

# Synthesis and Swelling Behaviors of graft copolymer Based on Chitosan-g-poly(AA-co-HEMA)

Mohammad Sadeghi

**Abstract**—In this work, Acrylic acid (AA) and 2-hydroxyethyl methacrylate (HEMA) monomers were directly grafted onto chitosan using ammonium persulfate (APS) as an initiator and methylenebisacrylamide (MBA) as a crosslinking agent under an inert atmosphere. A mechanism for hydrogel formation was proposed and the structure of the product was established using FTIR spectroscopy and scanning electron microscopy. The water absorbency increased with increasing the AA amount in the monomer feed due to formation of polyelectrolyte. Results indicated that the swelling capacity decreased with an increase in the ionic strength of the swelling medium. Furthermore, the swelling of superabsorbing hydrogels was examined in solutions with pH values ranging between 1 and 13. The Chitosan-g-poly(Acrylic acid-co-HEMA) hydrogel exhibited a pH-responsive swelling-deswelling behavior in acidic and alkaline solution.

**Index Terms**—Synthesis; chitosan; polyacrylic acid; 2-hydroxyethyl methacrylate

## I. 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. Because of their exceptional properties, i.e. biocompatibility, biodegradability, renewability, and non-toxicity, polysaccharides are the main part of the natural-based superabsorbent hydrogels. Graft copolymerization of vinyl monomers onto polysaccharides is an efficient route to preparation of hydrogels. The hydrogel forming ability through graft copolymerization of vinyl monomers onto polysaccharides such as starch, chitosan, sodium alginate, carrageenan, and cellulose has been well documented [5]. Because of the presence of certain functional groups along the polymer chains, hydrogels are

often sensitive to the conditions of the surrounding environment, which are referred to as “intelligent materials” or “smart materials”. For example, the water uptake of these materials may be sensitive to temperature, pH, or ionic strength of the swelling solutions, or even to the presence of a magnetic field or ultraviolet light [4]. These smart hydrogels are of general interest for biomedical applications, such as artificial muscles or switches, biomedical separation systems, and controlled release systems.

Chitosan is a linear natural polysaccharide composed of a partially deacetylated material of chitin. It is a basic polymer, having amine side groups [3]. Due to its excellent biocompatibility and biodegradability, chitosan and its derivatives were widely applied to fabrication of biomedical materials, enzyme and cell immobilization, especially for drug delivery. Since chitosan is easily soluble in acidic solutions, crosslinking of chitosan to form a network is the only way to prepare chitosan hydrogels. When anionic monomer such as acrylic acid in present acrylonitrile monomer is grafted onto chitosan (in the presence of a divinyl crosslinking agent monomer), an ampholytic hydrogel containing both cationic and anionic charges is prepared. So, by introducing anionic charges ( $-\text{COO}^-$ ) onto chitosan, a hydrogel with swelling ability at various pHs is prepared. In the present work, we study the synthesis and characterization of chitosan-g-poly(NaAA-co-HEMA) hydrogels.

## II. EXPERIMENTAL

### A. Synthesis of Hydrogel

A general procedure for chemically crosslinking graft copolymerization of AA and HEMA onto Chitosan backbones was conducted as follows. Chitosan was dissolved in degassed, distilled water containing 2 wt% of acetic acid. In general, (0.25-0.65 g) of chitosan was dissolved in 35.0 mL of the acetic acid solution. The reactor was placed in a water bath preset at 70 °C. Then (0.05-0.15 g in 5ml H<sub>2</sub>O) APS was added to the chitosan solution and stirred for 10 min at 70 °C. Following this, AA (2.0-4.5 ml) and HEMA(0.5 -3.0 ml) were added to the chitosan solution. MBA (0.01-0.11 g in 5ml H<sub>2</sub>O) as a crosslinker was added to the reaction mixture after the addition of monomer, and the mixture was continuously stirred for 1 h under argon atmosphere. After 60 min, the reaction product was allowed to be cooled to ambient temperature. The resulting hydrogel

Department of Chemistry, Science Faculty, Islamic Azad University, Arak Branch, Arak, Iran.

Corresponding author: E-mail: m-sadeghi@iau-arak.ac.ir, Tel : 0098 8613670017

was neutralized to pH 8 by addition of 1 N NaOH solution. Then methanol (500 mL) was added to the gel product while stirring. After complete dewatering for 24 h, the product was filtered, washed with fresh methanol (2×50 mL), and dried at 50 °C.

### B. Swelling Swelling Measurements Using Tea Bag Method

The tea bag (i.e. a 100 mesh nylon screen) containing an accurately weighed powdered sample ( $0.5 \pm 0.001$  g) was immersed entirely in 200 mL distilled water and allowed to soak for 2 h at room temperature. The sample particle sizes were 40 to 60 meshes (250-400  $\mu\text{m}$ )[6]. The tea bag was hung up for 15 min in order to remove the excess solution. The equilibrium swelling (ES) was calculated according to following equation:

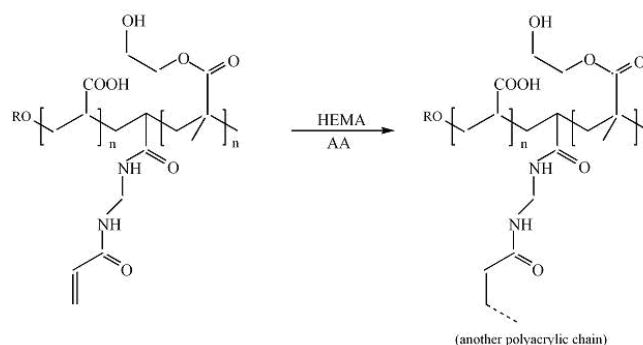
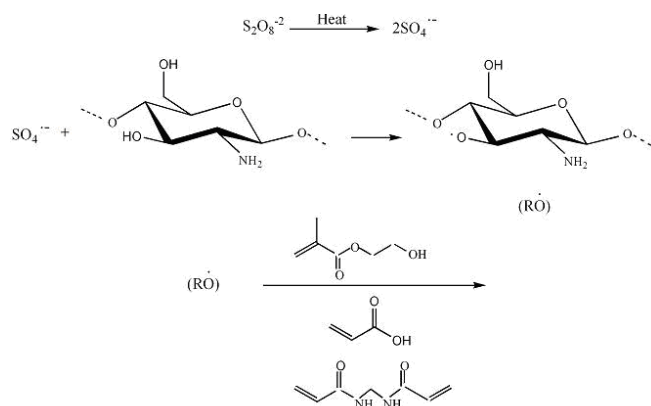
$$ES(g/g) = \frac{\text{Weight of swollen gel} - \text{Weight of dried gel}}{\text{Weight of dried gel}} \quad (1)$$

So, absorbency was calculated as grams of water per gram of resin (g/g). The accuracy of the measurements was  $\pm 3\%$ .

## III. RESULTS AND DISCUSSION

### A. Mechanism of Hydrogel Formation

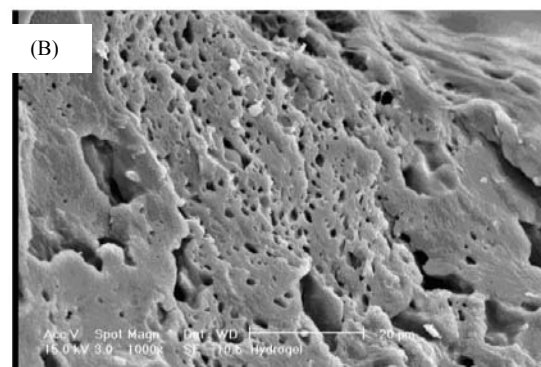
Superabsorbent hydrogels were prepared by graft copolymerization of acrylic acid and 2-hydroxyethyl methacrylate onto chitosan in the presence of MBA as a crosslinking agent. Ammonium persulfate was used as an initiator. The persulfate is decomposed under heating and produced sulfate anion-radicals that remove hydrogen from -OH groups of chitosan backbones[6]. So, this persulfate-saccharide redox system results in active centers capable to radically initiate polymerization of AA and HEMA leading to graft copolymer. Since the crosslinking agent, MBA, is presented in the system, the copolymer comprises a crosslink structure. A possible mechanism of the polymerization of acrylic acid and 2-hydroxyethyl methacrylate onto chitosan in the presence of MBA was shown in Scheme 1.



**Scheme 1** General mechanism for APS-initiated graft copolymerization of AA and HEMA onto chitosan in the presence of MBA.

For identification of the hydrogel, infrared spectroscopy and SEM were used. The FTIR spectra of pure chitosan and superabsorbent hydrogel based on chitosan are shown in Figure 1. In Figure 1(a) a broad band at 3418  $\text{cm}^{-1}$  corresponds to the associated -OH stretching vibrations of the hydroxyl groups, and the peak at 1611  $\text{cm}^{-1}$  corresponds to the N-H deformation bending of chitosan. The superabsorbent hydrogel product comprises a chitosan backbone with side chains that carry sodium carboxylate and ester functional groups that are evidenced by New peaks at 1570.4 and 1736.6  $\text{cm}^{-1}$  respectively. The very intense characteristic band at 1576  $\text{cm}^{-1}$  is due to C=O asymmetric stretching in carboxylate anion that is reconfirmed by another sharp peak at 1435  $\text{cm}^{-1}$  which is related to the symmetric stretching mode of the carboxylate anion. To obtain an additional evidence of grafting, a similar polymerization was conducted in absence of the crosslinker. After extracting the homopolyAA and homopolyHEMA (2.8%), appreciable amount of grafted chitosan was concluded. The graft copolymer spectrum was very similar to Fig. 1(a).

For more confirming structure of hydrogels, we applied 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 2 shows an SEM micrograph of the polymeric hydrogels obtained from the fracture surface[2-3].



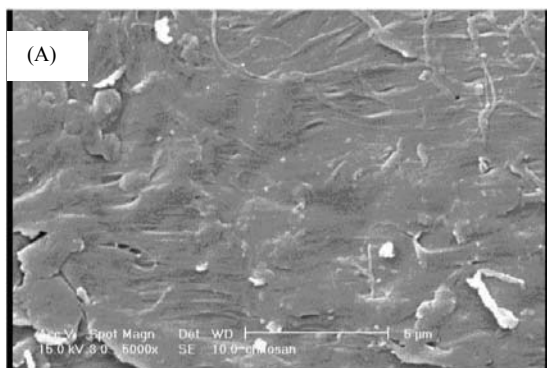


Figure 2. SEM photograph of chitosan(A), and the optimized superabsorbent hydrogel(B)

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

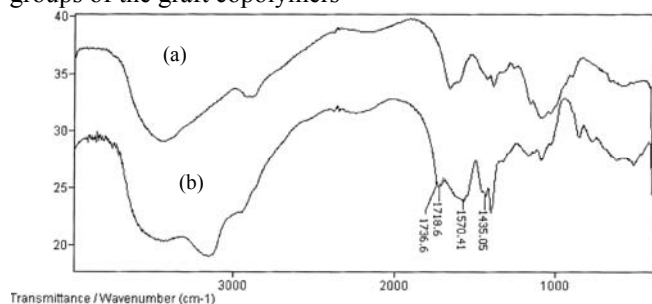


Figure 1. FTIR spectra of (a) chitosan and (b) chitosan-g-Poly(NaAA-co-HEMA) superabsorbent.

### C. Effect of pH on equilibrium swelling

Figure 3 represents pH dependence of the equilibrium swelling for Chitosan-g-poly(NaAA-co-HEMA) 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 [4]. In addition, it has been reported that the swelling properties of polybasic gels are influenced by buffer composition (composition and  $pK_a$ )<sup>19</sup>. 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  $pK_a$  for chitosan is 6.5 and that for carboxylic acid groups is  $\sim 4.7$ . In Figure 3, the dependence of the equilibrium swelling of the Chitosan-g-poly(NaAA-co-HEMA) hydrogel is characterized by a curve with two maximum at pH=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 Chitosan-g-poly(NaAA-co-HEMA) hydrogel includes chitosan, poly(acrylic acid) and poly(2-hydroxyethyl methacrylate) structures. The structure of chitosan and PAA are unizable. Therefore, based upon  $pK_a$  of PAA ( $\sim 4.7$ ) and  $pK_a$  of chitosan (6.5), the involving species are  $NH_3^+$  and  $COOH$  (at pH=1-3),  $NH_2$  and  $COO^-$  (at pH=7-13) and  $NH_3^+$  and  $COO^-$  or  $NH_2$  and  $COOH$  (at pH=4-7). Under acidic conditions, the swelling is controlled mainly by amino group

( $NH_2$ ) on the C-2 carbon of the chitosan component. It is a weak base with an intrinsic  $pK_a$  of about 6.5, 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.

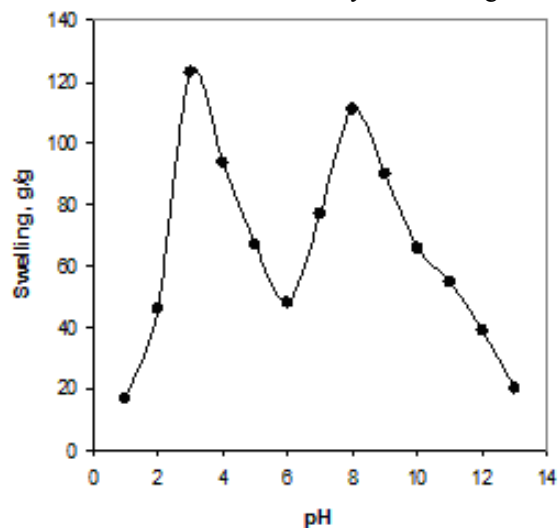


Figure 3. Swelling dependency chitosan-g-poly(AA-co-HEMA) superabsorbent on pH.

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 polyacid is about  $\sim 4.7$ , its 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 pH 9-13.

### D. Swelling dependency chitosan-g-poly(AA-co-HEMA) superabsorbent in salt solutions

The swelling ratio is mainly related to the characteristics of the external solution, i.e. the charge number and ionic strength, as well as the nature of polymer, i.e. the elasticity of the network, the presence of hydrophilic functional groups, and the extent of crosslinking density. For instance, swelling ability of "anionic" hydrogels in various salt solutions is appreciably decreased comparing 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 non-perfect anion-anion electrostatic repulsion. Therefore, the osmotic pressure resulted from the mobile ion concentration difference

between the gel and aqueous phases decreased and consequently the absorbency amounts diminished. In addition, in the case of salt solutions with multivalent cations, "ionic crosslinking" at surface of particles causing an appreciable decrease in swelling capacity[3].

In this series of experiments, the swelling capacity was measured in various salt solutions (Fig.4). It is obvious that swelling decrease is strongly depended on the "type" of salt added to the swelling medium. The effect of cation type (cations with different radius and charge) on swelling behavior is shown in Fig. 4. With increasing the charge of cation, degree of crosslinking is increased and swelling is consequently decreased. Therefore, the absorbency for the hydrogel in the studied salt solutions is in the order of monovalent > divalent > trivalent cations. The effect of cation radius on swelling may also been observed from Fig. 4. As reported by Pass et al[4], the carboxylate anion interacts with small cations, e.g.  $\text{Li}^+$ , stronger than with large cations, e.g.  $\text{Cs}^+$ . The stronger interactions of carboxylate-small cation have been observed using measurement of activating coefficients of various cations in several salt solutions. As a result, the absorbency in monovalent and divalent cation salt solutions is in the order of  $\text{CsCl} > \text{KCl} > \text{NaCl} > \text{LiCl}$  and  $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ , respectively.

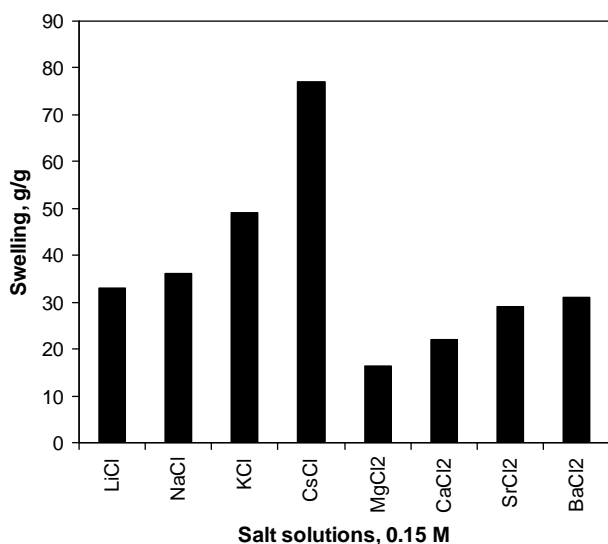


Figure4. Swelling capacity of the hydrogel in different chloride salt solutions (0.15M).

### III. CONCLUSION

Superabsorbent hydrogels, Chitosan-g-poly(AA-co-HEMA) hydrogel, were synthesized through grafting of AA and HEMA monomers onto chitosan using ammonium persulfate (APS) as an initiator and methylene bis acrylamide (MBA) as a crosslinking agent under an inert atmosphere. Swelling capacity of the hydrogels was found to affect by monomers and crosslinker concentrations. The swelling of the hydrogels exhibited a high sensitivity to pH in 3 and 8. Net effect of  $\text{H}^+/\text{OH}^-$  concentration was examined at various pHs in absence of any buffer solution. One sharp and large volume change was observed for Chitosan-g-poly(NaAA-co-HEMA) versus small pH variations in. 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. We investigated their swelling in different salt solutions and in media with a wide range of pHs. The pH-reversibility of the hydrogels (swelling/deswelling process) at pH 3.0 and 8.0 was also studied. This hydrogel polyampholytic network intelligently responding to pH may be considered as an excellent candidate to design novel drug delivery systems.

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**Khorramabad**, Lorestan, Iran on 15/06/1973. Educational backgrounds are: High School Diploma (GPA 15.5/ out of 20), Shahid taleghani High School, khorramabad, lorestan, 1992. B.Sc. In Pure Chemistry (GPA 14.50/ out of 20), Lorestan University, khorramabad, 1996. M.Sc. In Organic Chemistry -Polymer (GPA 15.95/ out of 20), Sharif University of Technology, Tehran, 2000. Ph.D. in Organic Chemistry (Polymer Chemistry), Sharif University of Technology, 2004 .

He is associate professor at Islamic Azad University ,Arak Branch. his works are:

1. 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
2. Studies on graft copolymerization of 2-hydroxyethylmethacrylate onto kappa-carrageenan initiated by ceric ammonium nitrate, *Journal of The Chilean Chemical Society*, 55N<sup>4</sup> (2010)
3. 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:

1. 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.

2. 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 (flocclants), 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:

1. Synthesis of novel superabsorbent hydrogels with high pH and low salt sensitivity
2. Synthesis of intelligent hydrogels as excellent candidate in cotrolled release drug delivery systems.
3. Synthesis of composite hydrogels for preparing of new superabsorbents with high mechanical stability.
4. Modification of natural polymers via free radical graft copolymerization of vinylic monomers.

**Dr.Sadeghi** is associate Professor at Islamic Azad University, Arak Branch.He is member of Iranian Polymer Association, member of Iranian Chemistry Association, member of American Plastic Association, The fifth person in Chemistry Olymiad in Iran, the best researcher in the Province, district, and also university for several years.