

Studies on Swelling Kinetics and Temperature-Sensitive Superabsorbent Hydrogels Based on Carboxymethylcellulose

MOHAMMAD SADEGHI*, SOUDEH SAFARI, ANAHITA GUDARZI, HADIS SHAHSAVARI and HOSSEIN SADEGHI

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

*Corresponding author: E-mail: m-sadeghi@iau-arak.ac.ir

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To develop materials with improved controllability and specificity, we have investigated swelling kinetics and temperature-sensitive properties using thermal cross-linking of a superabsorbing hydrogel based on carboxymethylcellulose and N-isopropylacrylamide and methacrylamide in a homogeneous solution. The hydrogels exhibited tem-sensitivity and cation exchange properties. The temperature and pH-reversibility properties of the hydrogels make the smart polymers as good candidates for considering as potential carriers for bioactive agents, *e.g.*, drugs. The swelling variations of hydrogels were also explained according to swelling theory based on the hydrogel chemical structure.

Key Words: Carboxymethyl cellulose, Superabsorbent, Hydrogel, N-Isopropylacrylamide, Methacrylamide.

INTRODUCTION

Superabsorbent can absorb tremendous amounts of water without dissolving in water because they contain considerable amounts of hydrophilic groups and have a three-dimensional structure. In fact, the network can swell in water and hold a large amount of water while maintaining the structure. Superabsorbent hydrogels are useful for many applications, such as disposable pads, sheets and towels for surgery, adult incontinence and female hygiene products, even through they were originally developed for agricultural applications to improve the water-holding capacity of soils to promote the germination of seeds and plant growth¹⁻³.

In particular, among the temperature-sensitive hydrogels reported to date, poly(N-isopropylacrylamide) (PNIPAAm) and its copolymers have been widely used for cell separation as well as for pharmaceutical and tissue engineering applications because of their unique thermal properties^{4,5}. PNIPAAm undergoes a reversible temperature-sensitive phase transition in aqueous solutions at approximately 32 °C (the lower critical solution temperature, LCST), which is between room temperature (25 °C) and body temperature (37 °C).

In addition to its use as on-off switches for the attachment/detachment of cells, this reversible deswelling event of PNIPAAm at below and above the LCST is also used as a means to control the release of various drugs. The collapse of PNIPAAm by raising temperatures above its LCST has been used to release various therapeutic agents including proteins

from PNIPAAm-based materials. In addition, it should be noted that a significant problem associated with protein release technology is the loss of biological activity of the protein due to denaturation. By varying temperatures, temperature-sensitive polymers can be used to load proteins in a passive and non-denaturing manner⁵⁻⁷.

The present work reveals simultaneously graft copolymerization of methacrylamide and N-isopropylacrylamide monomers onto CMC in the presence of methylenebisacrylamide (MBA) as a crosslinking agent.

EXPERIMENTAL

Preparation of hydrogel: Carboxymethylcellulose (CMC) solution was prepared in a 1 L reactor equipped with mechanical stirrer and gas inlet. CMC was dissolved in degassed distilled water. In general, 0.50 g of CMC was dissolved in 30 mL of distilled degassed water. The reactor was placed in a water bath preset at 60 °C. Then 0.10 g of ammonium persulfate (dissolved in 5 mL water) as an initiator was added to CMC solution and was allowed to stir for 10 min at 60 °C. After adding initiature, variable amounts of MAAm and NIPAAm were added to the CMC solution. Methylenebisacrylamide as a crosslinker (0.050 g in 5 mL water) was added to the reaction mixture after the addition of monomer and the mixture was continuously stirred for one hour under argon. The total volume of reaction was 40 mL. After 1 h, the reaction product was allowed to cool to ambient temperature and methanol (500 mL) was added to the gelled product. After complete dewatering

for 24 h, the product was filtered, washed with fresh methanol (2 mL × 50 mL) and dried at 50 °C^{8,9}.

Instrumental analysis: Fourier transform infrared (FTIR) spectroscopy absorption 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).

Swelling measurements: A CMC-g-PMAAm-co-PNIPAAm sample (0.10 g) was put into a weighed teabag and immersed in 100 mL distilled water and allowed to soak for 2 h at room temperature. The equilibrated swollen gel was allowed to drain by removing the teabag from water and hanging until no drop drained (*ca.* 0.5 h). The bag was then weighed to determine the weight of the swollen gel. The absorbency (equilibrium swelling) was calculated using the following equation, Flory¹⁰:

$$\text{Absorbency} = \frac{(W_s - W_d)}{W_d} \quad (1)$$

where W_s and W_d are the weights of the swollen gel and the dry sample, respectively. So, absorbency was calculated as grams of water per gram of copolymer (g/g). The accuracy of the measurements was ± 3 %.

RESULTS AND DISCUSSION

Effect of reaction temperature: The swelling capacity of the hydrogels prepared with various reaction temperatures, is shown in Fig. 1. Higher temperatures favour the rate of diffusion of monomers to the CMC 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, ammonium persulfate^{11,12}.

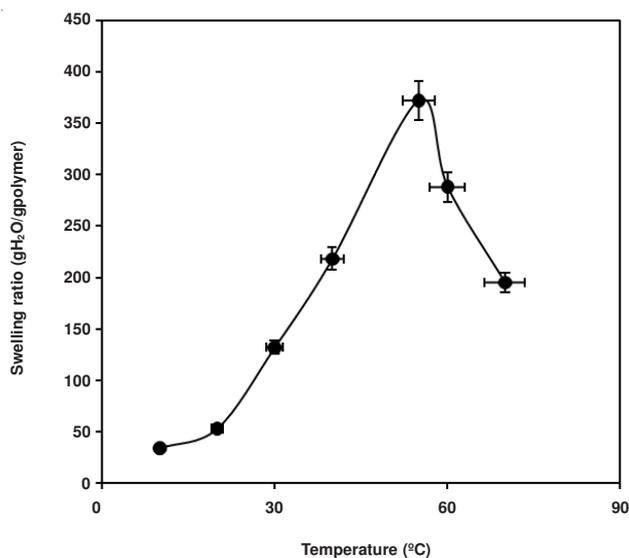
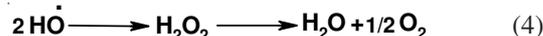


Fig. 1. Effect of reaction temperature on swelling capacity of the CMC-based hydrogels

The temperatures higher than the optimum value (55 °C), however, lead to low-swelling superabsorbents. This swelling-

loss may be attributed to (a) oxidative degradation of CMC chains by sulfate radical-anions (**Scheme-I**), (b) increasing the rate of termination and chain transfer reactions and (c) decomposition of ammonium persulfate to give O₂ (a radical scavenger), which reacts with primary free radicals (eqns. 2 and 3)^{8,13}, resulting in decreased molecular weight and decreased swelling (the sulfate radical anions may react with water to produce hydroxyl radicals (eqn. 2) and finally oxygen (eqn. 3).



The rate of graft copolymerization (R_p) was calculated simply using the following empirical formula¹⁴, for four initial points of Fig. 1:

$$R_p (\text{mol L}^{-1} \text{ s}^{-1}) = \frac{1000m_H}{MTV} \quad (4)$$

where m_H (g) stands for the weight of produced dry hydrogel, M (g mol⁻¹) denotes the molecular weight of monomers, 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 $\ln R_p$ versus $1/T$ (Fig. 2) based on Arrhenius relationship [$k_p = A \exp(-E_a/RT)$]. Therefore, E_a for the graft copolymerization of monomers onto polysaccharide backbones was found to be 78.3 kJ/mol.

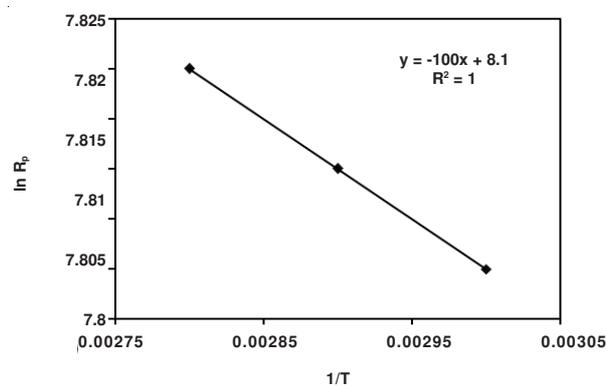
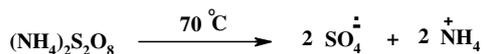


Fig. 2. Plot of $\ln R_p$ versus $1/T$

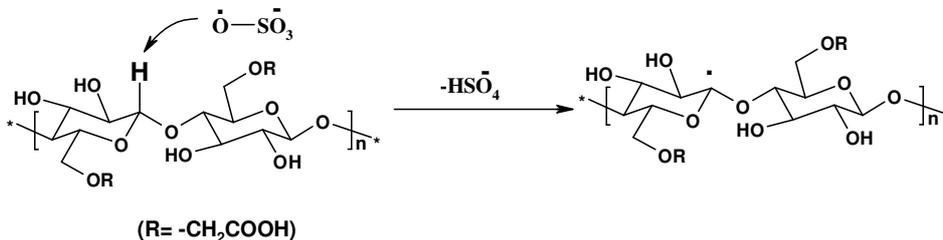
Thermo-sensitivity of the hydrogel: The dependence of swelling degree on temperature and time is shown in Fig. 3. It indicates that the swelling and deswelling of the hydrogels were reversible. The response to temperature change is very quick. An abrupt decrease of swelling ratio is observed from 20-55 °C.

pH-responsiveness behaviour of the hydrogel composite: Ionic superabsorbent hydrogels exhibit swelling changes at a wide range of pHs. Therefore, in this series of experiments, we investigated the reversible swelling-deswelling behaviour of this hydrogel in solutions with pH 2 and 8 (Fig. 4). At pH 8, the hydrogel swells due to anion-anion repulsive electrostatic forces, while at pH 2, it shrinks within a few minutes due to protonation of the carboxylate anions. This swelling-deswelling behaviour of the hydrogels makes them as suitable candidate for designing drug delivery systems^{13,15}.

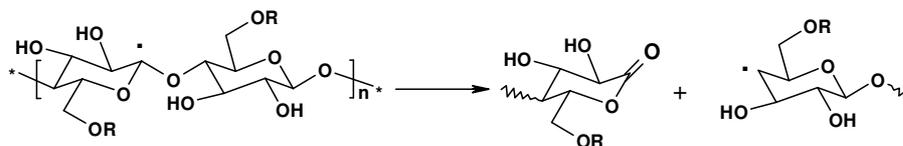
1. Thermal dissociation of APS



2. Hydrogen abstraction by sulfate anion-radical



3. Degradation of Carboxymethylcellulose macroradical



Scheme-I: A proposed mechanism for degradation of carboxymethylcellulose substrate by temperature

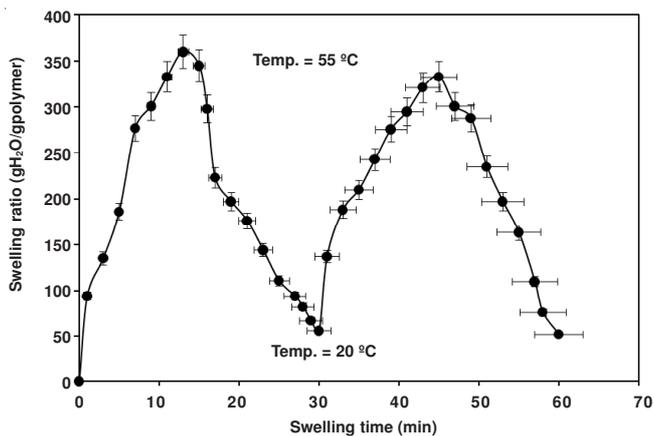


Fig. 3. Thermo-sensitivity of the hydrogel composite at 20, 55 °C

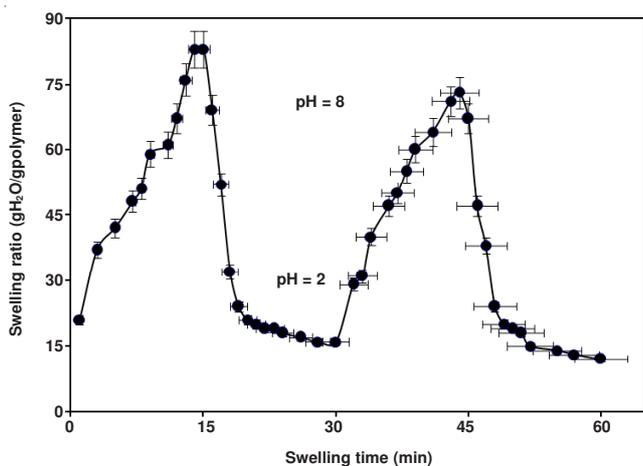
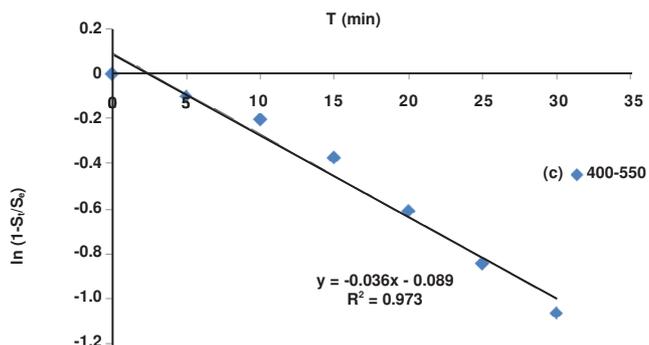
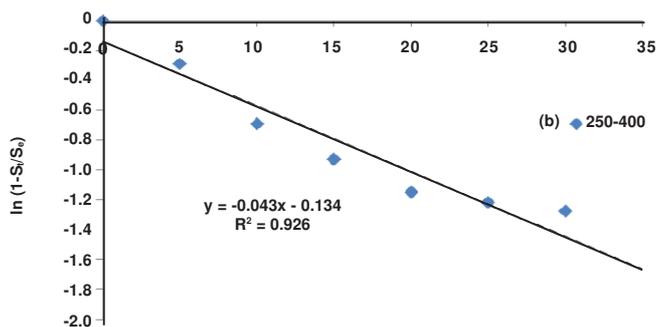
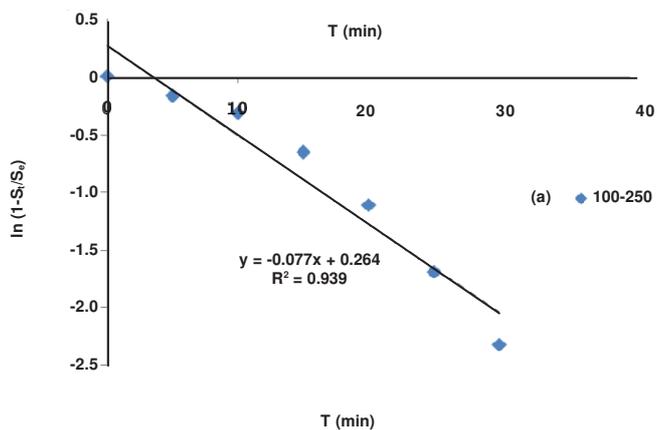


Fig. 4. On-off switching behaviour as reversible pulsatile swelling (pH 8) and deswelling (pH 2) of the hydrogel

Swelling kinetics: According to Fig. 5, the swelling values versus swelling time follow a power law trend. A “Voigt-based model” may be used for fitting the data¹⁶.



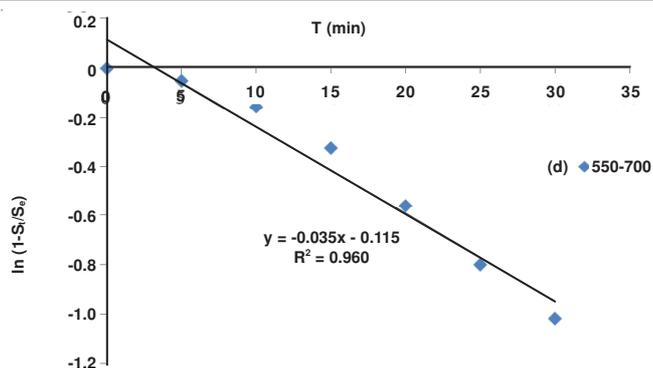


Fig. 5. Plot of $\ln(1 - S_t/S_e)$ versus time, according to eqn. 5 (first order kinetics) for the superabsorbent hydrogel with particle sizes 100-250 μm (a), 250-400 μm (b), 400-550 μm (c) and 550-700 μm (d)

$$S_t = S_e(1 - e^{-t/\tau}) \quad (5)$$

S_t is the swelling at time t , S_e is the equilibrium swelling (power parameter) and τ is the rate parameter. The rate parameters for superabsorbent are found to be 12.99, 23.25, 27.78 and 28.57 min for superabsorbent with particle sizes of 100-250, 250-400, 400-550 and 550-700 μm , respectively. It is well-known that the swelling kinetics for the superabsorbent polymers is significantly influenced by particle size of the absorbents¹⁷. With a lower the particle size, a higher rate of water uptake is observed. An increase in the rate of absorption would be expected from the increase in surface area with decreasing particle size of hydrogel.

For calculate the rate parameter, 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 parameters. 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 evaluating the rate of water absorbency of superabsorbent polymers on the condition that the particle size of the comparing samples are the same or, at least, in the same range¹⁶.

Conclusion

Superabsorbent hydrogels, CMC-g-poly(MAAm-co-NIPAAm), were synthesized through grafting of methacryl-

amide and N-isopropylacrylamide monomers onto CMC using ammonium persulfate (APS) as an initiator and methylene bis acrylamide (MBA) as a crosslinking agent under an inert atmosphere. The superabsorbent hydrogels exhibited high sensitivity to pH (in 2.0 and 8.0) and media temperature. therefore, we investigated the pH- and tem[-sensitivity of the hydrogel. Ionic repulsion between charge 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. This superabsorbent network intelligently responding to pH and temperature may be considered as an excellent candidate to design novel drug delivery systems. Finally, dynamic swelling kinetics of the hydrogel composite show that the rate of absorbency is increased with decreasing the particle size of superabsorbing samples.

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