

Optimization of Environmental-Chemical Factors Affecting on Swelling Capacity of a Novel Protein-Based Hydrogel

HOSSEIN HOSSEINZADEH

Department of Chemistry, Payame Noor University, 19395-4697, Tehran (Iran).
E-mail: h_hoseinzadeh@pnu.ac.ir

(Received: October 18, 2011; Accepted: November 30, 2011)

ABSTRACT

Novel biopolymer-based superabsorbent hydrogels were prepared by grafting crosslinked poly(acrylic acid-co-methacrylic acid) chains onto gelatin backbones through a free radical polymerization method. The graft copolymerization reaction was carried out in a homogeneous medium and in the presence of ammonium persulfate (APS) as an initiator and N,N'-methylene bisacrylamide (MBA) as a crosslinker. Under optimized reaction conditions, hydrogel has an absorbency of 340 g/g for distilled water. Swelling ratio in various salt solutions was also determined and additionally, the swelling of hydrogels was measured in solutions with pH ranged from 1 to 11.

Key words: Gelatin, Hydrogel, Acrylic acid, Methacrylic acid, Swelling behavior.

INTRODUCTION

Superabsorbent hydrogels are loosely crosslinked hydrophilic polymers that can absorb, swell and retain aqueous solutions up to hundreds of times their own weight¹. Since their response to changing environmental conditions such as temperature², pH³ and solvent composition⁴, these materials have been attracting much attention in medical and mechanical engineering fields. Although hydrogels made from synthetic polymers, such as polyacrylate, show 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 products⁵. Recently, attention has been focused on employing natural polymers such as cellulose⁶, gelatin⁷, chitosan⁸, alginate⁹ and protein¹⁰ to produce hydrogels with a specific response to a biological environment. The presence of the natural parts guarantees biocompatibility, biodegradability, and non-toxicity of the superabsorbing materials.

In the present report, we describe the preparation and characterization of a gelatin-based hydrogel as a new natural-based polymer. The effect of reaction variables affecting the water absorbency of the hydrogel and swelling behavior in various salt and pH solutions was investigated.

EXPERIMENTAL

Preparation of Hydrogel

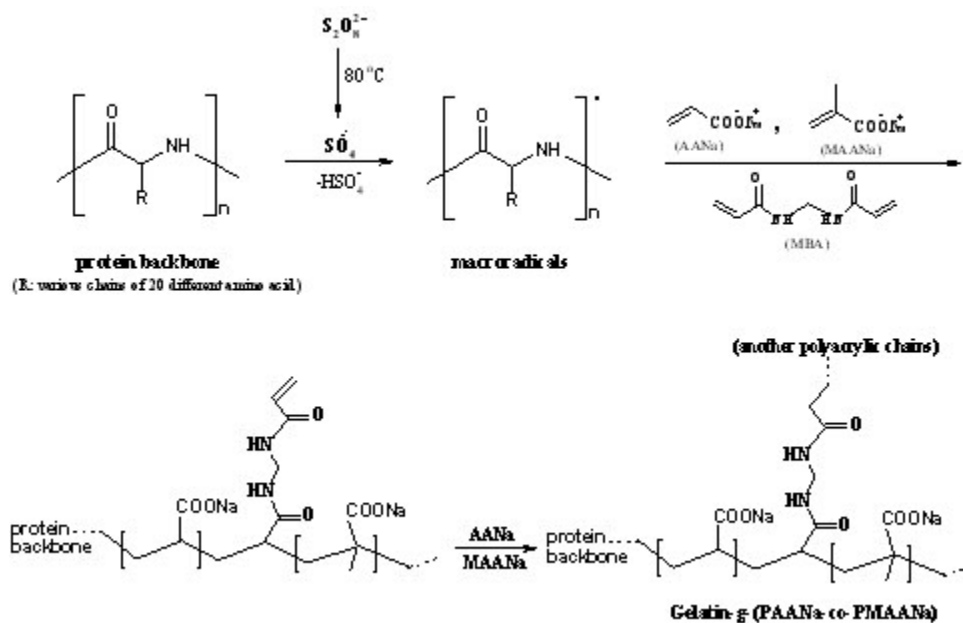
A general procedure for chemically crosslinking graft copolymerization of acrylic acid (AA) and methacrylic acid (MAA) onto gelatin backbones was conducted as follows: Gelatin (1.0 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021, three blade propeller type, 300 rpm), including 35 mL doubly distilled water. The reactor was immersed in a thermostated water bath preset at 80 °C). Then a definite amount of APS solution (0.1 g in 5 mL H₂O) was added to gelatin solution and was allowed to stir for 10 min. After adding APS, variable amounts of AA and MAA (neutralized to pH 8 by addition of

1N sodium hydroxide solution) were added simultaneously to the gelatin solution. MBA solution (0.03–0.08 g in 5 ml H₂O) was added to the reaction mixture after the addition of monomers and the mixture was continuously stirred. After 60 min, the reaction product was allowed to cool to ambient temperature. The hydrogel was poured to excess non solvent ethanol (200 mL) and kept for 3 h to dewater. Then ethanol was decanted and the product scissored to small pieces. Again, 100 mL fresh ethanol was added and the hydrogel was kept for 24 h. Finally, the filtered hydrogel is dried in oven at 50°C for 5 h. After grinding using mortar, the powdered superabsorbent was stored away from moisture, heat and light.

RESULTS AND DISCUSSION

Synthesis of hydrogel

The mixture of monomers, acrylamide and acrylic acid, was simultaneously grafted onto gelatin backbones in a homogeneous medium using APS as a radical initiator and MBA as a crosslinking agent. A general reaction mechanism for gelatin-g-poly(AA-co-MAA) hydrogel formation is shown in Scheme 1. At the first step, the thermally dissociating initiator, i.e. APS, is decomposed under heating to produce sulfate anion-radical. Then, the anion-radical abstracts hydrogen from one of the functional groups in side chains (i.e. COOH, SH, OH, and NH₂) of the substrate to form corresponding



Scheme 1: Proposed mechanistic pathway for synthesis of the gelatin-based hydrogels

radical. So, these macroradicals initiated monomer grafting onto gelatin backbones led to a graft copolymer. In addition, crosslinking reaction was carried out in the presence of a crosslinker, i.e., MBA, so that a three dimensional network was obtained.

Effect of crosslinker concentration

Crosslinks have to be present in a hydrogel in order to prevent dissolution of the hydrophilic polymer chains in an aqueous

environment. The crosslinked nature of hydrogels makes them insoluble in water. Efficiency of the incorporated crosslinker controls the overall crosslink density in the final hydrogel. Figure 1 shows the influence of the crosslinking agent on the swelling capacity of gelatin-g-poly(NaAA-co-AAm) hydrogel. As indicated in Figure 1, higher crosslinker concentration decreases the space between the copolymer chains and, consequently, the resulted highly crosslinked rigid structure cannot be expanded and hold a large quantity of water.

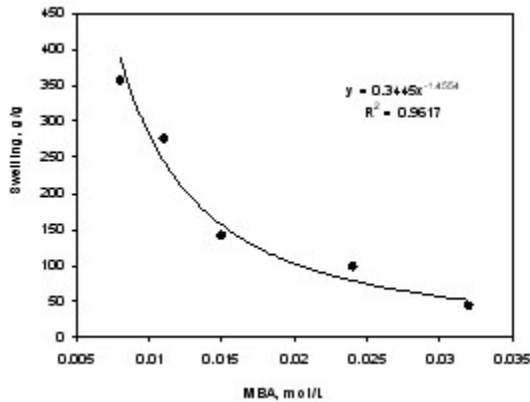


Fig. 1: Effect of crosslinker concentration on swelling capacity

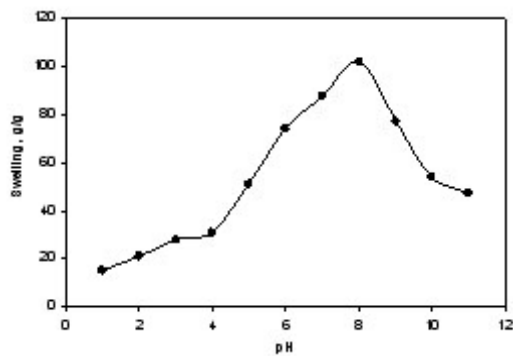


Fig. 2: Effect of pH of solution on swelling capacity of hydrogel

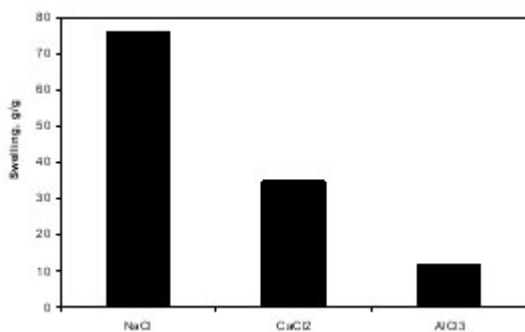


Fig. 3: Swelling capacity of the optimized hydrogel in different chloride salt solutions (0.15 M)

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 11.0 (Figure 2). Maximum swelling was obtained at pH 8. In acidic media, most carboxylate groups are protonated, so decreased repulsion of anionic groups leads to a decreased swelling ratio. At higher pHs (3–8), some carboxylate groups are ionized and the electrostatic repulsion between carboxylate 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 carboxylate anions and prevent effective anion–anion repulsion.

Swelling in Various Salt Solutions

Swelling capacity in salt solutions is of prime significance in many practical applications such as personal hygiene products and water release systems in agriculture. The 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 which causing a non-perfect anion–anion electrostatic repulsion. Also, in salt solution the osmotic pressure resulting from the difference in the mobile ion concentration between gel and the aqueous phases is decreased and consequently the absorbency amounts are diminished. In the present study, swelling capacity was studied in various chloride salt solutions (Figure 3). As shown in the Figure 3, multivalent cations decrease the swelling capacity considerably. This dramatic decrease of water absorbency in multivalent cationic solutions could be related to the complexing ability of the carboxylate groups inducing the formation of intramolecular and intermolecular complexes, which resulted in an increase in the crosslinking density of the network.

CONCLUSION

In the present study, collagen-g-(PAA-co-PMMA) superabsorbent hydrogel was synthesized in an aqueous solution using a persulfate initiator

and a hydrophilic crosslinker. Swelling capacity of the hydrogels is affected by the crosslinker (MBA) concentration, so that the swelling is decreased by increasing the MBA concentration. Swelling capacity of hydrogel in various pH solutions (1-11) exhibited high pH-sensitivity properties. This superabsorbent network intelligently responding to

pH may be considered as an excellent candidate to design novel drug delivery systems. 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.

REFERENCES

- 1 Po R., *J Macromol Sci-Rev Macromol Chem Phys C34*, 607-662 (1994).
- 2 Galaev I, Mattiasson B. *Smart Hydrogels, in: Smart Polymers, Applications in Biotechnology and Biomedicine*, Second Edition, CRC Press, Taylor & Francis Group (2007).
- 3 Ozturk V, Okay O. *Polymer* **43**: 5017-5026 (2002).
- 4 Qu X, Wirse'n A, Albertsson A.C. *Polymer* **41**: 4589-4598 (2000).
- 5 Hirokawa Y, Tanaka T. *J Chem Phys* **81**: 6379-6380 (1984).
- 6 Peppas LB, Harland RS. *Absorbent polymer Technology*, Elsevier, Amsterdam.
- 7 Zohuriaan-Mehr MJ, Pourjavadi, A. Salehi-Rad M. *Reac Func Polym* **61**: 23-31 (2004).
- 8 Jeanine A, Burmania GJ, Kao WJ. *Wiley Periodicals, Inc.* (2003).
- 9 Mahdavinia GR, Pourjavadi A, Zohuriaan-Mehr MJ. *J Appl Polym Sci* **99**: 1615-1619 (2006).
- 10 Bagheri Marandi G, Sharifnia N, Hosseinzadeh H. *J Appl Polym Sci* **101**: 2927-2937 (2006).