

Study Effect of Various Environmental Conditions on the Swelling Property of Biocopolymer Based on Carrageenan-g-polyMethacrylic acid Hydrogel

Mohammad Sadeghi*, Nahid Ghasemi¹ and Mojgan Yarahmadi²

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

¹Department of Chemistry, Science Faculty, Islamic Azad University, Arak Branch, Arak (Iran).

²Department of English, Faculty of Humanities, Arak Branch, Islamic Azad University, Arak (Iran).

(Received: 20 September 2011; accepted: 22 October 2011)

In this study, a series of highly swelling hydrogels based on carrageenan and polymethacrylic acid (PMAcA) was prepared via 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. A proposed mechanism for hydrogel formation was suggested and Infrared spectroscopy was carried out to confirm the chemical structure of the composite. Moreover, morphology of the samples was examined by scanning electron microscopy (SEM). Absorbency in various aqueous salt solutions indicated that the swelling capacity decreased with an increase in the ionic strength of the swelling medium. This behavior can be attributed to charge screening effect for monovalent cations, as well as ionic crosslinking for multivalent cations. However, due to the high swelling capacity in salt solutions, the hydrogels may be referred to as anti-salt superabsorbents. The swelling behavior of superabsorbing hydrogels was also measured in solutions with pH ranged from 1 to 13.

Key words: Carrageenan; Superabsorbent; Swelling behavior; Methacrylic acid monomer.

Superabsorbents polymers (SAPs) are hydrophilic three dimensional networks, which are able to absorb tremendous amount of water or biological fluids¹. In fact, the network can swell in water and hold a large amount of water while maintaining its original structure. Superabsorbent hydrogels are useful for many applications, such as disposable pads, sheets, and towels for surgery, adult incontinence, and other products, even through they were originally developed for

agricultural applications to improve the water-holding capacity of sandy soils to promote the germination of seeds and plant growth²⁻⁶.

Considerable interest has been focused on chemical modification of polysaccharides by grafting of synthetic polymers onto natural ones such as cellulose, chitosan, agar, Na-alginate, and starch^{5,7}. In order to synthesis of polysaccharides-based SAPs, vinylic Graft copolymerization can be carried out by different initiators and different mechanisms. Carrageenan is a collective term for linear sulfated polysaccharides obtained commercially by alkaline extraction of certain species of red seaweeds⁹. Schematic diagram of the idealized structure of the repeat units for the most well-known and most important type of carrageenan family.

* To whom all correspondence should be addressed.
Tel: +98-861-3410017, Fax: +98-861-3410017
E-mail: m-sadeghi@iau-arak.ac.ir

EXPERIMENTAL

Materials

The polysaccharide, kappa-carrageenan (κC), from Condinson Co., Denmark); N, N'-methylene bisacrylamide (MBA, from Merck) as a crosslinker, ammonium persulfate (APS, from Fluka) as a water soluble initiator, of analytical grade and methacrylic acid (MAcA from Total) as a monomer, were analyze grade and used without further purification.

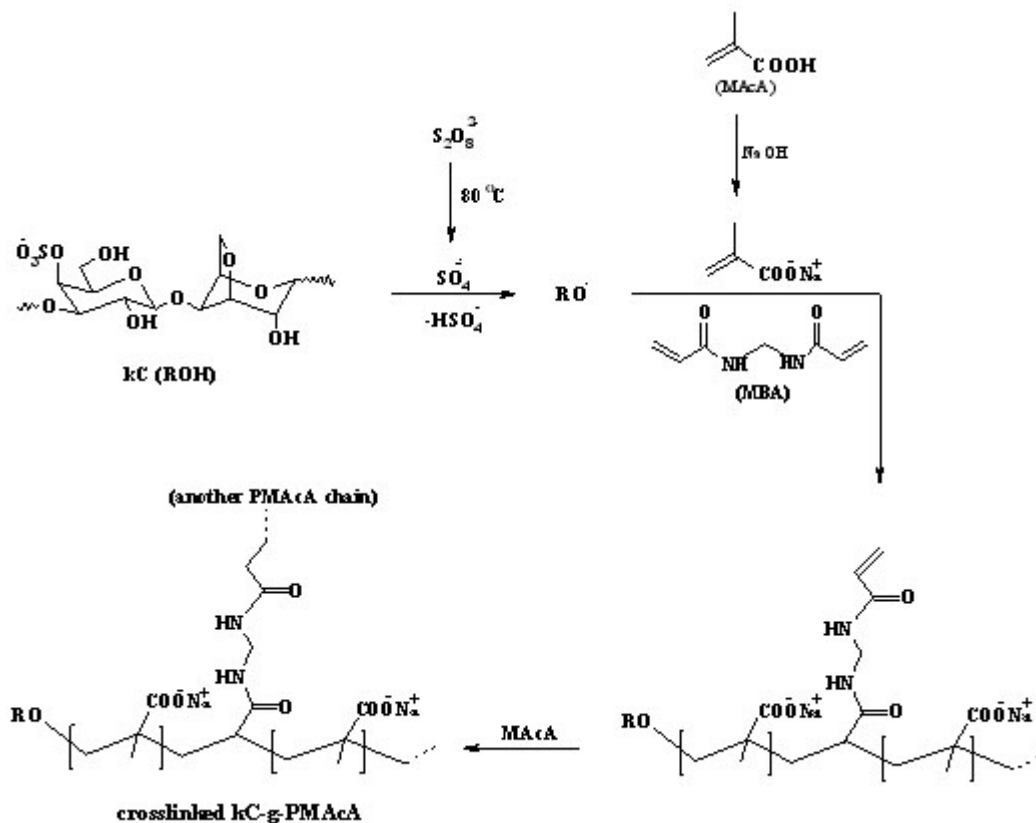
Instrumental Analysis

Samples were characterized as KBr pellets using a Mattson-1000 FTIR spectrophotometer. An atomic absorption spectrometer (Varian AA-5) was used for the measurements of the metal ion absorption.

Graft copolymerization

Certain amount of water (25ml) and κC (1.0 g) was added to a three-neck reactor equipped with a mechanical stirrer (Heidolph RZR 2021) at a

stirring rate of 400 rpm. The reactor was placed in a thermostated water bath preset at desired temperature (65 °C) for 15 min. After dissolving of and homogenizing of the mixture, the monomer, and the crosslinker, were simultaneously added and the reaction mixture was stirred for 15 min. Then, the APS initiator was added and gelation was observed after about 40 min. After 1h, the mixture was treated with 1N sodium hydroxide for partial neutralization (20-100%) of the carboxylic groups of the grafted poly (methacrylic acid). Finally, the obtained gel was poured into 100 ml of ethanol for 2h and then cut into small pieces (diameter 5 mm). Then the ethanol was decanted and 100 ml fresh ethanol was added. The hydrogel pieces were kept for 24 h in order to solidification complete dewatering. The dried gel particles were filtered and placed in an oven at for 6 h. After grinding, the powdered superabsorbent hydrogel was stored away from moisture, heat and light ⁸.



Scheme 1. A proposed mechanism for synthesis of H- κC -g-PMAcA superabsorbent hydrogel

Water Absorbency Measurement

Accurately weighted samples (0.1 ± 0.0001 g) of the powdered superabsorbents with average particles sizes between 40-60 meshes (250-350 μ m) immersed in 200 ml distilled water for 3 h. The equilibrium swelling (ES) capacity was measured twice at room temperature by "tea bag" method and calculated using the following formula:

$$ES \text{ (g/g)} = \frac{W_2 - W_1}{W_1} \quad \dots(1)$$

Where W_1 and W_2 are the weights of dry and swollen gel respectively

RESULTS AND DISCUSSION

Synthesis and mechanism aspects

Crosslinking graft copolymerization of methacrylic acid onto kappa-carrageenan was carried out using of APS as a free radical initiator and MBA as a hydrophilic crosslinker. The crosslinking graft copolymerization of acrylic acid onto kappa-carrageenan was carried out. Mechanism for the grafting and chemically crosslinking reactions are outlined in scheme 1. The persulfate initiator is decomposed under heating to generate sulfate anion-radical. The radical abstracts hydrogen from the hydroxyl group of the kappa-carrageenan to form alkoxy radicals on the substrate. So this persulfate-saccharide redox system results in active centers on the substrate to radically initiate polymerization of

MAcA led to a graft copolymer. Since a crosslinking agent, e.g. MBA, is presented in the system, the copolymer comprises a crosslinked structure. It should be pointed out that the sulfate ion-radical may also initiate MAcA homopolymerization. However, the probable crosslinked hydrophilic homopolymer (poly acrylic acid) does not cause appreciable undesired effects on absorbency properties of the final products. On the other hands, according to preliminary measurements, the sol (soluble) content of the hydrogel networks was as little as 2.5%. This fact practically supports the idea that all PMAcA is involved in the polymer network. So the PMAcA percent in the network will be very similar to that of the initial feed of reaction⁸⁻⁹.

Spectral characterization

The grafting was confirmed by comparing the FTIR spectra of the polysaccharide substrate with that of the grafted products. Fig. 1 shows the FTIR spectra of polysaccharide, (κ C), and κ C-g-PMacA. The IR spectrum of the κ C-g-PMacA

Table 1. Values k and n (as obtained from the curve fitting, Fig. 4) for the optimally prepared superabsorbent hydrogel, H-carrageenan-g-PMacA

Swelling medium	k	n
<i>NaCl</i>	8.2	0.41
<i>CaCl</i> ₂	8.3	0.52
<i>AlCl</i> ₃	8.4	0.65

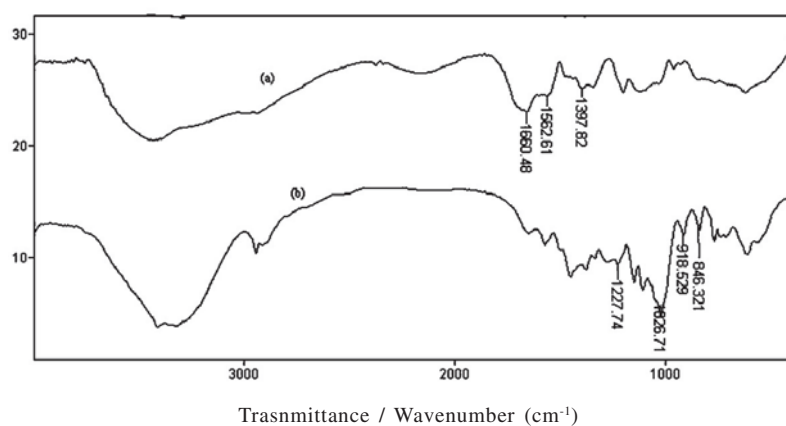


Fig. 1. FTIR spectra of κ C-g-PMacA hydrogel (a), and pure κ C (b)

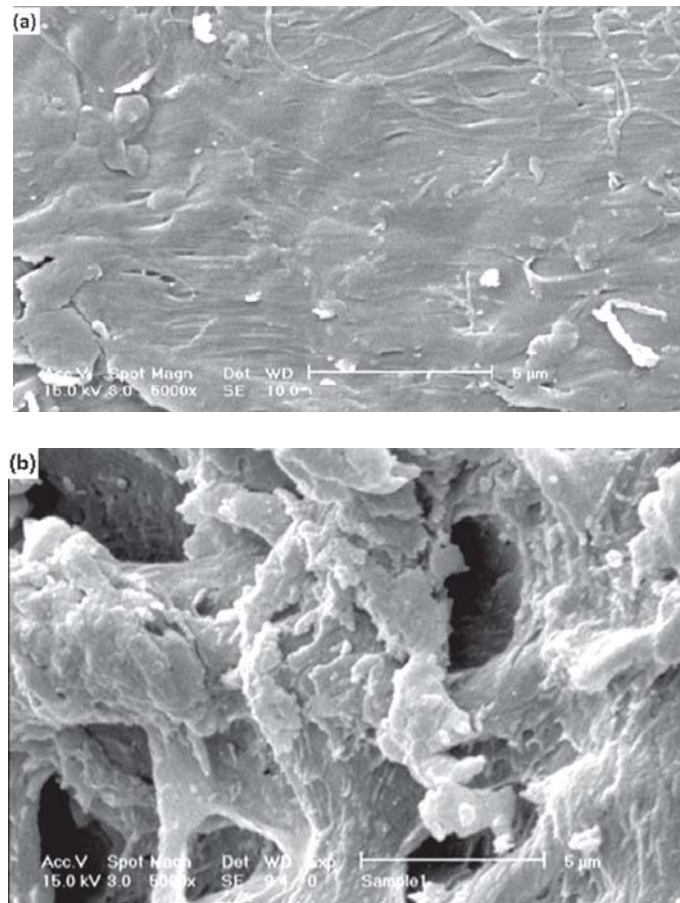


Fig. 2. SEM photograph of pure κ C (a) and the hydrogel (b). Surfaces of hydrogel was taken at a magnification of 5000, and the scale bar is 5 μ m

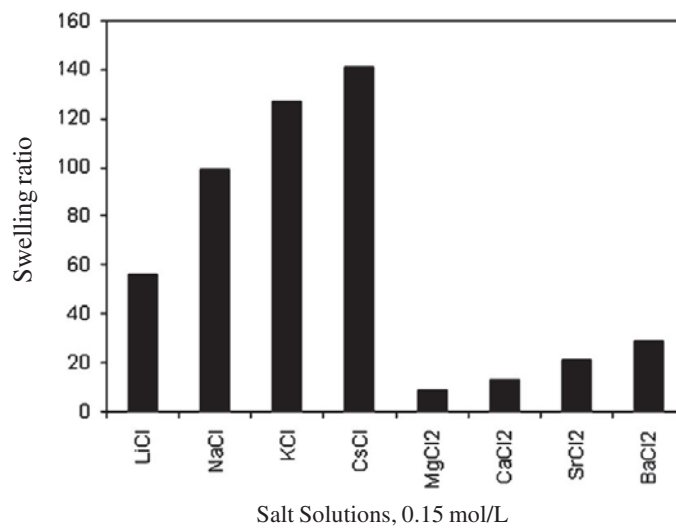


Fig. 3. Swelling capacity of the hydrogel, H- κ C-g-PMACa, in different chloride salt solutions (0.15M)

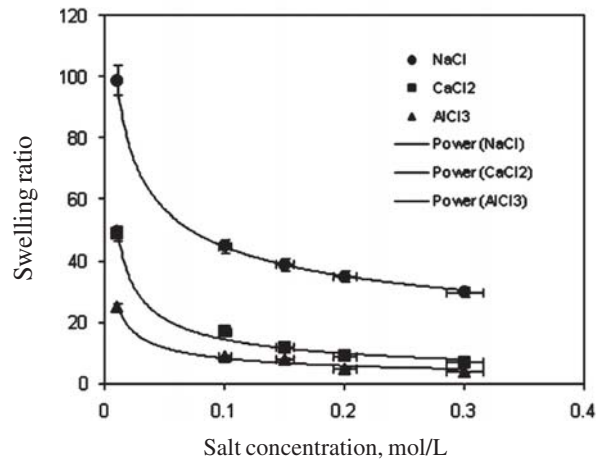


Fig. 4. Swelling capacity variation of H-carrageenan-g-PMACa superabsorbent in saline solutions with various concentrations

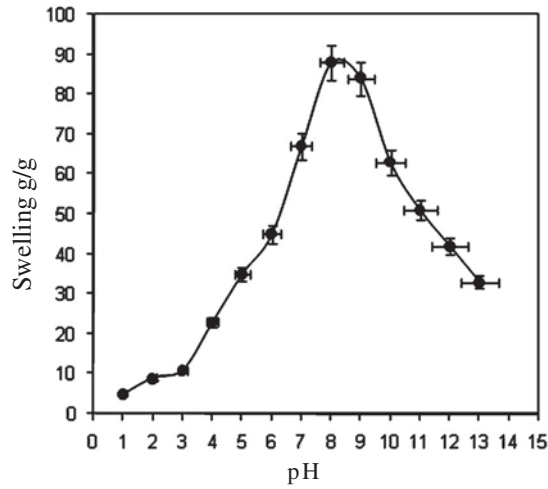


Fig. 5. Effect of pH of solutions on swelling capacity of H-carrageenan-g-PMACa hydrogel

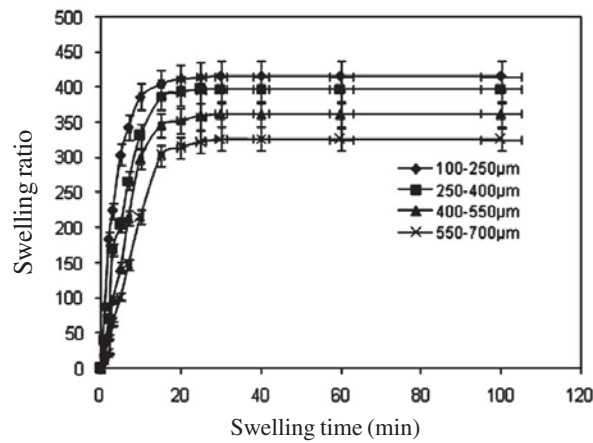


Fig. 6. Representative swelling kinetics of a superabsorbent hydrogel with various particle sizes

(Fig. 1a) shows three new characteristic absorption bands at 1660, 1562 and 1397 cm^{-1} verifying the formation of graft copolymer product⁹. These peaks attributed to carbonyl stretching of the carboxylic acid groups and symmetric and asymmetric stretching modes of carboxylate groups, respectively. The bands observed at 846, 918, 1026 and 1227 cm^{-1} can be attributed to D-galactose-4-sulfate, 3,6-anhydro-D-galactose, glycosidic linkage and ester sulfate stretching of κC backbone, respectively (Fig. 1b). The broad band at 3340 cm^{-1} is due to stretching of $-\text{OH}$ groups of κC .

Morphology of superabsorbent hydrogel

The morphology of the crosslinked hydrogel was observed by scanning electron microscope (SEM). Although the water inside the hydrogel was sublimed to make cavities, the structure of the hydrogel was preserved. Figure 2 shows an SEM micrograph of the polymeric hydrogels 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.

Effect of salinity on swelling capacity

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 repulsion⁹. Therefore, the osmotic pressure resulted from the mobile ion concentration difference between the gel and aqueous phases decreased and consequently the absorbency amounts decreased. In addition, in the case of salt solutions with multivalent cations, "ionic crosslinking" at surface of particles causing an appreciable decrease in swelling capacity. It is obvious that swelling decrease is strongly depended on the "type" and "concentration" 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. 3. With increasing the charge of cation, degree of crosslinking is increased and swelling is consequently decreased¹². Therefore, the absorbency for H-carrageenan-g-PMaCA 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. 3. As reported by Pass *et al.*⁹, the carboxylate anion interacts with small cations, e.g. Li^+ , stronger than with large cations, e.g. 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 water absorbency in monovalent and divalent cations 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.

Fig. 4 illustrates a reverse and power law relationship between concentration of salt solutions (NaCl , CaCl_2 , and AlCl_3) and swelling capacity of the hydrogel, H-carrageenan-g-PMaCA. Again, charge screening effect and ionic crosslinking are the main explanations for the intense loss of swelling. The known relationship between swelling and concentration of salt solution is stated as following equation¹²:

$$\text{Swelling} = k [\text{salt}]^{-n} \quad \dots(2)$$

where k and n are constant values for an individual superabsorbent. The k value is swelling at a high concentration of salt and n value is a measure of salt sensitivity.

Figure 4 indicates that changing of the salt concentrations higher than ~ 0.2 M has no appreciable influence on superabsorbency of the superabsorbent. As given in Table 1, the k values are almost the same (~ 8) for the swelling in various salt solutions. The n values are proportionally changes with the cation valency enhancement. Here, the effect of the ionic crosslinking acts as more effective factor against swelling rather than the charge screening effect of the cation. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems¹³.

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 H-carrageenan-g-PMaCA hydrogel was

measured in different pH solutions ranged from 1.0 to 13.0 (Fig. 5). 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 (88 g/g) was obtained at pH 8. In acidic media, the most of carboxylate groups are protonated, so decreased repulsion of anionic groups leads to a decreased swelling ratio. 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 is “charge screening effect” of excess Na⁺ in the swelling media which shield the carboxylate anions and prevent effective anion-anion repulsion. Similar swelling-pH dependencies have been reported in the case of other hydrogel systems¹³.

Kinetics of swelling

In practical applications, not only a higher swelling capacity is required, but also a higher swelling rate is needed. Buchholz has suggested that the swelling kinetics for the superabsorbents is significantly influenced by factors such as swelling capacity, size distribution of powder particles, specific size area and composition of polymer¹. Figure 13 represents the dynamic swelling behavior of H-carrageenan-*g*-PMAcA superabsorbent samples with various particle sizes in water. Initially, the rate of water uptake sharply increases and then begins to level off. The time required to reach the equilibrium swelling capacity was achieved after ~20 min. A power law behavior is obvious from Fig. 6. The data may be well fitted with a Voigt-based equation (Eq. 3):

$$S_t = S_e (1 - e^{-t/\tau}) \quad \dots(3)$$

where S_t (g/g) is swelling at time t , S_e is equilibrium swelling (power parameter, g/g), t is time (min) for swelling S_t , and τ (min) stand for the “rate parameter”. The rate parameters for superabsorbent are found to be 0.5, 1.5, 3.2 min for superabsorbent with particle sizes of 100-250, 250-400 and 400-550 μm , respectively. It is well-known

that the swelling kinetics for the superabsorbent polymers is significantly influenced by particle size of the absorbents. 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^{9,12}.

CONCLUSION

A new salt-responsive superabsorbent based on H-carrageenan-*g*-PMAcA was synthesized through crosslinking and graft copolymerization of methacrylic acid onto carrageenan. The maximum water absorbency of hydrogel is found to be 315 g/g. The study of FTIR, SEM spectra provide the graft copolymerization and crosslinking do takes place. Swelling measurement of the synthesized hydrogels in different salt solutions showed appreciable swelling capacity, especially in solutions with monovalent cations. However, swelling loss in salt solutions, in comparison with town-water, can be attributed to charge screening effect and ionic crosslinking for mono- and multi-valent cations, respectively.

REFERENCES

1. Buchholz, F.L., Graham, A.T. *Modern Superabsorbent Polymer Technology*, New York: Wiley, (1997).
2. Chu, L.Y., Kim, J.W., Shah, R.K., Weitz, D.A. *Adv. Funct. Mater.*, **17**: 3499-3504 (2007).
3. Crescenzi, V., Cornelio, L., Di Meo, C., Nardocchia, S., Lamanna, R. *Biomacromolecules*, **8**: 1844-1850 (2007).
4. J. Lin, J. Wu, Z. Yang, M. Pu, *Polymers & Polymer Composites.*, **9**: 469-471 (2001).
5. J. Wu, J. Lin, M. Zhou, C. Wei, *Macromol. Rapid Commun.*, **21**: 1032-1034 (2000).
6. Hoffman, A. S. *Polymeric Materials Encyclopedia*, Salamone, J. C.; Ed.; CRC Press, Boca Raton, FL., **5**: 3282 (1996).
7. J. Wu, Y. Wei, J. Lin, S. Lin, *Study, Polymer.*, **44**: 6513-6520 (2003).
8. Kirk RE, Othmer DF. *Encyclopedia of Chemical Technology*, Vol. 4, Kroschwitz JI, Howe-Grant M. (eds). John Wiley & Sons: New York, 942 (1992).
9. Pourjavadi A, Ghasemzadeh H, Hosseinzadeh

- H. *e-Polymers*, No. 027(2004).
10. Sadeghi, M, Yarahmadi, M, *Oriental Journal of Chemistry*, **27**(2): 417-427 (2011)
 11. Sadeghi, M, Yarahmadi, M, *Oriental Journal of Chemistry*, **27**(2): 529-536 (2011)
 12. Sadeghi, M, Yarahmadi, M, *Oriental Journal of Chemistry*, **27**(2): 453-460 (2011).
 13. G. R. Mahdavinia, A. Pourjavadi, H. Hosseinzadeh, M.J. Zohuriaan-Mehr, *Eur. Polym. J.*, **40**: 1399-1407 (2004).