

# Fast Responsive Poly(acrylic acid-*co*-*N*-isopropyl acrylamide) Hydrogels Based on New Crosslinker

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**ABSTRACT:** Novel dual temperature- and pH-sensitive poly(acrylic acid-*co*-*N*-isopropylacrylamide), AA/NIPAAm, hydrogels were successfully prepared by chemical crosslinking with crosslinkers. Copolymers of AA/NIPAAm were crosslinked in the presence of different mol % of *N,N*-methylene bisacrylamide (MBA) and melamine triacrylamide (MAAm) as crosslinkers by bulk radical polymerization. The resultant xerogels were characterized by extracting the soluble fractions and measuring the equilibrium water content. Lower critical solution transition temperatures (LCST) were measured by DSC. The properties of crosslinked AA/NIPAAm series are evaluated in terms of compositional drift of polymerization, heterogeneous crosslinking, and chemical structure of the relevant components. Soluble fractions of the crosslinked networks were reduced by varying the MAAm and MBA

concentrations. The influence of environmental conditions such as temperature and pH on the swelling behavior of these polymeric gels was investigated. The swelling behaviors of the resulting gels show pH sensitivity. The prepared MAAm type AA/NIPAAm hydrogels exhibited a more rapid deswelling rate than MBA type AA/NIPAAm hydrogels in ultra pure water in response to abrupt changes from 20°C to 50°C. The results of this study provide valuable information regarding the development of dual stimuli-sensitive hydrogels with fast responsiveness. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 114–122, 2009

**Key words:** hydrogels; pH- and temperature sensitive gels; *N*-isopropylacrylamide; melamine triacrylamide crosslinkers

## INTRODUCTION

A hydrogel is a network of hydrophilic polymers that can swell in water and hold a large amount of water while maintaining the structure. A three-dimensional network is formed by crosslinking polymer chains. Crosslinking can be provided by covalent bonds, hydrogen bonding, van der Waals interactions, or physical entanglements.<sup>1,2</sup> The types of environment-sensitive hydrogels are also called “Intelligent” or “smart” hydrogels.<sup>3</sup> Many physical and chemical stimuli have been applied to induce various responses of the smart hydrogel systems. The physical stimuli include temperature, electric fields, solvent composition, light, pressure, sound, and magnetic fields, whereas the chemical or biochemical stimuli include pH, ions, and specific molecular recognition events.<sup>4,5</sup>

Hydrogels that are responsive to both temperature and pH can be modified by incorporating ionizable and hydrophobic functional groups to the same

hydrogels. When a small amount of anionic monomer, such as acrylic acid, is incorporated in a thermoreversible polymer, the lower critical solution temperature (LCST) of the hydrogel depends on the ionization of the pendant carboxyl groups, that is, the pH of the medium. As the pH of the medium increases above the pKa of the carboxyl groups of polyanions, LCST shifts to higher temperatures due to the increased hydrophilicity and charge repulsion.<sup>6–9</sup> In the previous work,<sup>10</sup> a new method is proposed for introducing new crosslinkers to prepare pH- and temperature-sensitive hydrogels. The new crosslinkers are prepared by simple reaction of melamine with both methacryloyl- and acryloylchlorides to produce monomers with the same chemical structures as *N*-isopropyl acrylamide (NIPAAm). Our work was extended to prepare crosslinked HEMA-VP copolymers using the new crosslinkers to produce intelligent gel with novel properties.<sup>11</sup> In the present article, the prepared new crosslinker can be used to prepare novel dual temperature- and pH-sensitive poly(acrylic acid-*co*-*N*-isopropylacrylamide), AA/NIPAAm, hydrogels by chemical crosslinking with crosslinkers. Measurements of pH and temperature sensitivity of the prepared gels are another goal of the present study.

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## EXPERIMENTAL

### Materials

Melamine and acryloyl chloride (AC) were supplied by (Aldrich). Triethylamine (Aldrich, Germany), 1-methyl-2-pyrrolidone (NMP) (Aldrich, Germany), tetrahydrofuran (THF) (Aldrich, Germany), and toluene (Aldrich, Germany) were used as received. Acrylic acid (AA) and *N*-isopropyl acrylamide (NIPAAm) were supplied by Aldrich. *N,N'*-methylene bis acrylamide, (MBA), (Aldrich, Germany) was used as crosslinker. The initiator, ammonium persulfate (APS), was supplied from Merck (Darmstadt, Germany). Double distilled and deionized water were used in hydrogel preparation and in swelling measurements. The experiments were carried out in a thermostatic water bath (Fryka, kaltechnik KB 300 Germany) equipped with both cooling and heating systems.

### Synthesis and purification of *N*-melamine acrylamide crosslinker

Method of preparation and purification of *N*-melamine acrylamide can be described as following<sup>10</sup>: melamine (0.1 mol) was reacted with (0.3 mol) of AC in the presence of NMP (100 mL) and triethylamine (0.3 mol) as acid acceptor in a four-necked round bottom flask fitted with a mechanical stirrer, thermometer, nitrogen inlet, and dropping funnel. AC was added over a period of 2 h and the reaction temperature was not allowed above 10°C. Precipitation of the triethylamine hydrochloride appeared immediately. This temperature was adjusted for 6 h. The reaction mixture was stirred for 48 h at room temperature and the precipitate was removed by filtration. The filtrate was diluted with THF and the unreacted melamine was removed by addition of saturated hot NaCl aqueous solution. THF was evaporated from the filtrate under vacuum. The remaining products were diluted with toluene and the solid product was removed by filtration. The final viscous products were recovered after evaporation of toluene and NMP by rotary evaporation under vacuum. The products were characterized by elemental analysis, melting point, FTIR, and <sup>1</sup>H NMR spectroscopy. The monomers produced from the reaction between AC with melamine is designated here as MAAm.

### Synthesis of crosslinked AA/NIPAAm copolymers

The crosslinked AA/NIPAAm copolymers were prepared by solution polymerization using water as solvent in the presence of APS (0.02 wt %) as inhibitor and the MAAm or MBA (1 wt %). The monomer ratios, ranging from 0.1 to 0.9 mol %, were used in

the preparation of crosslinked AA/NIPAAm copolymers. The copolymerization reactions were performed in siliconized test tubes under N<sub>2</sub> atmosphere at 65°C for 24 h. The polymer rods were postcured at 110°C in air for 24 h to ensure complete polymerization.

### Characterization of crosslinked AA/NIPAAm copolymers

The sol fraction percentage (SF%) in the crosslinked xerogel discs was determined from the weight of the dried gel before and after solvent Soxhelt extraction. SF values are calculated according to the equation:  $SF = (W_o - W) 100/W_o$ ; where  $W_o$  and  $W$  are the weight of the discs before and after extraction, respectively.

The dried discs were subjected to swelling measurements at different pH and temperatures. The swelling lower critical transition temperatures (LCSTs) of the crosslinked AA/NIPAAm copolymers were measured using differential scanning calorimetry (DSC) (Du Pont 910 DSC).

For the swelling measurements, dried cylindrical disks with diameter 11 and 5 mm thickness were immersed in a solution of desired pH (2–12), ionic strength,  $I$  (0.01–0.2M), and temperature (10–50°C).

### Measurement of swelling parameters

The xerogel discs having dimensions (5 mm × 11 mm) were swollen (after SF extraction) to equilibrium in different pH aqueous solutions at different temperatures (10–50°C) on both heating and cooling. The swelling ratio ( $q$ ) was obtained as:  $q = W_h/W_x$ ; where  $W_h$  and  $W_x$  are the weights of hydrogel and xerogel, respectively. Equilibrium water content (EWC), volume fraction of polymer ( $\phi_p$ ), and volume fraction at crosslinking ( $\phi_r$ ) were calculated from swelling measurements as described in a previous article.<sup>10,11</sup> EWC values are calculated according to the equation:  $EWC = (W_h - W_x) 100/W_h$ . Although  $\phi_p$  and  $\phi_r$  values are determined according to the equations:  $\phi_p = (d/d_o)^3$ ,  $\phi_r = q \phi_p$ , where  $d_o$  and  $d$  are the diameters of xerogel and hydrogel discs, respectively.

### Measurement of thermoreversibility

The dried gels were immersed in an excess of deionized water at 25°C for 24 h. Each swollen gel was removed to fresh deionized water at 50°C, and the shrunken gel was weighed at various time intervals. Finally, the gel was reswelled in deionized water at 25°C and the swollen sample was weighed at various intervals. To measure the change in swelling

ratio of the gel, this operation was repeated for three cycles.

### Kinetics of swelling/deswelling

Thin discs (0.2 mm × 11 mm) were used to measure the swelling/deswelling response rate. The water uptake capacity ( $W_u$ ) is calculated from the equation:  $W_u = (W_t - W_x)100/W_e$ , where  $W_x$ ,  $W_t$ , and  $W_e$  are the weight of xerogel, gel at time  $t$ , and gel at equilibrium, respectively. The same equation was used to calculate deswelling kinetics at 50°C.

### Measurement of swelling ratios in various pH solutions and pH reversibility

The measurement of  $q$  values for the copolymeric gels under various pH solutions was the same as that in deionized water. The pH values of various solutions adjusted by aqueous solution of HCl and NaOH were measured with a pH meter (Radiometer pH M 95) calibrated by standard buffer solution. The pH reversible experiments were carried out at pH 3 and pH 10 for 0.01M buffer solution at 25°C.

## RESULTS AND DISCUSSION

The number of polymeric gels capable of a thermotropic collapse was strongly limited. These polymers are reported as poly(*N*-alkylacrylamides)<sup>12</sup>, poly(*N*-vinyl caprolactam),<sup>13</sup> and poly(vinyl methyl ether) crosslinked by  $\gamma$ -radiation.<sup>14,15</sup> These gels were synthesized by several methods, which include: forming a heterogeneous networks through a phase separation method<sup>16</sup>; introducing free ends grafts through polymeric chains<sup>17</sup>; use of silane crosslinking agents<sup>18</sup>; cold polymerization methods<sup>19</sup>; using of polyethylene glycol as a pore-forming agent during the polymerization reaction<sup>20</sup>; and two-step polymerization methods.<sup>21</sup> In addition, it was reported that a thermo-sensitive gel could also be prepared as a result of binding of the cationic surfactant, tetraphenyl-phosphonium chloride, to a negatively charged polyelectrolyte gel.<sup>22</sup> It was demonstrated previously that novel crosslinkers based on tris-*N,N,N*-acrylamido melamine (MAAm), which have either methacrylate or acrylate groups, can be used as crosslinkers to synthesize thermo-responsive gels.<sup>10,11</sup> Asoh et al.<sup>23</sup> developed rapid response porous poly(*N*-isopropylacrylamide) networks and poly(acrylic acid) linear chains. Kishi et al.<sup>24</sup> prepared fast responsive and pH-/thermo-responsive copolymer hydrogels by creating microporous structures with  $\gamma$ -ray irradiation treatment. However, because of their appeal, dual thermo- and pH-sensitive hydrogels with rapid responsiveness continue to increasingly attract attention. Thus, to promote new

applications, it remains essential to develop dual stimuli-sensitive hydrogels with new architectures by new synthetic strategies. Zhang et al.<sup>25</sup> aimed to develop a novel method for creating dual thermo- and pH-sensitive hydrogels with rapid response behavior. They developed a novel strategy to improve the response rate of dual stimuli-responsive hydrogels through a modification of the molecular structure. They prepared a dual temperature- and pH-sensitive P(NIPAAm-*co*-AA) hydrogel with comb-type grafted chains. The PNIPAAm graft chains were introduced into the crosslinked network by copolymerization of PNIPAM macromonomers with NIPAM monomers and AAc monomers. The effect of the graft chains with freely mobile ends on the deswelling changes was compared with the behavior of normal-type gels containing random copolymers of NIPAAm and AAc in given temperature and pH conditions. Moreover, they investigated for the first time the effects of simultaneous changes of both temperature and pH value on the prepared dual thermo- and pH-sensitive hydrogels. The specific methods used to purify and characterize the chemical structure of MAAm has been previously discussed.<sup>10,11</sup> The properties of polymeric hydrogels are highly influenced by crosslink density and also, in the majority of cases, on the functionality of crosslinkers.<sup>23,24</sup> Wide varieties of acrylate crosslinkers have been used to form crosslinked networks. In bulk or solution polymerization, the choice of crosslinkers is quite broad. However, the solubility of many crosslinkers in water-phase polymerization becomes marginal. Much effort has been expended on attaining high levels of purity in the monomers, but the literature indicates otherwise with regard to the crosslinking agents. In this respect, a simple method was used to synthesize two crosslinkers based on polyfunctional acrylate and methacrylate. The ability to use these new crosslinkers to synthesize novel series of temperature and pH sensitive hydrogels is the main goal of the present investigation. In the present investigation, MAAm and MBA crosslinkers were used to synthesis thermo-sensitive hydrogels based on AA and NIPAAm monomers in their network structures. In this respect, APS at 0.1 (wt %) was used as initiator to polymerize AA and NIPAAm monomers. Different mol % of crosslinkers were used to investigate the variation of crosslinker types and concentrations on polymerization.

### Crosslinked AA/NIPAAm copolymers

Crosslinked AA/NIPAAm copolymers were prepared via solution polymerization using water as solvent and different weight percentage of MAAm and MBA crosslinkers ranging from 0.5 to 4%. The monomer ratios of AA/NIPAAm 0.9 : 0.1, 0.7 : 0.3,

**TABLE I**  
SF, LCST, and Swelling Parameters at 20°C of Crosslinked AA/NIPAAm Copolymer Hydrogels

| Copolymers<br>AA/NIPAAm<br>(mol/mol) | Swelling parameters<br>(crosslinked with 1% MBA) |      |             |             | Swelling parameters<br>(crosslinked with 1% MAAM) |      |             |             | SF (%) |      | LCST (°C) |      |
|--------------------------------------|--|------|-------------|-------------|---|------|-------------|-------------|--------|------|-----------|------|
|                                      | EWC  | $q$  | $\varphi_p$ | $\varphi_r$ | EWC   | $q$  | $\varphi_p$ | $\varphi_r$ | MAAm   | MBA  | MAAm      | MBA  |
| Poly(NIPAAm)                         | 96.0   | 25.3 | 0.036       | 0.93        | 91.73   | 12.1 | 0.077       | 0.94        | 2.2    | 10.1 | 32.2      | 34.1 |
| 10/90                                | 90.5   | 10.5 | 0.082       | 0.86        | 82.4  | 5.7  | 0.172       | 0.98        | 3.1    | 7.8  | 32.4      | 33.3 |
| 30/70                                | 87.9   | 8.3  | 0.093       | 0.77        | 96.5  | 28.8 | 0.033       | 0.94        | 6.2    | 5.6  | 33.6      | 35.5 |
| 50/50                                | 80.7   | 5.2  | 0.141       | 0.73        | 97.8  | 45.6 | 0.018       | 0.83        | 9.3    | 4.5  | 34.5      | 36.6 |
| 70/30                                | 75.6   | 4.1  | 0.149       | 0.61        | 98.1  | 53.4 | 0.015       | 0.78        | 11.4   | 3.3  | 35.7      | 37.7 |
| 90/10                                | 72.2   | 3.6  | 0.167       | 0.60        | 98.4  | 60.8 | 0.012       | 0.72        | 13.1   | 1.2  | 36.4      | 38.5 |
| Poly(AA)                             | 96.9   | 32.1 | 0.031       | 1           | 97.7  | 43.4 | 0.002       | 1           | 15.3   | 2.3  | 38.3      | –    |

0.5 : 0.5, 0.3 : 0.7, and 0.1 : 0.9 (mol/mol %) were used in all cases. AA/NIPAAm copolymers could be crosslinked due to the presence of  $\text{—C=C—}$  groups of MBA and MAAM grafts that can react with another monomers or with crosslinkers in presence of initiators. In this respect, MBA or MAAM was used at different concentrations (0.5–4 wt %) as a crosslinker for all AA/NIPAAm copolymers. The crosslinking was carried out in presence of MBA or MAAM and APS as initiator. In the present investigation, AA/NIPAAm gels were obtained at two different crosslinkers as described in the experimental section. The crosslinking mechanism of these copolymers is based on radical polymerization of double bonds of AA/NIPAAm with a tetra functional and hexafunctional MBA and MAAM crosslinkers, respectively.

The SF values of the prepared AA/NIPAAm copolymers crosslinked with 1% of both MAAM and MBA crosslinkers were measured, using Soxhlet extraction with water after 48 h, and the results are listed in Table I. The effect of weight percentage of both MAAM and MBA crosslinkers on AA/NIPAAm (with 0.5 mol ratio of AA) on SF values were determined and listed in Table II. The data listed in Tables I and II show that the SF values decreased with incorporation of MAA. However, the SF value in the case of MBA crosslinker is less than the SF value of copolymers crosslinked with MAAM crosslinker. Accordingly, this finding may lead to speculate that the reactivity of MBA towards copoly-

mers is much higher than MAAM crosslinker. This speculation runs in harmony with a previous finding<sup>26,27</sup> at which the SF value was related to the reactivity ratio and the relative reactivity between the mixture components. This would include AA (and/or NIPAAm), the initial double bonds of MBA or MAAM crosslinker, and the various double bonds of crosslinkers that are pendant to the polymer chain after incorporation of the crosslinker in the polymer network. The prepared MAAM crosslinker having three double bonds would be expected to have the same reactivity with AA, NIPAAm, and AA/NIPAAm polymers. It is proposed that after incorporation of one double bond, the second and third double bonds are not reactive because of steric hindrance or shielding and thus remain as dangling double bonds.<sup>27</sup> This model is based on the variation of the reactivity ratio of copolymers and the condition of copolymerization such as pH, temperature, and structure of crosslinkers. Based on this finding, it was found that the crosslinked AA/NIPAAm having high AA copolymers crosslinked with MAAM content has higher SF values than those containing high MBA content. On the other hand, SF data of AA/NIPAAm crosslinked with MAAM show higher values than crosslinked with MBA. This may be ascribed to the different crosslinking densities of such xerogels with MBA and MAAM crosslinkers. This can be attributed to that AA is a good solvent for MAAM crosslinker, consequently, the incorporation of crosslinker with copolymers having high AA content is

**TABLE II**  
SF, LCST, and Swelling Parameters at 20°C of Crosslinked AA/NIPAAm (50 mol/50 mol) Copolymer Hydrogels

| Crosslinker<br>contents<br>(mol %) | Swelling parameters<br>(crosslinked with 1% MBA) |      |             |             | Swelling parameters<br>(crosslinked with 1% MAAM) |      |             |             | SF (%) |     | LCST (°C) |      |
|------------------------------------|--|------|-------------|-------------|---|------|-------------|-------------|--------|-----|-----------|------|
|                                    | EWC  | $q$  | $\varphi_p$ | $\varphi_r$ | EWC   | $q$  | $\varphi_p$ | $\varphi_r$ | MAAm   | MBA | MAAm      | MBA  |
| 0.005                              | 93.5   | 15.3 | 0.054       | 0.82        | 98.2  | 55.1 | 0.016       | 0.88        | 13.1   | 7.8 | 36.9      | 38   |
| 0.01                               | 80.7   | 5.2  | 0.141       | 0.73        | 97.8  | 45.6 | 0.018       | 0.83        | 9.3    | 4.5 | 34.5      | 36.6 |
| 0.02                               | 77.3   | 4.4  | 0.161       | 0.71        | 96.7  | 30.2 | 0.022       | 0.65        | 7.8    | 3.1 | 33.2      | 35.2 |
| 0.04                               | 71.4   | 3.5  | 0.194       | 0.68        | 96.0  | 25.1 | 0.022       | 0.55        | 4.4    | 2.3 | 32.1      | 34.1 |

decreased into the network. It was also noted that the increment of crosslinker concentrations decreases SF values of the prepared AA/NIPAAm copolymers. This can be attributed to the formation of high crosslink density copolymers. The high crosslink density of the present system is based on crosslinking by other than a normal crosslinking mechanism.

### Swelling behavior

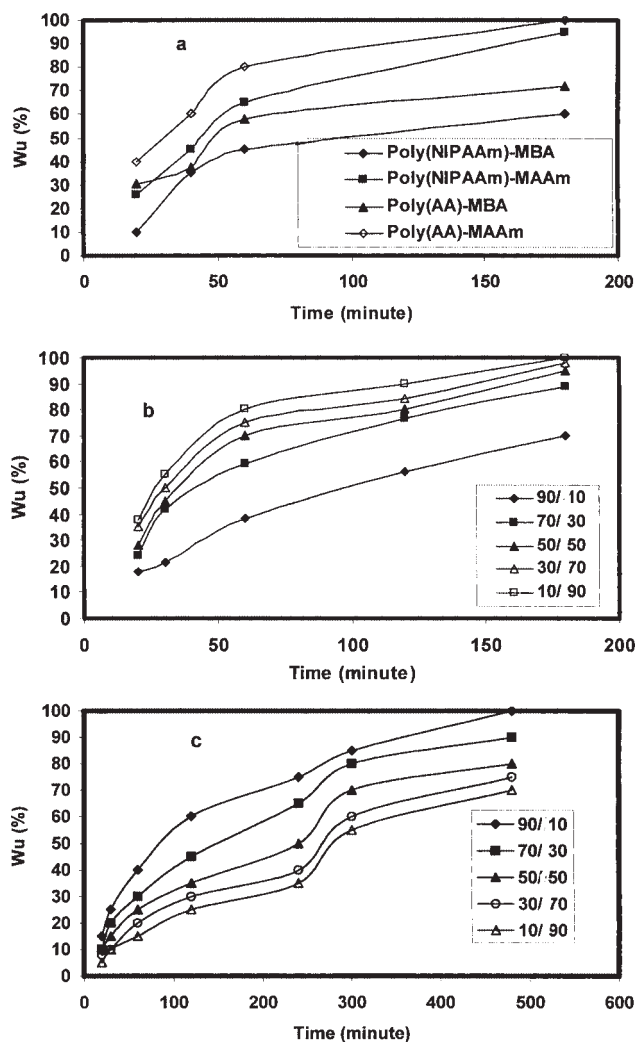
From the earlier discussion it is believed that the crosslinked AA/NIPAAm copolymers with MAAm crosslinker consists of very heterogeneous networks having dangling chains formed (especially) at the end of the crosslinking. The inhomogeneous network structures of AA/NIPAAm copolymers originated by the incorporation of MAAm crosslinker that can affect the behaviors of the network in aqueous media. The effect of both pH and temperature of aqueous media on the swelling and deswelling behaviors of crosslinked AA/NIPAAm copolymers is discussed in the coming section.

Swelling of ionic gel is a consequence of the balance between ionization of ionic group of the polymer network and constraint imposed by the polymer chains. Brannon Peppas and Peppas<sup>28</sup> reported that the polyacid hydrogels swelled abruptly when the pH of medium is raised above the  $pK_a$  value of the acid. In this respect, the crosslinked AA/NIPAAm copolymers have ionic moieties based on acrylic acid. It is well known that the  $pK_a$  value of acrylic acid is 4.75. On the other hand, the prepared gels were fully swelled in deionized water (pH 5.5) at 20°C. In this respect, the swelling parameters EWC,  $q$ ,  $\Phi_p$ , and  $\Phi_r$  values of AA/NIPAAm gels in deionized water at 20°C were determined and listed in Tables (I–II). It was found that the water content of crosslinked gels in presence of MBA was less than that crosslinked with MAAm. It was also noted that, AA/NIPAAm crosslinked with MBA have higher  $\Phi_p$  than that crosslinked with MAAm. This can be referred to the formation of high crosslink density network due to high reactivity of AA/NIPAAm copolymer with MBA crosslinker. On the basis of the Flory-Rehner,<sup>29</sup> the crosslink density of polymers decreases when polymer volume fraction at crosslinking  $\Phi_p$  increases. On the other hand, the high crosslink density of polymer networks increases the interaction between ionic carboxyl groups that decreases the swelling capacity. The data of the swelling capacities, listed in Tables (I–II), reveal that the swelling degree of AA/NIPAAm gels have two contradicts swelling behaviors. It is proved from the SF measurements that AA-NIPAAm copolymers have different crosslinking densities based on AA content. High crosslink densities stabilize the helicoidal structure through formation hydrogen bonds.

The structure is destroyed by crosslinking during the incorporation of NIPAAm.<sup>29</sup> This distortion increases the interaction of  $-\text{COOH}$  or  $-\text{NH}$  groups of AA/NIPAAm with water in the swelling process. On the other hand, presence of NIPAAm in AA/NIPAAm backbone decreases the interaction between  $-\text{COOH}$  and  $-\text{NH}$  groups of AA/NIPAAm as described in SF measurements. This allows networks to absorb unbounded water.<sup>29</sup> The SF measurements indicate that the crosslinking densities increase with increasing AA content when MBA crosslinker was used instead of MAAm crosslinker. Accordingly, the swelling capacities were increased with increment of AA content when MAAm replaced the MBA crosslinker. So, we can conclude that the crosslinking reaction produces more compact network that decreases the maximum swelling degree.

### Swelling and deswelling kinetics

In this section the influence of copolymer composition and crosslinker concentrations on swelling and deswelling behaviors of AA/NIPAAm copolymer in deionized water are considered. The swelling and deswelling kinetic curves of crosslinked AA/NIPAAm copolymers having different compositions at 20°C were determined and represented in Figure 1. The deswelling kinetics of these copolymers at 50°C were measured and plotted in Figure 2. The swelling kinetics of AA/NIPAAm copolymer crosslinked with different concentrations of both MAAm and MBA crosslinkers were determined were not represented here for brevity. The data of swelling show that the overall swelling attains its maximum at different times ranging between 1 and 3 h based on the copolymer composition and on the percentage of MAAm and MBA crosslinking agent. In this respect, the copolymers with 0.9, 0.7, 0.5, 0.3, and 0.1 AA mol ratios show different swelling times at 0.5, 1, 1.5, 2, and 3 h, respectively. It was also noted that, the times were increased when MBA used as crosslinker for AA/NIPAAm copolymers. It was also observed that the swelling time was decreased at high crosslinker content. These behaviors can be attributed to the increasing hydrophobicity of the copolymers owing to the formation of less elastic network structures due to high crosslinker content.<sup>23</sup> The deswelling kinetics of AA/NIPAAm hydrogels at 50°C is shown in Figure 2. Comparing the swelling time and deswelling times, it was found that the deswelling times are lower than the swelling times. This means that AA/NIPAAm deswells much faster than swelling especially for copolymers having high AA and crosslinker contents. The results can be attributed to the fact that the more heterogeneous network allows for faster shrinking upon water desorption.<sup>30</sup> This



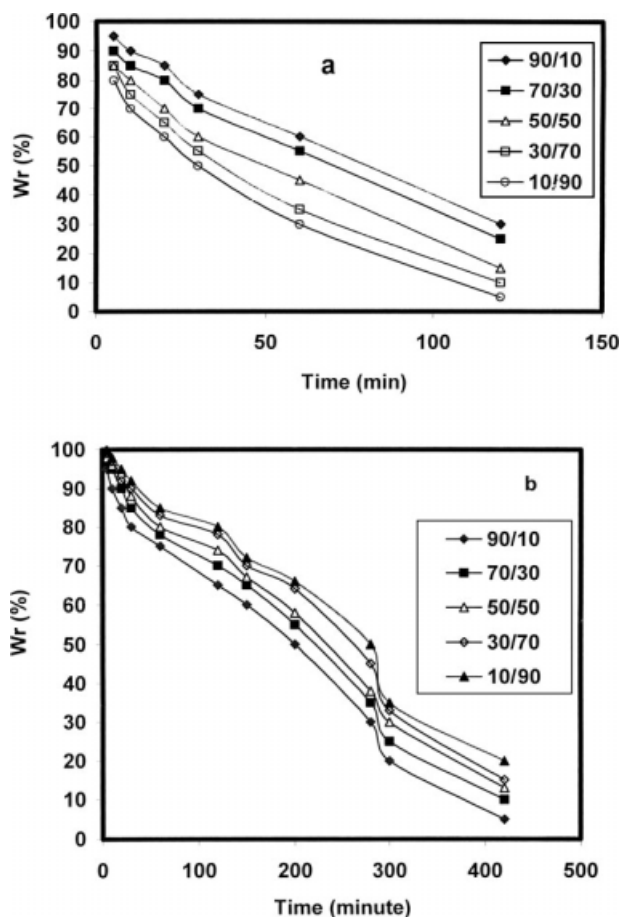
**Figure 1** Swelling kinetics of (a) poly(NIPAAm) and poly(AA), crosslinked AA/NIPAAm copolymers at 20°C crosslinked with (b) MAAM, and (c) MBA crosslinkers.

also can be explained on the basis that copolymers shrink from the swollen state at which the diffusion resistance of water is considered to be small.<sup>31</sup>

#### Effect of temperature on swelling parameters

The swelling degree of the hydrogels depends on the balance between the repulsive and attractive specific intermolecular interactions, that is, van der Waals forces, hydrophobic interaction, hydrogen bonding, and electrostatic interactions. Temperature is another parameter that affects the balance of interactions in some specific gels. The volume change of these gels may be referred to a thermodynamic characteristic of their linear polymers.<sup>32</sup> Hydrogels containing NIPAAm are among the most widely studied materials.<sup>33</sup> The coil- to globule transition of aqueous solutions of poly(NIPAAm) and their gels are referred to various types of interactions.<sup>34</sup> In this respect, AA/NIPAAm copolymers contain NIPAAm

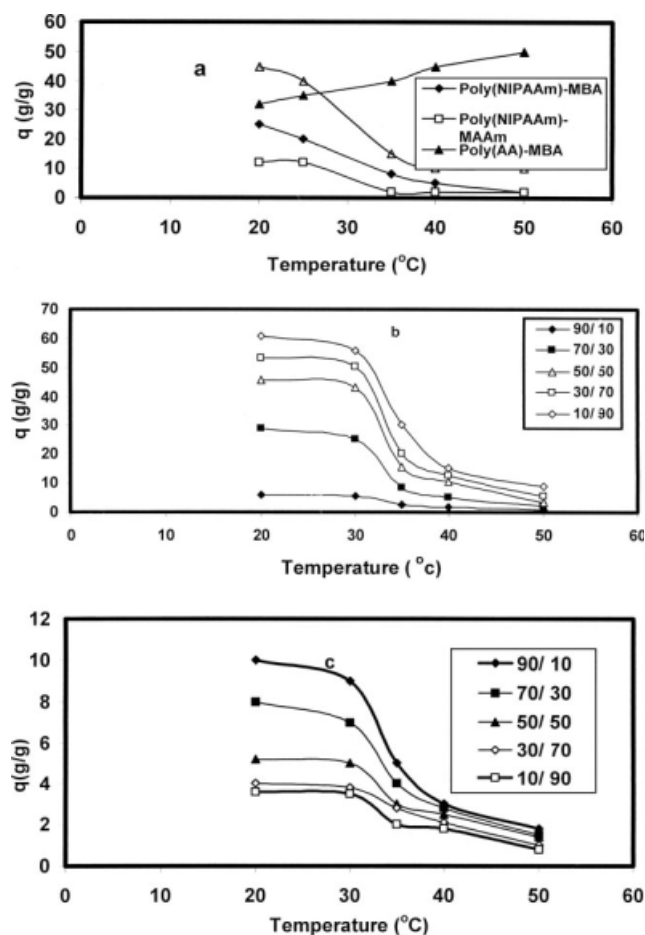
as side chain. The driving forces for swelling of these gels are referred to the formation of hydrogen bonds between  $-\text{COOH}$  of AA and  $\text{O}=\text{C}-\text{NH}$  of NIPAAm with water. Although hydrophobic interaction may be arises from interaction between isopropyl groups of NIPAAm and hydrophobic sites of MAAm crosslinker. All AA/NIPAAm xerogel discs were swollen in water at room temperature and all gels swelled uniformly, and had smooth edges and definite shape. The AA/NIPAAm gel has good mechanical properties. LCST values of the swelled gels were measured by DSC as described in the experimental section. LCST values for AA/NIPAAm having different composition of crosslinks with 1% of MAAm and MBA crosslinkers were determined and listed in Table I. The LCST values of crosslinked AA/NIPAAm gels (having AA mol ratio 0.5) with different weight ratios of MAAm and MBA were measured and listed in Table II. It was found that all AA/NIPAAm gels have LCST values. It was also observed that LCST values decrease with increase crosslinker contents. This can be attributed to the increase in hydrophobicity of the copolymers. Consequently, the network becomes more



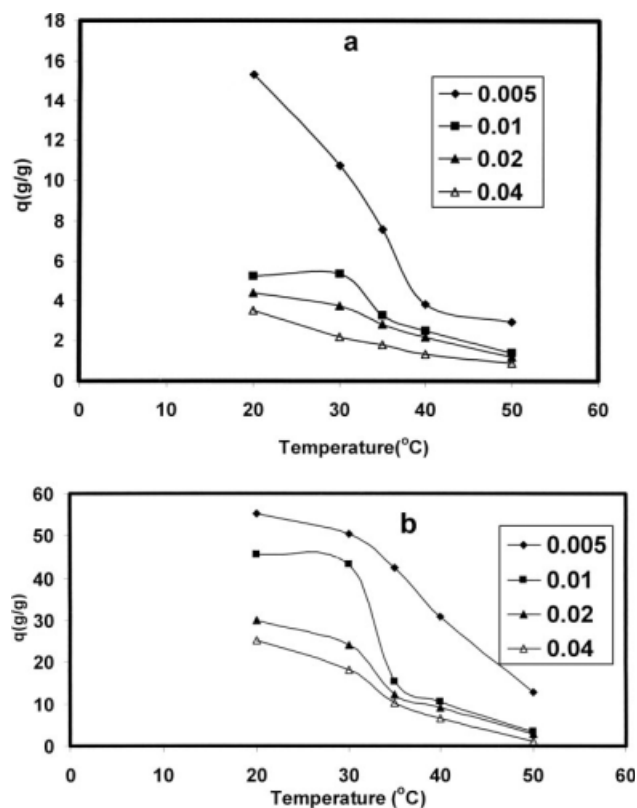
**Figure 2** Deswelling kinetics of crosslinked AA/NIPAAm copolymers at 50°C crosslinked with (a) MAAM and (b) MBA crosslinkers.

inhomogeneous due to the high possibilities of formation of end free chains by increment of crosslinker contents. It was also observed that AA/NIPAAm copolymers crosslinked with MBA have higher LCST values when compared with those crosslinked with MAAm crosslinker. This can be attributed to the formation of high crosslink density networks. This reflects on the low possibilities of AA/NIPAAm crosslinked with MBA to form less heterogeneous networks than those crosslinked with MAAm.

The effect of temperature on  $q$  values of crosslinked AA/NIPAAm with 1% of MAAm and MBA was measured and represented in Figure 3. The relation between  $q$  and temperature of swelling media for crosslinked AA/NIPAAm with different weight ratios of MAAm and MBA were plotted in Figure 4. In this respect, the gels were swelled to equilibrium at 25°C for 24 h and the swelling capacity will be measured at equilibrium. The gels were transferred to measure their swelling capacities at different temperatures. The gel swelling capacity was measured every hour until the gel reaches the equilibrium at

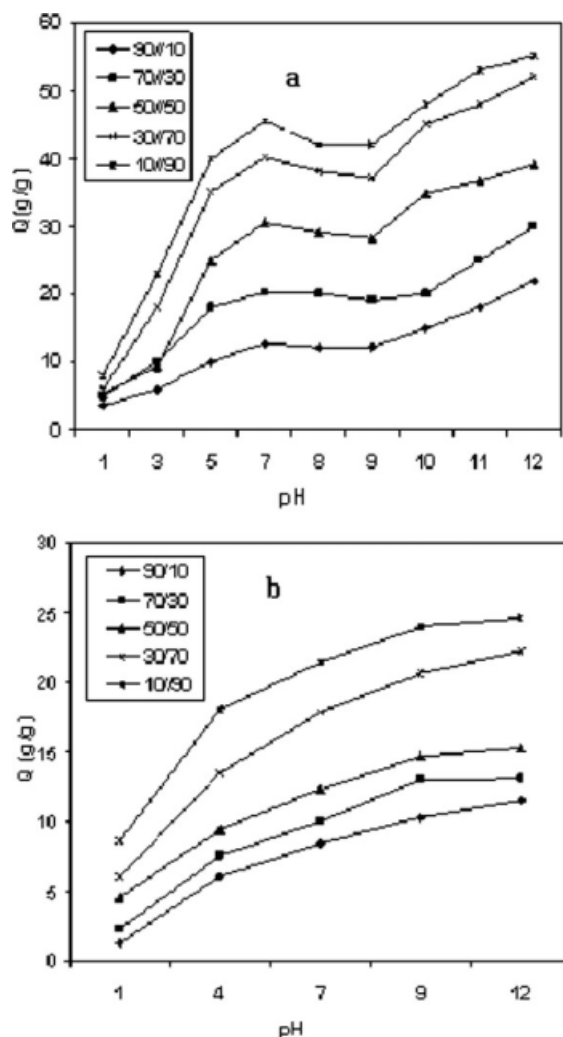


**Figure 3** Effect of temperature on the swelling capacities of the crosslinked (a) poly(NIPAAm) and poly(AA), AA/NIPAAm copolymers with 0.01 mol % of (b) MAAm, and (c) MBA crosslinkers.



**Figure 4** Effect of temperature on the swelling capacities of the crosslinked AA/NIPAAm copolymers with different concentrations of (a) MAAm and (b) MBA crosslinkers.

definite temperature of swelling. In this respect, the time of swelling at different temperature was changed according to gel composition and method of crosslinking. It was noted that the  $q$  values were changed at the same temperatures which were determined from DSC measurements. The increase in the swelling ratio above 26°C indicates that the copolymer contain more water with increasing temperature. This means that the hydration rate of AA/NIPAAm copolymers having high AA contents increases than the rate of dehydration which arises from the hydrophobic interaction of dangling chains and incorporation of AA above 25°C. The other curves of copolymers having high AA content show a fall in swelling capacities with increasing temperature, which becomes sharper. The reversible nature of swelling and deswelling was confirmed from the repeated swelling measurements of crosslinked AA/NIPAAm copolymers, which indicates that the same  $q$  values were recorded at the same temperatures. This behavior will be discussed in the swelling and deswelling kinetic measurements. On the other hand, it was observed that the swelling ratios for all AA/NIPAAm gels were decreased with increasing temperature near their LCSTs. However, AA/NIPAAm gels show different swelling ratios depending on AA contents. The phase transition



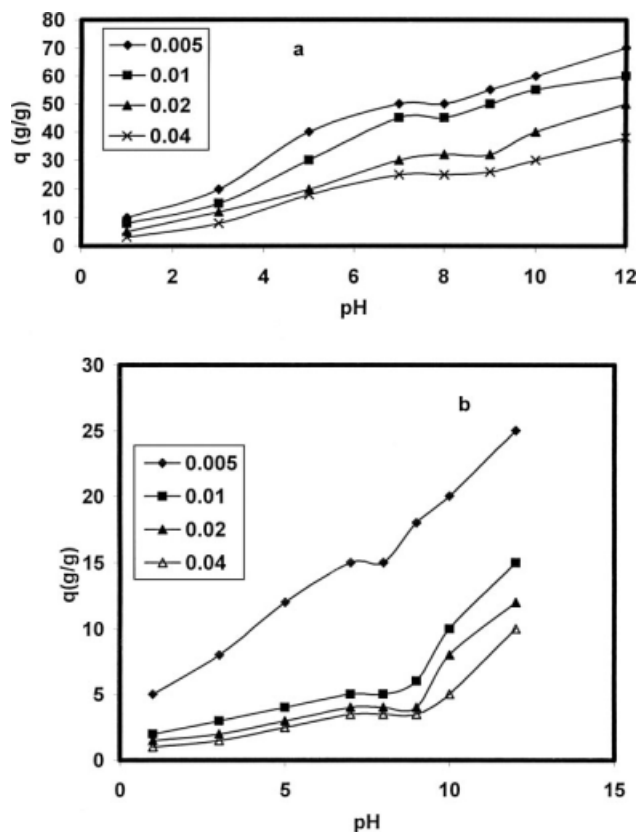
**Figure 5** Swelling and pH relations of the crosslinked AA/NIPAAm copolymers with 0.01 mol % of (a) MAAM and (b) MBA crosslinkers in aqueous solution and 0.1M KCl at temperature 20°C.

temperature of the grafts was shifted to higher temperature with increasing AA content. At the same time, the phase transition of AA/NIPAAm was shifted to lower value when the crosslinking was completed with MAAM crosslinker. This can be referred to the formation of dangling chain in the presence of MAAM crosslinker. Consequently, the hydrophilicity of gels decreases and the phase transition temperature was shifted to lower temperatures. It was also observed that the swelling ratio increases with increasing the temperature up to LCST. This can be referred to the formation of severance hydrogen bonding between amide groups of NIPAAm and  $-\text{COOH}$  groups of AA moieties.

#### Effect of pH on swelling parameters

pH-sensitive gels may be synthesized by crosslinking of weak or strong ionizable polyelectrolyte. pH

of the swelling medium induces a change in the degree of ionization of the polyelectrolyte and therefore in the swelling capacity of the hydrogel. The swelling behaviors of the prepared AA/NIPAAm gels were determined in saline solution at different pH to study the effect of pH on swelling parameters. The swelling ratios of AA/NIPAAm gels, cross-linked with 1% MBA or MAAM, were measured at different pH of the swelling medium in aqueous and 0.1M KCl solutions and represented in Figures 5–6. The data show that the AA/NIPAAm gels cross-linked with MBA attain maximum swelling ratios at pH 7 and remains constant thereafter up to pH 12 in both deionized and saline solution. However, the swelling ratio of gels was remained unchanged at pH about 3. This value was found between the first  $\text{pK}_a$  values of AA ( $= 4.75$ ).<sup>35</sup> Although, the cross-linked AA/NIPAAm gels with MAAM were fully swelled from pH 9–12. This stepwise swelling is probably due to the delayed acid dissociation of the acrylic acid of AA/NIPAAm gels crosslinked with MAAM.<sup>36</sup> The dissociation of the first few AA shields the residual acid units of the same polymer.<sup>37</sup> These observations may be explained on the basis that the AA/NIPAAm gels crosslinked with



**Figure 6** Swelling and pH relations of the crosslinked AA/NIPAAm copolymers with different concentrations of (a) MAAM and (b) MBA crosslinkers in aqueous solution and 0.1M KCl at temperature 20°C.



MAAm have lower crosslinked density and possess flexible network than that crosslinked with MBA. Therefore, the charged carboxylate group, formed during the acid dissociation process due to increment pH the swelling medium, may have a greater shielding effect on the remaining pendant maleic acid that increases  $pK_a$  of the residual AA of AA/NIPAAm.<sup>37</sup> It was also noted that the swelling ratio of AA/NIPAAm was decreased in saline salt solution. This was explained on the basis that an additional electrostatic swelling should be completely screened at high salt concentrations.<sup>38</sup>

### CONCLUSIONS

Fast responsive temperature and pH-sensitive hydrogels based on AA/NIPAAm copolymers have been successfully prepared by chemical crosslinking. The swelling measurements of AA/NIPAAm show that the polymer crosslinked with MAAm have higher swelling ratios than that crosslinked with MBA. The crosslinked AA/NIPAAm gel (crosslinked with MBA) attains maximum swelling ratios at pH 7, Whereas the crosslinked AA/NIPAAm (crosslinked with MAAm) swells step wisely at pH 2–7 and attains their maximum swelling ratios at pH 9–12. The swelling behaviors of AA/NIPAAm gels are closely correlated with the dissociation of the pendant acrylic acid. Sensitivity of AA/NIPAAm gels to pH variations was referred the delayed acid dissociation of the pendant acrylic acid.

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