

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230519269>

# PH sensitivity and swelling behavior of partially hydrolyzed formaldehyde-crosslinked poly(acrylamide) superabsorbent hydrogels

ARTICLE *in* JOURNAL OF APPLIED POLYMER SCIENCE · JULY 2008

Impact Factor: 1.77 · DOI: 10.1002/app.28205

---

CITATIONS

23

---

READS

112

6 AUTHORS, INCLUDING:



**Gholam Bagheri Marandi**

University of Tehran

29 PUBLICATIONS 215 CITATIONS

SEE PROFILE



**Saeid Sadeh**

University of British Columbia - Vancouver

4 PUBLICATIONS 43 CITATIONS

SEE PROFILE



**Gholam Reza Mahdavinia**

University of Maragheh

43 PUBLICATIONS 833 CITATIONS

SEE PROFILE

# pH Sensitivity and Swelling Behavior of Partially Hydrolyzed Formaldehyde-Crosslinked Poly(acrylamide) Superabsorbent Hydrogels

G. Bagheri Marandi,<sup>1,2</sup> K. Esfandiari,<sup>1</sup> F. Biranvand,<sup>1</sup> M. Babapour,<sup>1</sup> S. Sadeh,<sup>1</sup> G. R. Mahdavinia<sup>3</sup>

<sup>1</sup>Department of Chemistry, Islamic Azad University, Karaj, Iran

<sup>2</sup>Department of Soil Science, Faculty of Agriculture, University of Tehran, Karaj, Iran

<sup>3</sup>Faculty of Science, Department of Chemistry, University of Maragheh, Maragheh, Iran

Received 21 May 2007; accepted 3 December 2007

DOI 10.1002/app.28205

Published online 15 April 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Poly(acrylamide) superabsorbent hydrogel was synthesized through crosslinking method. Formaldehyde was used as a crosslinking agent. To achieve a hydrogel with high swelling capacity, the resulted hydrogels were saponified using NaOH solution at high temperature. During saponification, ammonia gas is produced from hydrolysis reaction of amide groups. The arising of ammonia produces porous structure in hydrogels, which is confirmed using scanning electron microscopy. The conversion of amide groups to carboxylate groups was identified by FTIR spectroscopy. The reaction variables in both crosslinking and hydrolysis reactions that affect the swelling of hydrogels were optimized. The swelling of the hydrogels in vari-

ous salt solutions with various valencies and radii was studied. Also, the absorbency under load was measured. The hydrogels exhibited pH-sensitivity characteristics. A sharp swelling change was observed in lieu of pH variations in a wide range (1–13). The swelling variations were explained according to the swelling theory based on the hydrogel chemical structure. The pH-reversibility and on-off switching behavior makes the intelligent hydrogels as good candidates for considering as potential drug carries. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1083–1092, 2008

**Key words:** poly(acrylamide); hydrogel; crosslinking; pH-sensitivity; swelling

## INTRODUCTION

Superabsorbent polymers are loosely crosslinked networks that can absorb a large amount of water in a short time and retain water under pressure.<sup>1</sup> Superabsorbent hydrogels have been paid much more attention in recent years for its wide application in many fields, such as drug delivery system,<sup>2</sup> separation processes,<sup>3</sup> stimulus responsive materials,<sup>4</sup> disposable diapers,<sup>5</sup> and soil-improvement agent.<sup>6</sup> The hydrogels responding to external stimuli such as heat, pH, electric field, chemical environments, etc., are often referred as intelligent or smart hydrogels.<sup>7</sup> Among these, pH-sensitive hydrogels have been extensively investigated for potential applications in controlled release systems. All the pH-responsive polymers contain pendant acidic (e.g., carboxylic) or basic (e.g., amine) groups that release or accept protons in response to change in environmental pH.

Poly(acrylamide) (PAAm) hydrogels and their derivatives is the subject of many studies.<sup>8–10</sup> PAAm hydrogels have proven capability of water absorption and biocompatibility with physiologic body fluids. Many routes were reported by researchers to prepare hydrogels based on PAAm. The polymeriza-

tion or copolymerization of acrylamide monomer in the presence of crosslinker is the main route.<sup>11–13</sup>

Researchers<sup>14,15</sup> have investigated the mechanism of crosslinking and thermal behavior of PAAm with formaldehyde using <sup>13</sup>C NMR and differential scanning calorimetry. They have suggested that crosslinking of PAAm using formaldehyde can take place inter- or intra-molecular. At high temperature, intra-molecular crosslinking takes place.<sup>14</sup>

The main aim of this work is to study hydrogel formation of PAAm using formaldehyde as crosslinker and investigate the effect of synthesis condition as well as the swelling media on the swelling capacity of hydrolyzed PAAm hydrogels. Therefore, first we attempt to investigate the effect of reaction variables (crosslinking and hydrolysis conditions) on the swelling of hydrolyzed PAAm hydrogels. Then, we investigated the effect of ionic media on the swelling of hydrolyzed PAAm hydrogels. In addition, the pH-sensitivity and pH-reversibility of the hydrogel as well as the absorbency under load (AUL) were investigated.

## EXPERIMENTAL

### Materials

PAAm was synthesized through the method mentioned in the literature.<sup>16</sup> In brief, AAm (Merck, Ger-

Correspondence to: G. B. Marandi (marandi@kiaui.ac.ir).

**TABLE I**  
**Effect of Reaction Variables in Both Crosslinking and Hydrolysis**  
**Conditions on the Sol%**

Temperature (°C)				Time (min)				NaOH	
T-C	Sol%	T-H	Sol%	t-C	Sol%	t-H	Sol%	Normality	Sol%
65	12.4	60	4.5	30	13.1	15	3.4	0.5	3.5
75	7.5	70	7.2	60	9.7	30	5.5	1	4.2
85	4.1	80	9	90	7.1	45	6.8	1.5	6.5
95	2.5	90	14.5	120	4.7	75	13	2	10.5
–	–	–	–	150	2.3	105	15.5	2.5	15

T-C: Temperature of Crosslinking; T-H: Temperature of Hydrolysis, t-C: time of Crosslinking; t-H, time of Hydrolysis.

many) solution was prepared in a 1-L three-necked reactor equipped with mechanical stirrer, gas inlet, and reflux condenser. Thirty grams of AAm was dissolved in 300 mL of distilled water and degassed for 15 min using N<sub>2</sub> gas. To control the reaction temperature, the reactor was placed in a water bath preset at 60°C. Then, 0.2 g of potassium persulfate (Fluka, Switzerland) was added to the AAm solution and allowed to complete the polymerization at 60°C for 2 h. The resulted PAAm was poured into 1 L of ethanol for dewatering for 24 h. After this time, dewatered PAAm was dried at 80°C in an oven for constant weight. To crosslink PAAm, formaldehyde (Merck, 37%) was used without purification. All other materials (Merck) were used as received.

### Synthesis of PAAm hydrogels

PAAm (5.0 g) was added in 100 mL of distilled water and it was stirred to achieve a homogenous solution. The pH of this solution was adjusted at 5 using HCl. To control the reaction temperature (65–95°C), the reactor was placed in a thermostated water bath. Then, desired concentration of formaldehyde aqueous solution (1.85–4.32 mM) was added to the mixture. The crosslinking reaction was allowed to proceed for desired time (30–180 min). Crosslinked polymer was allowed to cool to room temperature and then was poured in ethanol (500 mL) and allowed to dewater for 48 h. The dewatered hydrogel was dried at 50°C in an oven to constant weight.

The crosslinked polymer (2 g) was then saponified using 50 mL aqueous NaOH solution (0.5–2.5N) in a three-necked reactor fitted with a mechanical stirrer and a reflux condenser at the desired temperature (hydrolysis temperature = 60–90°C). The mixture was allowed to stir for a certain time (alkalization time: 15–180 min). The hydrolyzed PAAm product was allowed to cool to ambient temperature and neutralized to pH 8.5 by addition of 10 wt % acetic acid solution. Ethanol (300 mL) was added to the gel product while stirring. After complete dewatering (for 24 h), the product was filtered, washed with

fresh ethanol (2 × 50 mL), and dried in an oven at 50°C.

### Sol content measurement

A certain amount of dried hydrogel (0.10 g) was put into distilled water for 48 h. Then the swollen hydrogels were filtered and poured in 200 mL ethanol for dewatering. Then, the hydrogels were dried in an oven at 50°C for constant weight. The lost weight in hydrogel content is attributed to the sol content [(lost weight/initial weight of hydrogel) × 100]. The results of these experiments were illustrated in Table I.

### Swelling measurements

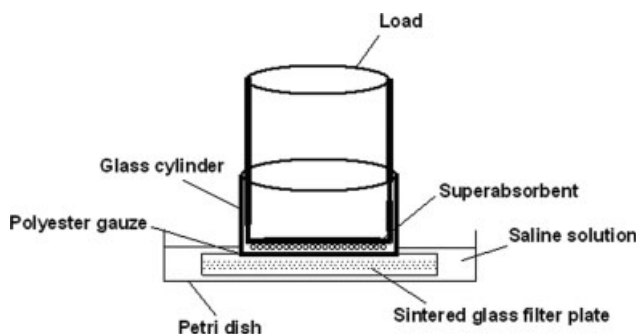
A certain amount (0.1 ± 0.001 g) of hydrogel sample with certain average particle sizes was put into a weighed tea bag (i.e., a 100-mesh nylon screen) and immersed in 100 mL distilled water, in buffer solution (30 mL) or in salt solution (30 mL), and allowed to soak for 2 h at room temperature. The equilibrated swollen gel was allowed to drain by removing the tea bag from water (~ 20 min). The bag was then weighed to determine the weight of the swollen gel. The absorbency (equilibrium swelling) was calculated using the following equation:

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

where  $W_s$  and  $W_d$  are the weights of the samples swollen in water and in dry state, respectively.

### Absorbency under load

AUL was measured using a piston assembly allowing addition of weights on top of the superabsorbent sample. These series of experimental were done in Sharif University of Technology in Iran. This system is similar to the apparatus that is used in Iran Polymer and Petroleum Institute.<sup>17</sup> The used apparatus was shown in Scheme 1.<sup>17</sup> A macroporous sintered glass filter plate (porosity 0,  $d = 80$  mm,  $h = 7$  mm)



**Scheme 1** The apparatus used for determination of Absorbency of Under Load (Ref. 17).

was placed in a petri dish ( $d = 118$  mm,  $h = 12$  mm), and weighed dried hydrogel ( $0.5 \pm 0.01$  g) was uniformly placed on the surface of polyester gauze located on the sintered glass. A cylindrical solid load (Teflon,  $d = 60$  mm, variable height) was put on the dry hydrogel particles while it can be freely slipped in a glass cylinder ( $d = 60$  mm,  $h = 50$  mm). Desired load (applied pressure 2068, 4137, and 6205 Pa) was placed on the hydrogel sample. Then, 0.9% saline solution was added so that the liquid level was equal to the height of the sintered glass filter. Whole of the set was covered to prevent surface evaporation and probable change in the saline concentration. After 60 min, the swollen particles were weighed again, and AUL was calculated according to eq. (1).

### pH reversibility

pH reversibility of the hydrogel was investigated in terms of swelling and deswelling of the final product at two basic (pH 8.0) and acidic (pH 2.0) solutions, respectively. Swelling capacity of the hydrogels at each pH was measured according to eq. (1) at consecutive time intervals (30 min).

### Swelling kinetic

For studying the absorbency rate of the hydrogels, certain amount of samples ( $0.1 \pm 0.001$  g) with various particle sizes were poured into numbers of weighed tea bags and immersed in 200 mL distilled water. At consecutive time intervals, the water absorbency of the hydrogels was measured according to the aforementioned method.

### FTIR spectroscopy and SEM micrographs

FTIR spectra of samples were taken in KBr pellets using an ABB Bomem MB-100 FTIR spectrophotometer. The hydrogel was analyzed by scanning electron microscopy (Philips, Model Stemi SV8).

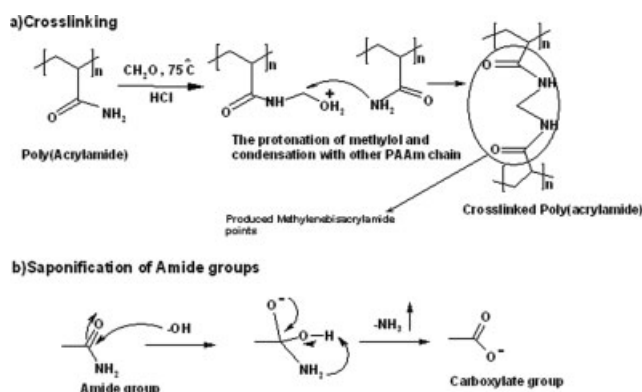
## RESULTS AND DISCUSSIONS

### Synthesis and characterization

PAAm hydrogels was synthesized through crosslinking of PAAm using formaldehyde as crosslinker [Scheme 2(a)]. In the reaction between PAAm and formaldehyde at acidic pH and high temperature, crosslinking is due to methylene bisacrylamide formation intramolecularly.<sup>14</sup> In acidic pH, formaldehyde reacts with amide groups to produce methylol. These methylols react through condensation with other amide groups of other PAAm chains.<sup>15</sup> Three-dimensional PAAm hydrogel contains hydrophilic amide groups ( $-\text{CONH}_2$ ). To achieve a hydrogel with high swelling capacity, crosslinked PAAm was saponified. During saponification the amide groups convert to carboxylate groups. Under this reaction the ammonia gas evolves from the mixture [Scheme 2(b)].

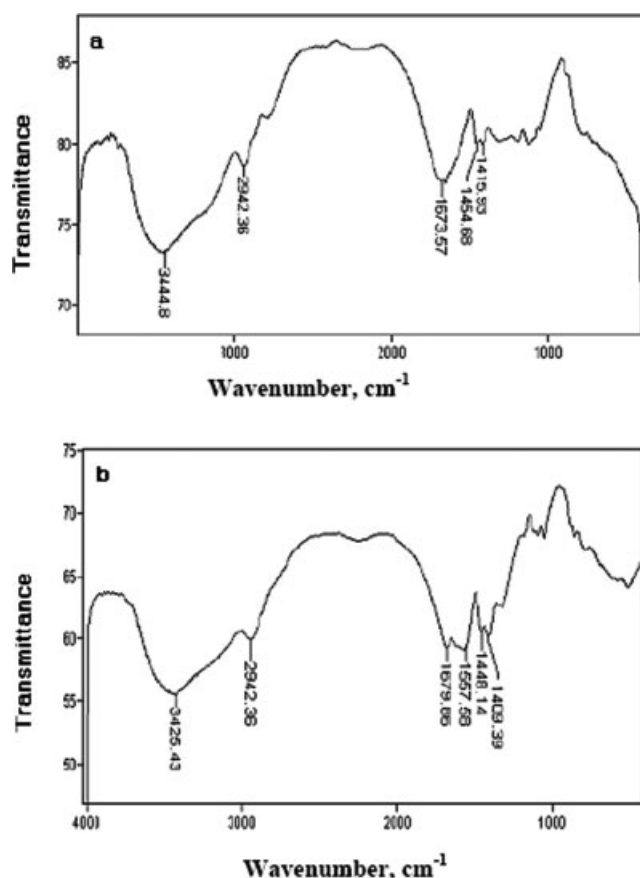
For identification and characterization of the PAAm hydrogels, FTIR spectroscopy and SEM micrograph were used. In the spectrum of the non-hydrolyzed hydrogel [Fig. 1(a)], the peaks at  $\sim 3200$  and  $1673$   $\text{cm}^{-1}$  can be attributed to NH stretching and carbonyl stretching in carboxamide functional groups, respectively.<sup>18</sup> In the spectrum of hydrolyzed hydrogel [Fig. 1(b)], the very intense characteristic band at  $1557$   $\text{cm}^{-1}$  is due to C=O asymmetric stretching in carboxylate anion that is reconfirmed by another sharp peak at  $\sim 1409$   $\text{cm}^{-1}$  which is related to the symmetric stretching mode of the carboxylate anion. This confirmed the conversion of amide groups ( $-\text{CONH}_2$ ) to the carboxylate functional groups ( $-\text{COO}^-$ ).

The SEM micrographs of crosslinked PAAm and partially hydrolyzed PAAm hydrogels are shown in Figure 2. The hydrolyzed PAAm hydrogels shows a porous surface [Fig. 2(c,d)]. However, a relatively planar surface with some pleats was generated when PAAm is crosslinked with formaldehyde [Fig. 2(a,b)].



**Scheme 2** (a) Crosslinking of PAAm chains to form methylenebisacrylamide groups and (b) proposed mechanism for saponification of amide with hydroxyl to produce carboxylate group.





**Figure 1** Infrared spectrum of crosslinked PAAm (a), and hydrolyzed PAAm hydrogel (b).

The porous surface of the hydrolyzed hydrogel may be attributed to the evolving of ammonia gas during saponification reaction.

### Study of reaction variables on swelling

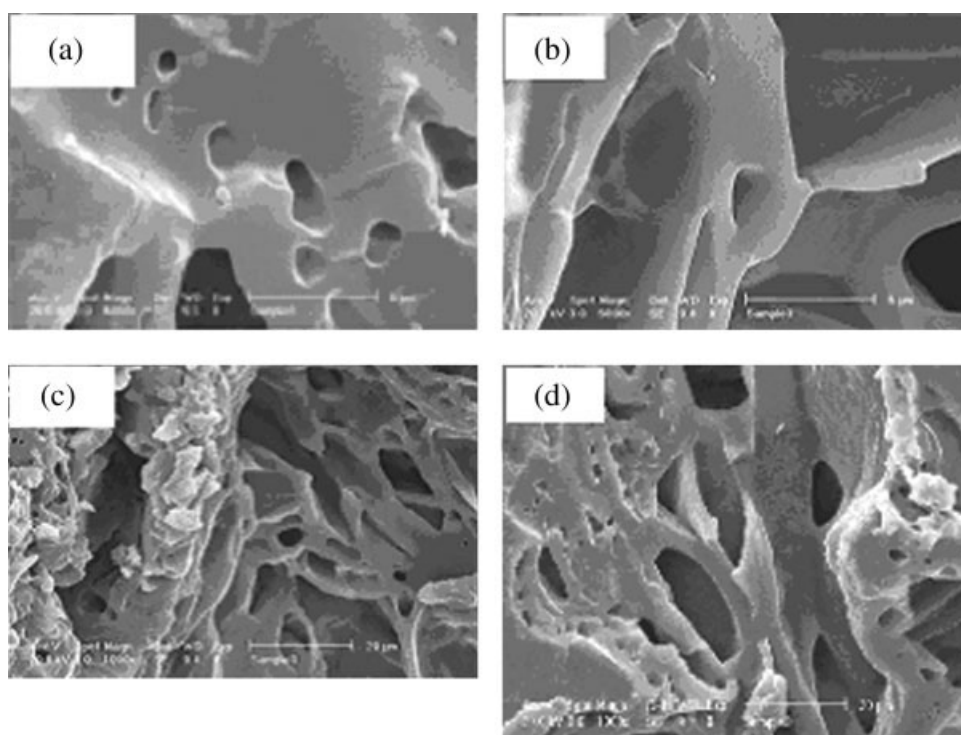
The relationship between the swelling ratio and network structure parameters given by Flory is usually used as the following equation<sup>19</sup>:

$$q_m^{5/3} \cong \frac{(i/2v_u S^{*1/2}) + (1/2 - \chi_1)v_1}{v_e/V_0} \quad (2)$$

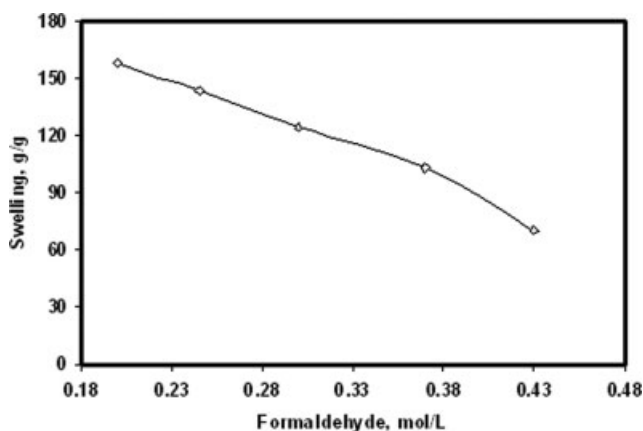
Here,  $i/2v_u$  is the concentration of the fixed charges of the unswollen networks, and  $S^*$  is the ionic strength in the external solution;  $v_e/V_0$  is the cross-link density which refers to the number of effectively crosslinked points between chains in unit volume. The term  $(1/2 - \chi_1)v_1$  represents the interaction parameter, i.e., affinity of the hydrogel to water. The  $q_m$  term is the swelling ratio of the hydrogel.<sup>20</sup>

### Effect of crosslinker on swelling

The effect of the extent of crosslinking on water absorbency of hydrolyzed PAAm hydrogel is shown in Figure 3. In this series of reactions, the formaldehyde concentration was varied from 1.85 to 4.32 mM. According to this figure, with increase in crosslinker concentration, the water absorbency is



**Figure 2** SEM micrographs of crosslinked PAAm (a and b) and hydrolyzed PAAm hydrogels (c and d).

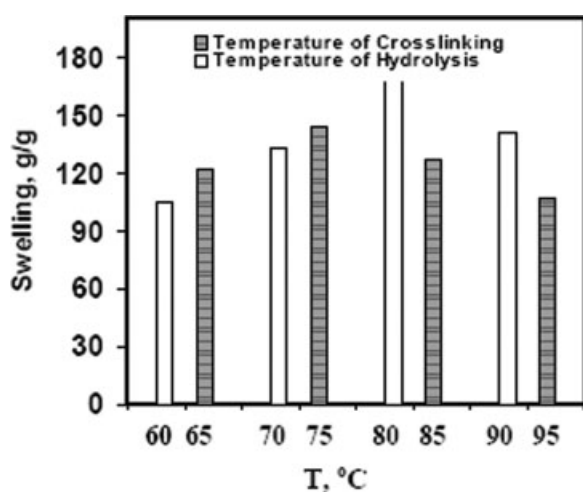


**Figure 3** Swelling dependency of PAAm hydrogel on formaldehyde crosslinker concentrations. Crosslinking conditions: PAAm, 5 g; time, 105 min;  $T = 75^\circ\text{C}$ ; pH 5. Hydrolysis conditions: NaOH, 1N; time, 60 min;  $T = 80^\circ\text{C}$ .

decreased. Higher crosslinker concentration produces more crosslinked points in polymeric chains and increases the extent of crosslinking of the polymer network, which results in less swelling when it is brought into contact with water. Similarly Li and Wang have reported similar observation for superabsorbent composite.<sup>21</sup> According to the eq. (2), at high values of crosslinker, the  $v_e/V_0$  parameter was increased. So, the water absorbency ( $q_m$ ) is decreased.

#### Effect of temperature on swelling

Effect of temperature on the water absorbency of the hydrogels was studied in both crosslinking and hydrolysis conditions (Fig. 4). In the case of crosslink-



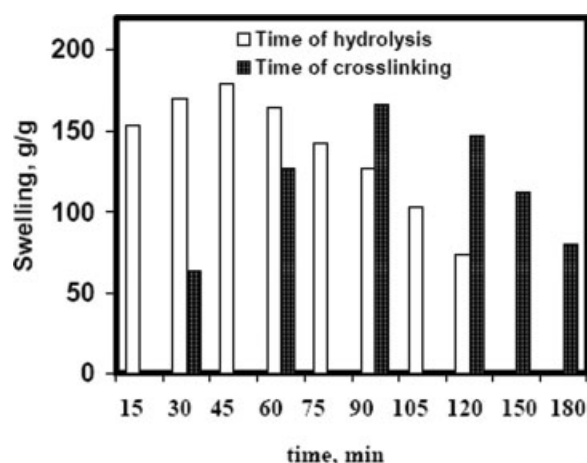
**Figure 4** Effect of crosslinking and hydrolysis temperature on the swelling of PAAm hydrogels. Crosslinking conditions: PAAm, 5 g; formaldehyde, 1.85 mM; time, 105 min; pH 5. Hydrolysis conditions: NaOH, 1N; time, 45 min.

ing temperature, the water absorbency is increased up to  $75^\circ\text{C}$ . The results of Table I indicate that with increasing the temperature of crosslinking reaction up to  $75^\circ\text{C}$ , the sol content is decreased. So, increase in swelling is attributed to the decrease in sol content. But beyond  $75^\circ\text{C}$ , in spite of decrease in sol content, the water absorbency is decreased. It may be attributed to producing of more crosslinking points.<sup>14</sup>

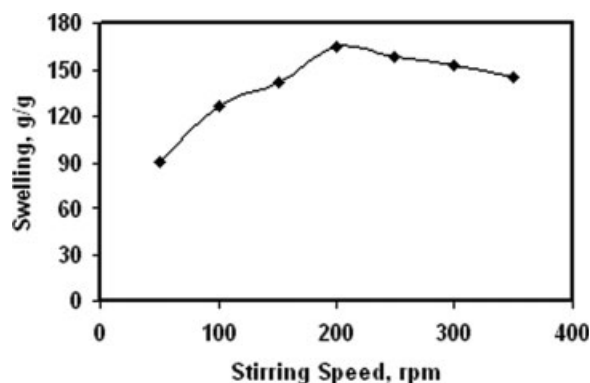
The effect of temperature of hydrolysis on water absorbency of the hydrogels shows that the swelling is increased up to  $80^\circ\text{C}$ . In spite of increase in sol content with increasing the temperature of hydrolysis, the water absorbency is increased. It is well known that high temperature favors the kinetic of converting of amide to carboxylate up to  $80^\circ\text{C}$  [high fixed charges on the hydrogel ( $i/2v_u$ ) are produced]. The higher the anionic groups in hydrogel, the higher is the water absorbency. Increase in sol content may be attributed to the attack of hydroxyl groups to crosslink point and subsequently polymeric chains part with each other. The temperature higher than  $80^\circ\text{C}$ , however, leads to low swelling of hydrogels. According to Table I, the sol content is increased in high content beyond  $80^\circ\text{C}$ . This decrease in swelling may be attributed to some sort of unwanted alkaline degradation of the polymer chains of the hydrogel occurring at high temperature.

#### Effect of reaction time on swelling

The effect of reaction time of crosslinking and hydrolysis on the swelling is shown in Figure 5. In the crosslinking reaction, water absorbency of the hydrogel increased with increasing time up to 90 min. The



**Figure 5** Effect of crosslinking and hydrolysis time on the swelling capacity of the synthesized hydrogel. Crosslinking conditions: PAAm, 5 g; formaldehyde, 1.85 mM; pH 5. Hydrolysis conditions: NaOH, 1N; temperature,  $80^\circ\text{C}$ .



**Figure 6** Swelling dependencies of hydrogels on stirring speed of crosslinking and hydrolysis reactions. Crosslinking conditions: polyacrylamide, 5 g; formaldehyde, 1.85 mM; time, 90 min; pH 5. Hydrolysis conditions: NaOH, 1N; time, 60 min; temperature, 80°C.

results of Table I show that with increasing the time of reaction, the sol content is decreased. Low sol content causes high swelling capacity. But, beyond 90 min, in spite of decrease in sol content, the water absorbency is decreased which can be attributed to produce more crosslink points in hydrogel. According to eq. (2), more crosslink points in hydrogel result in low swelling capacity.

As shown in Figure 5, swelling of the hydrogel is increased by increasing the time of hydrolysis from 15 to 45 min, and then decreased. The increase of water absorbency up to 45 min is attributed to: (a) increase of carboxylate groups ( $i/2v_{ii}$  in eq. (2)). Wu et al. have reported similar conclusion in the hydrolysis of starch-g-PAAm/mineral powder.<sup>22</sup> They have demonstrated that with increasing time of hydrolysis, the carboxylate groups are increased. (b) In the presence of alkaline, some crosslink points are attacked by hydroxyl groups of soda and so the crosslink density is decreased. Decrease in crosslink density causes the high swelling capacity. When the time increases to more than 45 min, the water absorbency is decreased, that is, in agreement with increase in sol content. Also, this decrease in swelling may be attributed to the unwanted alkaline degradation of the crosslink point and subsequently the polymeric chains part with each other. This phenomenon causes high sol content (Table I).

#### Effect of stirring speed on swelling

The influence of stirring speed of both crosslinking and hydrolysis reaction was studied. In the crosslinking reaction, the water absorbency is increased significantly for stirrer rates from 50 to 200 rpm and then decreased gradually (Fig. 6). The swelling enhancement from 50 to 200 rpm attributed to effective mixing and mass transfers. However, the higher

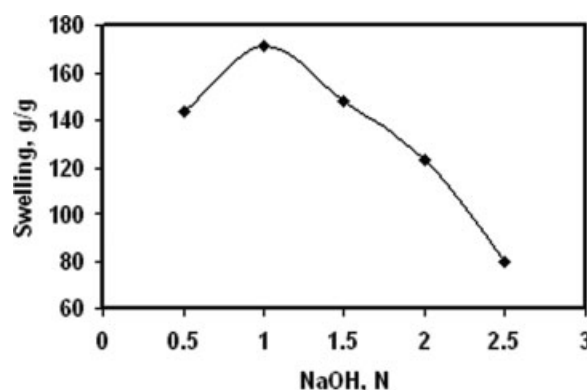
rpm shear forces may be also degrading the macromolecular chains, leading to decrease in molecular weight and subsequent loss of swelling. The result of hydrolysis reaction is similar to crosslinking reaction. In fact, the saponification reaction speed from 50 to 200 rpm results in increasing of water absorbency, but beyond 200 rpm, the higher rpm shear forces may degrade the macromolecular chains leading to decrease in molecular weight and subsequent loss of swelling. These results are similar to the conclusions that have been reported by Hosseinzadeh et al.<sup>23</sup>

#### Effect of NaOH concentration on swelling

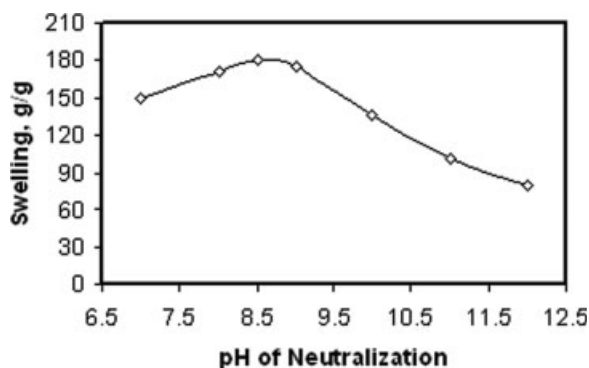
The alkaline hydrolysis of crosslinked PAAm was performed using different concentrations of the hydroxyl ion, ranging from 0.5 to 2.5N. Optimum water absorbency was achieved at 1.0N of NaOH solution (Fig. 7). The increase in swelling with increasing soda concentration up to 1N is attributed to (a) the enhancement of the carboxylate anions,<sup>24</sup> and (b) the increase in soda concentration causes the degradation of crosslink point, which causes the reduction of crosslink density and therefore the swelling is increased. The effect of high concentration of soda on degradation of crosslink point is clearly obvious according to Table I. As shown in this table, higher than 1N, the sol content is increased sharply. In fact, at high soda concentration, the polymeric chains easily part with each other and causes high sol content.

#### Effect of postneutralization

In this series of experiments, after the alkaline hydrolysis, excess NaOH was neutralized by acetic acid solution to a desired pH value (Fig. 8). Without the postneutralization stage ( $\text{pH} > 9$ ), the decreased



**Figure 7** Swelling dependency of the synthesized hydrogel as a function of NaOH concentration. Crosslinking conditions: polyacrylamide, 5 g; formaldehyde, 1.85 mM; temperature, 75°C; pH 5; time, 90 min. Hydrolysis conditions: time, 60 min, temperature 80°C.

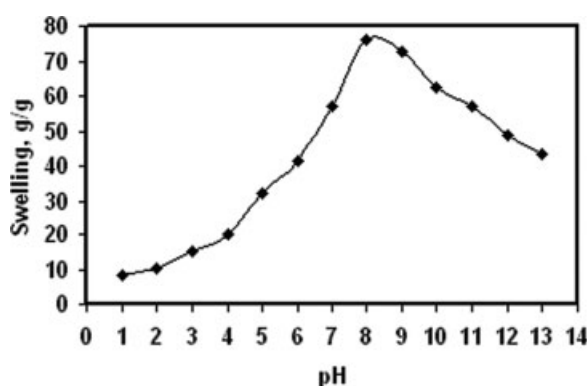


**Figure 8** Effect of neutralizing pH on swelling capacity of the synthesized hydrogel. Crosslinking conditions: polyacrylamide, 5 g; formaldehyde, 1.85 mM; temperature, 75°C; pH 5; time, 90 min. Hydrolysis conditions: NaOH, 1N; time, 45 min; temperature, 80°C.

absorbency is related to screening effect of excess  $\text{Na}^+$  ions in the swelling.<sup>19</sup> In acidic media, a similar behavior is observed because of different phenomena. At pH 8–8.5, the carboxylate groups become completely ionized, and the electrostatic repulsive force between the charged sites ( $\text{COO}^-$ ) causes an increase in swelling. According to Figure 8, the best pH adjusted after hydrolysis was found to be 8.5.

#### pH responsiveness and pulsatile swelling behavior of hydrolyzed hydrogel

Partially hydrolyzed PAAm hydrogels contain carboxylate groups ( $-\text{COO}^-$ ) that either accept or release protons in response to changes in environmental pH.<sup>25</sup> Swelling of the hydrogels was measured in solutions buffered at various pH values, from 1.0 to 13.0. The maximum swelling of the hydrogel (76.1 g/g) was achieved at pH 8 (Fig. 9). The partially hydrolyzed hydrogel comprises carboxylate groups ( $-\text{COO}^-$ ). The  $\text{pK}_a$  value of the carboxylic acid is  $\sim 4.7$ . So, the carboxylic groups are ionized at  $\text{pH} > 4.7$ , while at  $\text{pH} < 4.7$ , they will be



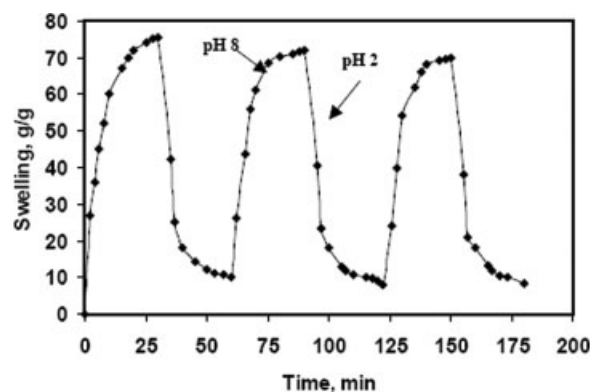
**Figure 9** Effect of pH of solutions on the swelling capacity of the optimized hydrogel.

protonated. At higher pH (above the  $\text{pK}_a$  of carboxylic groups), the carboxylic acid groups become ionized and the electrostatic repulsive force between the charged sites ( $\text{COO}^-$ ) causes an increase in swelling (increase in  $i/2v_u$  term). Under acidic pH ( $\text{pH} < 4.7$ ), most of the carboxylate anions are protonated, and so the main anion–anion repulsive forces are eliminated and consequently swelling values are decreased. At pH 8, the carboxylic acid groups become completely ionized and the electrostatic repulsive force between the charged sites ( $\text{COO}^-$ ) causes an increase in swelling. However, at basic conditions ( $\text{pH} > 8$ ), a screening effect of the counter ions, i.e.,  $\text{Na}^+$ , shields the charge of the carboxylate anions and prevents an efficient repulsion [according to eq. (2) increase in  $S^*$  results in decrease of swelling]. As a result, a remarkable decrease in equilibrium swelling is observed (gel collapsing).

The pH-dependent swelling reversibility of the hydrogels was examined in buffered solutions (Fig. 10). The figure demonstrates the hydrogel reversibility to absorb water upon changing the pH in acidic and basic region (pH 8 and 2). At pH 8, the hydrogel swells up to 75 g/g because of anion–anion repulsive electrostatic force, while at pH 2 it shrinks within few minutes because of the protonation of carboxylate groups. This sudden and sharp swelling–deswelling behavior at different pH values makes the system highly pH-sensitive and suitable for tailoring pulsatile (on–off swelling) drug-delivery systems.

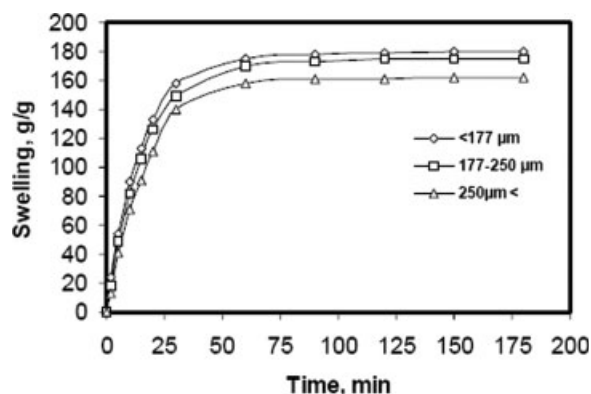
#### Swelling kinetics

Particle size of hydrogels is an effective parameter that affects the swelling of the superabsorbent hydrogels. So, in these series of experiments, we examined the swelling of the hydrogel as a function of particle sizes. According to Figure 11, the swelling values versus swelling time follow a power law trend.



**Figure 10** On–off switching behavior as reversible pulsatile swelling (pH 8.0) and deswelling (pH 2.0) of the optimized hydrogel.



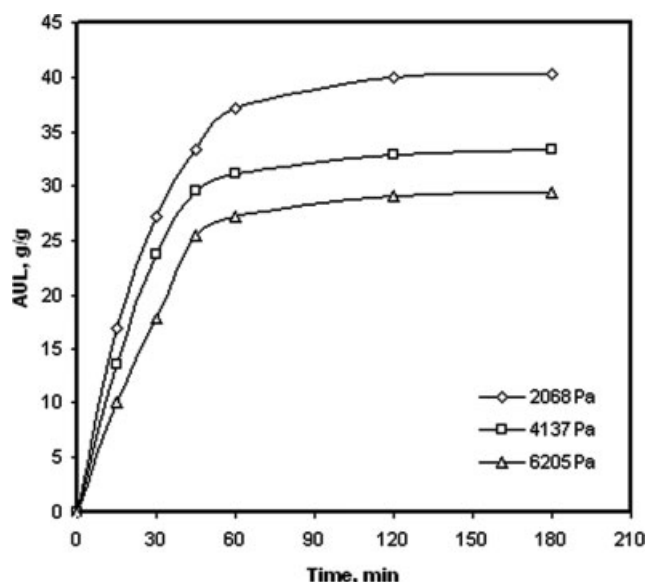


**Figure 11** Representative swelling kinetics of the optimized hydrogel.

A "Voigt-based model" may be used for fitting the data.<sup>26</sup>

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

$S_t$  (g/g) is the swelling in time  $t$  (min),  $S_e$  is the equilibrium swelling (power parameter; g/g), and  $\tau$  (min) is the rate parameter. The power parameters according to Figure 11 are 162, 175, and 180 g/g for  $>250$ , 177–250, and  $<177$   $\mu\text{m}$  of particle sizes, respectively. To calculate the rate parameter, by using the above formula and a little rearrangement, one can plot  $\ln[1 - (S_t/S_e)]$  versus time ( $t$ ). The slope of the straight line fitted (slope =  $-1/\tau$ ) gives the rate parameter ( $\tau = 23.2$ , 10.4, and 9.1 min for  $>250$ , 177–250, and  $<177$   $\mu\text{m}$  of particle sizes, respectively). It should be pointed out that the rate parameter (which is a measure of the swelling rate) is totally dependent upon the particle size of the swelling gel. With



**Figure 12** Time dependence of the AUL values for optimized sample with 177–250  $\mu\text{m}$  particle sizes.

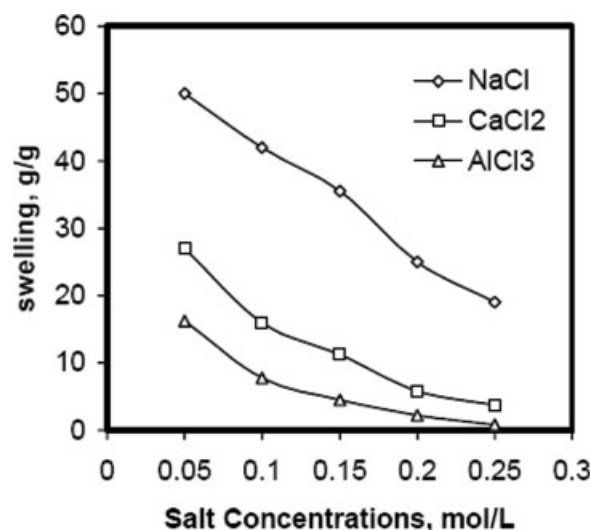
decrease in particle size, the rate parameter is decreased. This indicates that permeation resistance became smaller as the particle size becomes smaller, presumably as a result of the increase in surface area accessible to the water.

#### Absorbency under load

AUL is an important factor in the practical application of superabsorbents to determine the swollen gel strength.<sup>17,27</sup> The absorbencies measured under different loads are shown in Figure 12. As shown, the minimum time needed for the highest AUL in the case of each load was determined to be  $\sim 60$  min. After this time, the AUL values were unchanged. In addition, the curves expectedly exhibit that AUL decreases with increasing the amount of loading.

#### Swelling in salt solutions

Figure 13 shows the effect of salt solution concentration on the swelling behavior of the hydrogels. The increase of ionic strength in the solution leads to a decrease in the swelling ratio of the hydrogels. The behavior can be explained on the basis of osmotic pressure or screening effect developed because of unequal distribution of ions in the medium and the polymer network.<sup>28</sup> The ions attached to the polymer network are immobile and considered to be separated from the external solution by a semipermeable membrane. When the hydrogels are placed in water, there is maximum osmotic pressure developed and hence the maximum swelling. When the polymer is in salt solutions the osmotic pressure developed is much lower because the external solution contains



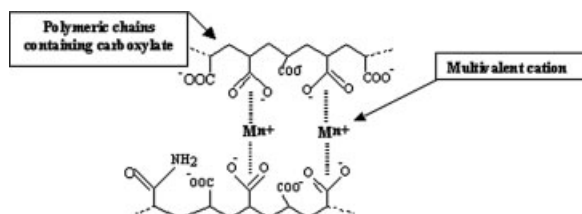
**Figure 13** Swelling capacity variation of the optimized hydrogel in various salt solutions with different concentrations.

$\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Cl}^-$  (increase in  $S^*$  in eq. (2) causes a decrease in swelling). So the swelling is drastically reduced. As shown in this figure, the swelling capacity decreases with an increase in charge of the metal cation ( $\text{Al}^{3+} < \text{Ca}^{2+} < \text{Na}^+$ ). This can be explained by the exchange capacities of the different valency cations. The higher the cation valency, the higher is the exchange capacity of the cation. It may be explained by the complexing ability arising from the coordination of the multivalent cations with carboxylate groups (Scheme 3). Anionic groups from various polymeric chains connected together electrostatically through multivalent cations and subsequently result in high crosslink points in hydrogel composition. This ionic crosslinking mainly occurs at the surface of particles and makes them rubbery and very hard when they swell in  $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$  solutions, respectively. In contrast, the hydrogel particles swollen in NaCl solution and water exhibit lower strength of swelled gel.

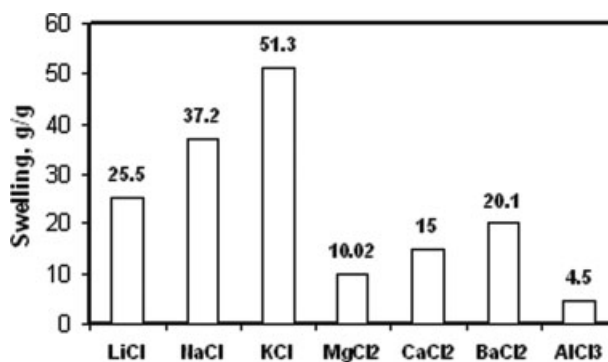
The effect of cation radius on swelling can also be observed from Figure 14. As reported by Pass et al.,<sup>29</sup> the carboxylate anion interacts with small cations, e.g.,  $\text{Li}^+$ , stronger than with large cations, e.g.,  $\text{K}^+$ . The stronger interactions of carboxylate–small cation 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  $\text{KCl} > \text{NaCl} > \text{LiCl}$  and  $\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ , respectively.

## CONCLUSIONS

We prepared hydrogels composed of PAAm by crosslinking with formaldehyde. In our reaction conditions,  $-\text{CO}-\text{NH}-\text{CH}_2-\text{NH}-\text{CO}-$  crosslink is formed from reaction of amide groups and formaldehyde. The optimum conditions of crosslinking reaction were achieved at  $75^\circ\text{C}$ , 200 rpm of stirring speed, pH 5, and 90 min crosslinking time. In the hydrolysis reaction, 200 rpm of stirring speed,  $t = 80^\circ\text{C}$ , 1N of NaOH concentration, 45 min time of hydrolysis, and pH of postneutralization 8.5 were optimum conditions. The swelling of the hydrogels



**Scheme 3** Crosslinking interactions between multivalent metal cations and anionic groups of hydrolyzed PAAm hydrogel.



**Figure 14** Swelling capacity variation of the optimized hydrogel in various salt solutions with same concentrations (0.15 mol/L).

in salt solution indicates that increase in salt concentration causes a decrease in water absorbency. Also, the results show that increase in radius of cations of salts (salt solutions with same concentration and same anions) leads to increase in the swelling capacity of the hydrogel. In addition, the water absorbency of the hydrogels exhibits that AUL decreases with increasing the amount of loading. The pH reversibility of the swelling–deswelling process (pH 2.0 and 8) was also studied. The abrupt pH-dependency of the swelling might be a key factor to their successful application in many technologies, such as controlled delivery of bioactive agents. Therefore, besides superabsorbency, PAAm hydrogels can also be considered as good candidates for designing drug-delivery systems.

## References

- Po, R. J. *Macromol Sci Rev Macromol Chem Phys* 1994, C34, 607.
- Park, S. E.; Nho, Y. C.; Lim, Y. M. *J Appl Polym Sci* 2004, 91, 636.
- Cussler, E. L.; Stokar, M. R.; Varberg, J. E. *AIChE J* 1984, 30, 578.
- Brannon, P. L.; Peppas, N. A. *Chem Eng Sci* 1991, 46, 715.
- Dursun, S.; Erdener, K.; Olgun, G. *Polym Bull* 1998, 41, 577.
- Donlar Corporation, U.S. Pat. 5,998,491 (1999).
- Kost, J. In *Encyclopedia of Controlled Drug Delivery*, Vol. 1; Mathiowitz E., Ed.; Wiley: New York, 1999; p 445.
- Saraydin, D.; Karadag, E.; Oztop, N.; Guven, O. *Biomaterials* 1994, 15, 917.
- Saraydin, D.; Karadag, E.; Cetinkaya, S.; Guven, O. *Radiat Phys Chem* 1995, 46, 1049.
- Karadag, E.; Saraydin, D.; Guven, O.; *Macromol Mater Eng* 2001, 286, 34.
- Guyen, O.; Sen, M.; Karadag, E.; Saraydin, D. *Radiat Phys Chem* 1999, 56, 381.
- Kasgoz, H.; Ozgumus, S.; Orbay, M. *Polymer* 2003, 44, 1785.
- Yao, K. J.; Zhou, W. J. *J Appl Polym Sci* 1994, 53, 1533.
- Fong, D. W.; Kowalski, D. J. *J Polym Sci Part A: Polym Chem* 1993, 31, 1625.
- Singhal, R.; Sachan, S.; Rai, J. S. P. *Iran Polym J* 2002, 11, 143.
- Lin, H. R. *Eur Polym J* 2001, 37, 1507.

17. Ramazani-Harandi, M. J.; Zohuriaan-Mehr, M. J.; Yousefi, A. A.; Ershad-Langroudi, A.; Kabiri, K. *Polym Test* 2006, 25, 470.
18. Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed.; Wiley: New York, 1998.
19. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
20. Buchholz, F. L.; Graham, A. T. *Modern Superabsorbent Polymer Technology*; Wiley: New York, 1998.
21. Li, A.; Wang, A. *Eur Polym J* 2005, 41, 1630.
22. Wu, J.; Wei, Y.; Lin, J.; Lin, S. *Polymer* 2003, 44, 6513.
23. Hosseinzadeh, H.; Pourjavadi, A.; Mahdavinia, G. R.; Zohuriaan-Mehr, M. J. *J Bioact Compat Polym* 2005, 20, 475.
24. Krul, L. P.; Nareiko, E. I.; Matusevich, Y. I.; Yakimtsova, L. B.; Matusevich, V.; Seeber, W. *Polym Bull* 2000, 45, 159.
25. Qiu, Y.; Park, K. *Adv Drug Deliver Rev* 2001, 53, 321.
26. Omidian, H.; Hashemi, S. A.; Sammes, P. G.; Meldrum, I. *Polymer* 1998, 39, 6697.
27. Pourjavadi, A.; Kurdtabar, M. *Eur Polym J* 2007, 43, 877.
28. Castel, D.; Ricard, A. R. *J Appl Polym Sci* 1990, 39, 11.
29. Pass, G.; Philips, G. O.; Wedlock, D. J. *Macromolecules* 1977, 10, 197.