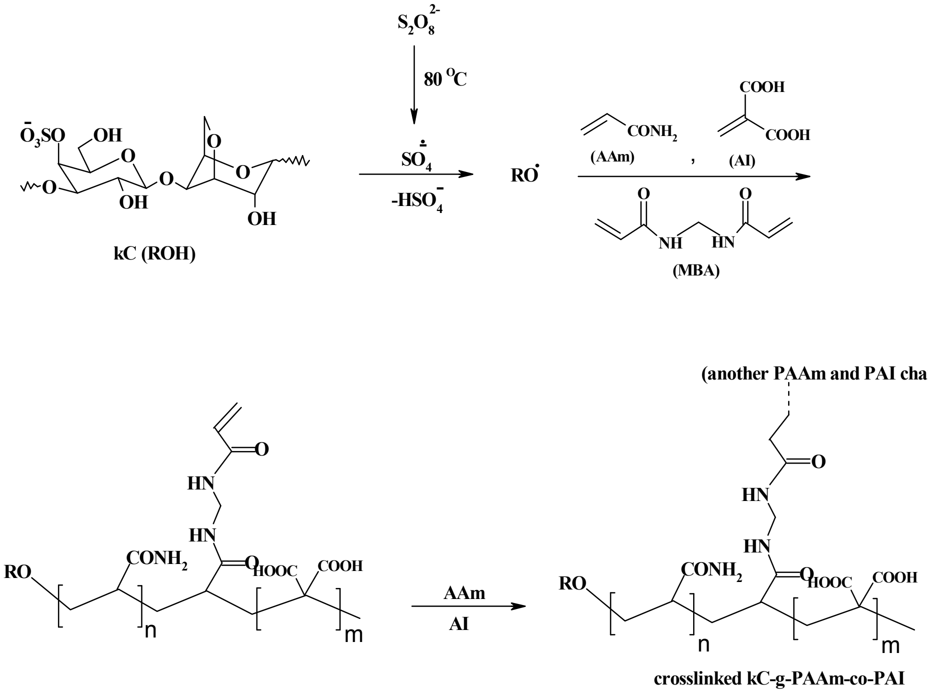

Fig. 1: Proposed mechanistic pathway for synthesis of κC-based hydrogels Transmittance/Wavenumber(cm^{-1})

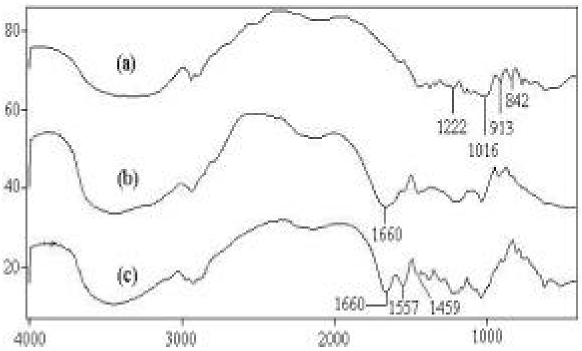

Fig. 2: (a,b&c) FTIR spectra of κC (a),H- κC-g-PAM (b) and H-κC-g-PAM-co-PAI (c).

To obtain an additional evidence of grafting, a similar graft copolymerization reaction was conducted in absence of the crosslinker. After extracting the copolymer (PAAm-co-AI), appreciable amount of synthetic polymer percentage of the graft copolymer (88%) were concluded. The graft copolymer spectrum was very similar to Fig. 2c. 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 AAm and AI monomers are involved in the polymer network. So, the monomers percent in the network will be very similar to that of the initial feed of reaction.

Scanning Electron Microscopy: One of the most important properties that must be considered is hydrogel microstructure morphologies. The surface morphology of the samples was investigated by scanning electron microscopy. Figure 3c shows an SEM micrograph of the polymeric hydrogels (H-κCg-PAAm-co-AI) obtained from the fracture surface. The hydrogel has a porous structure. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

Optimization of the Grafting Conditions: In this work, optimization of the grafting conditions (i.e. concentration of κC, MBA, AAm,AI and APS and bath temperature reaction) as well as the swelling behavior of the resulted pH-responsive superabsorbent hydrogels were investigated.

Effect of MBA Concentration: Figure 4 demonstrates the effect of the crosslinker concentration on swelling capacity of H-Kc-g-PAAm-co-AI product. According to this figure, the absorbency is decreased with increasing the MBA concentration. 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 [2]. In fact, more crosslinking concentration causes to the higher crosslinking density and decreases the space

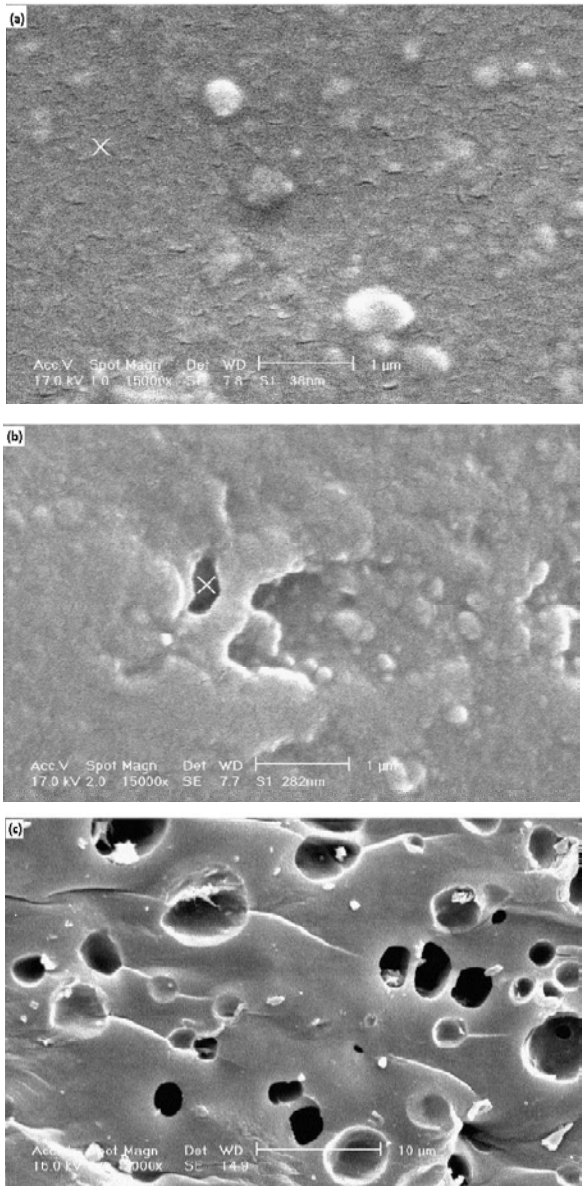

Fig. 3: (a,b&c). SEM photograph of the kappa-carrageenan (a) and H-κC-g-PAAm hydrogel (b) and H-κC-g-PAAm-co-PAI hydrogel Surfaces with scale bar 10 µm(c).

between the copolymer chains and consequently, the resulted highly crosslinked rigid structure can not be expanded and hold a large quantity of water. Such well-known behavior was reported by pioneering scientists [2, 9, 16]. Figure 4 exhibits a power law behavior of swelling-[MBA], with K=0.719 and n=11.65 which is obtained from the curve fitted with Eq. 2.

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

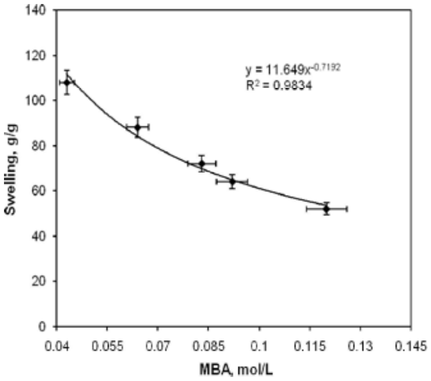

Fig. 4: Swelling dependency of H-κC-g-Poly(AAm-co-AI) hydrogel on crosslinker concentration. Grafting conditions: κC 1.5 g, AAm 0.5 mol/L, AI 1.2 mol/L, APS 0.025 mol/L, 80°C, 1h.

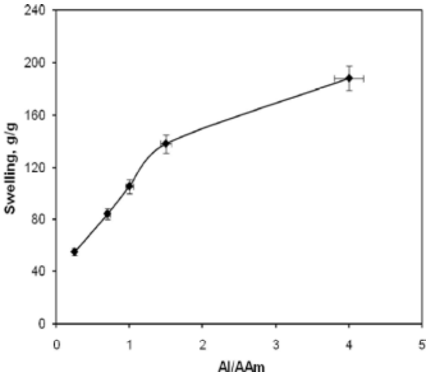

Fig. 5: Swelling dependency of H-κC-g-PMAM hydrogel as a function of monomers concentration.Grafting conditions: κC 1.5 g, MBA 0.043 mol/L, APS 0.025 mol/L, 80°C, 1h.

The K and n 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.

Effect of Monomer Ratio on Swelling Capacity: The swelling capacity of the hydrogels prepared with various ratios of monomers is shown in Fig. 5. Since pH of the polymerization mixture was adjusted at 8.0 after the reaction, the superabsorbency of H-κC-g-PNaAI-PAAm hydrogel is due to both functional groups of ionic carboxylate (from neutralized AI) and ionic carboxamide (from AAm). The presence of the ionic groups in polymer chains results in increasing of swelling because the ionized groups are more strongly solvated rather than ionic groups (non-ionized) in the aqueous medium.

Higher swelling capacities are obtained from employing higher initial ratios of NaAI/AAm. Therefore, the swelling enhancement versus higher NaAI/AAm ratio can be attributed to the formation of high carboxylate groups in the synthesized samples.

Effect of APS Concentration: The influence of initiator concentration on final swelling capacity of the hydrogel has been studied by varying the APS concentration from 0.005 to 0.039 mol/L (Fig. 6). Maximum swelling (210 g/g) was obtained at 0.02 mol/L of initiator concentration. More or less than this concentration gives hydrogel with decreased swelling capacity. The number of active free radicals on the κC backbone is decreased at lower concentrations than 0.02 mol/L which, in turn, resulting in lower graft polymerization extent and consequently lower final water absorbency. Subsequent swelling loss can be explained on the basis of (a) an increase in terminating step reaction via bimolecular collision, which is referred to as 'self-crosslinking' by Chen and Zhao [20] and (b) the decrease in molecular weight (MW) of grafted PMAM of the hydrogel causes to decrease swelling value. The latter reason is due to the inverse relationship between MW and initiator concentration [21]. Also, 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 [14]. A similar oxidative degradation of chitosan chains by potassium persulfate is recently reported by Hsu *et al*. [22].

Effect of Bath Temperature on Swelling Capacity: To study the influence of reaction temperature on water absorbency, the graft copolymerization of AI and AAm onto carrageenan was carried out at six temperatures ranging from 30 to 80°C and the results are presented in Figure 7. Swelling capacity of the hydrogels is increased with increasing the temperature from 30 to 65°C and then decreased. At 65°C, maximum swelling (294 g/g) was obtained.

Corresponding increase in water absorbency up to 65°C could be attributed to the following factors: increased the number of free radicals formed on the carrageenan backbone, increased propagation of the graft copolymerization onto carrageenan, enhanced diffusion of monomers and initiator into and onto backbone structure and increased in mobility of the monomers molecules and their higher collision probability with the backbone macroradicals [18]. However, swelling capacity decreased as the bath temperature was raised beyond 65°C. This can be accounted for in terms of chain radical termination at higher temperatures [22].

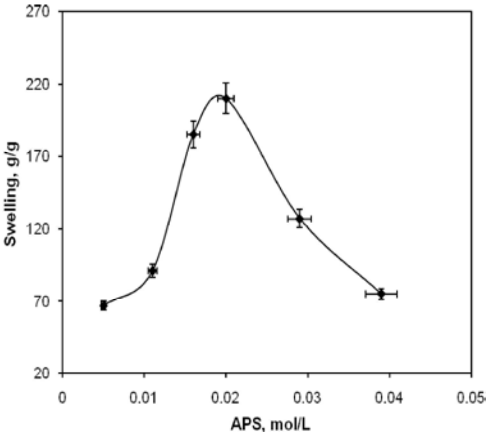

Fig. 6: Effect of initiator concentration on swelling capacity. Grafting conditions: κC 1.5 g, MBA 0.043 mol/L, AAm 0.4 mol/L, AI 1.6 mol/L, 80°C, 1h.

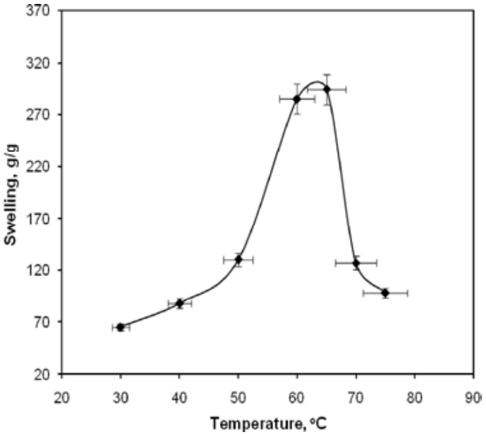

Fig. 7: Effect of hydrolysis temperature on swelling capacity of H-κC-g-PMAM superabsorbent hydrogel.Grafting conditions: κC 1.5 g, MBA 0.043 mol/L, APS 0.02 mol/L, AAm 0.4 mol/L, AI 1.6 mol/L, 1h.

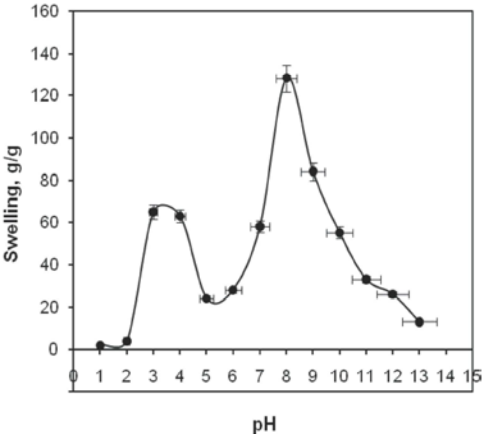

Fig. 8: Swelling dependency of H-κCg-PAAm-co-PNaAI superabsorbent on pH

Effect of Ph on Equilibrium Swelling: Figure 8 represents pH dependence of the equilibrium swelling for H-κCg-PAAm-co-PNaAI hydrogels at ambient temperature (25°C). The equilibrium swelling (ultimate absorbency) of the hydrogels were studied at various pHs ranged from 1.0 to 13.0. No additional ions (through buffer solution) were added to medium for setting pH because absorbency of a superabsorbent is strongly affected by ionic strength. In addition, it has been reported that the swelling properties of polybasic gels are influenced by buffer composition (composition and pK_a). Therefore, stock NaOH (pH 13.0) and HCl (pH 1.0) solutions were diluted with distilled water to reach desired basic and acidic pHs, respectively.

The effective pKa for kappa-carrageenan is 4.9 and that for carboxylic acid groups is ~4.6. In Figure 8, the dependence of the equilibrium swelling of the H-κCg-PAAm-co-PNaAI hydrogel is characterized by a curve with two maximum at pHs 3 and 8. The remarkable swelling changes are due to the presence of different interacting species depending on pH of the swelling medium. It can be assumed that H-κCg-PAAm-co-PNaAI hydrogel includes kappa-carrageenan, poly (itaconic acid) and poly (acrylamide) structures. The structure of kappa-carrageenan and PAI are ionizable. Therefore, based upon pK_a of PAI (~4.6) and pK_a of carrageenan (4.9), the involving species are NH_3^+ and COOH (at pHs 1-3), NH_2 and COO^- (at pHs 7-13) and NH_3^+ and COO^- or NH_2 and COOH (at pHs 4-7). Under acidic conditions, the swelling is controlled mainly by NH_2 groups on the acrylamide components. It is a weak base with an intrinsic pK_a of about 4.9, so it gets protonated and the increased charge density on the polymer should enhance the osmotic pressure inside the gel particles because of the NH_3^+-NH_3^+ electrostatic repulsion. This osmotic pressure difference between the internal and external solution of the network is balanced by the swelling of the gel. However, under a very acidic condition (pH<3), a screening effect of the counter ion, i.e. Cl^-, shields the charge of the ammonium cations and prevents an efficient repulsion.

As a result, a remarkable decreasing in equilibrium swelling is observed (gel collapsing). At pH>4.7, the carboxylic acid component comes into action as well. Since the pK_a of the weak poly acid is about ~4.7, it's ionization occurring above this value, may favor enhancing absorbency. But under pH 6.4, or in a certain pH range 4-7, the majority of the base and acid groups are as NH_3^+ and COO^- or NH_2 and COOH forms and therefore ionic interaction of NH_3^+ and COO^- species (ionic crosslinking) or hydrogen bonding between amine and carboxylic acid (and probably carboxamide groups) may lead to a kind of crosslinking followed by decreased swelling. At pH 8, the carboxylic acid groups become ionized and the electrostatic repulsive force between the charged sites (COO^-) causes increasing in swelling. Again, a screening effect of the counter ions (Na^+) limits the swelling at pHs 9-13[25-32].

CONCLUSSION

In this work, we prepared a novel superabsorbent hydrogel, H-κC-g-Poly(AAm-co-AI), by graft copolymerization of AAm and AI monomers onto κC backbones. The maximum water absorbency (294 g/g) was achieved under the optimum conditions that found to be MBA 0.043mol/L, Aam 0.4 mol/L, AI 1.6 mol/L, APS 0.02 mol/L, reaction temperature 65°C and time 1h. The swelling of the hydrogels exhibited a high sensitivity to pH in 3 and 8. Net effect of H^+/OH^- concentration was examined at various pHs in absence of any buffer solution. One sharp and large volume change was observed for hydrogels versus small pH variations. Ionic repulsion of protonated groups in acidic solutions causes volume change. Ionic repulsion between charged groups incorporated in the gel matrix by an external pH modulation could be assumed as the main driving force responsible for such abrupt swelling changes. It also exhibited ampholytic nature of pH-responsiveness in swelling behavior.

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