

# Uses of Electron-Beam Irradiation to Prepare pH- and Temperature-Sensitive Hydrogels from Reactive Poly(vinyl alcohol) Grafts

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**ABSTRACT:** Thermosensitive poly(vinyl alcohol)-graft-(maleic anhydride), PVA-MA, and poly(vinyl alcohol)-graft-(*N*-isopropylacrylamide maleic anhydride) (PVA-MA-NIPAAm) copolymers containing carboxyl groups were prepared using electron beam irradiation at dose 80 kGy. The swelling ratios of the cross-linked gels were measured at various temperatures. The LCST values were measured using DSC technique. The temperature dependence of the swelling ratios of the cross-linked copolymers and terpolymers were measured at different temperatures. The swelling ratios of copolymers increased with increasing temperature up to 25–38°C, then decreased. The swelling

behavior of both copolymers and terpolymers was referred to formation of hydrogen bonds between amide group of NIPAAm moieties and carboxyl group in MA moieties and to hydrophobic interaction due to methyl groups of NIPAAm. The swelling behaviors of these gels were analyzed in buffer solution at various pH. Swelling ratios of all gels were relatively high and they showed reasonable sensitive to pH. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 1706–1715, 2008

**Key words:** thermosensitive polymer; pH-sensitive polymer; poly(vinyl alcohol); grafts; hydrogen bonding; swelling

## INTRODUCTION

Poly(vinyl alcohol), PVA, is one of the synthetic biodegradable polymers and has excellent physical properties. Its water solubility transparency and modulus can be modified by attaching substituents like acetates, acetals, or urethanes to some of the secondary OH groups of the backbone. The remaining alcohol groups act as physical cross-linking forming a three-dimensional network with a considerable stability. However, this physical gelation is thermally reversible. There are different types of modification that were used to synthesize chemically cross-linked PVA gels.<sup>1–3</sup> Hydrogels of PVA, chemically cross-linked with glutaraldehyde, were investigated by McKenna and Horkay.<sup>4</sup> PVA can be cross-linked by using difunctional agents that condense with hydroxyl groups.<sup>5</sup> PVA has been used as the material for artificial tendon and artificial larynx; in addition, membranes for kidney dialysis and wound coverings can be prepared from PVA.<sup>6</sup>

Hydrogels that contain ionizable groups change their dimensions with pH solution. Several pH-sensitive hydrogels have been investigated for their possi-

ble application in thermosensitive polymers. PVA that contains a different number of carboxylic groups has been applied in several industrial fields.<sup>7</sup> The hydroxyl groups of PVA are largely transformed to ester by reaction with acid chlorides or acid anhydrides. PVA hydrogels were prepared by reaction of diglycidyl aromatic compounds with pendant monosuccinate or phthalate ester of PVA to provide highly cross-linked materials.<sup>8,9</sup> In previous studies, the preparation of new ionic gels by using different dose rate of electron-beam irradiation was reported.<sup>10,11</sup> The aim of the present work is to introduce ionic groups onto PVA by introducing active unsaturated anhydride groups onto hydroxyl groups by chemical reaction. This reaction was completed by grafting maleic anhydride onto PVA hydroxyl groups. On the other hand, we have used electron beam irradiation to obtain cross-linked ionic gels based on grafting and cross-linking of *N*-isopropyl acrylamide monomer (NIPAAm) and polymer (PNIPAAm) without use cross-linker. The aim to use both NIPAAm and PNIPAAm is to introduce thermosensitive moieties onto PVA grafts. On the other hand, the mechanism of cross-linking and grafting of both NIPAAm and PNIPAAm by electron beam irradiation is discussed in the present article. The effects of pH and temperature of the swelling medium on the swelling degrees of the obtained gels are another objective of this study.

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## EXPERIMENTAL

### Materials

*N*-isopropylacrylamide monomer, NIPAAm (Aldrich Chemical, Germany) was crystallized from hexane. A free radical solution polymerization of NIPAAm in 1,4-dioxane (Aldrich Chemical, Germany, HPLC-grade) was performed using 2,2' azobis-isobutyronitrile (ABIN, supplied by Aldrich Chemical, Germany) at 70°C for 6 h. The obtained poly(*N*-isopropylacrylamide), NIPAAm, was precipitated with diethyl ether and purified by redissolution in acetone and reprecipitated in diethyl ether (yield: 87%,  $M_w$ : 173,000 g/mol by light scattering (LS) in THF). PVA having degree of hydrolysis 87–89% and weight average molecular weight ( $M_w$ ) 146,000 g/mol was obtained from Aldrich Chemical (Germany). It is designed as partially hydrolyzed PVA (PPVA). PVA having degree of hydrolysis 99–99.8% and  $M_w$  145,000 g/mol was purchased from Fluka. It is designed as fully hydrolyzed PVA (FPVA). Maleic anhydride (MA) and dimethylsulfoxide (DMSO) of reagent grade were obtained from Aldrich Chemical (Germany). Ammonium persulfate, APS, was obtained from Merck. All solvents having analar grade were used as supplied. The water employed for swelling measurements was deionized.

### Techniques

Synthesis of cross-linked poly(vinyl alcohol)-graft-(maleic anhydride) and PNIPAAm polymers

Graft copolymerization of MA onto PVA was carried out according to reported method.<sup>12</sup> Cross-linking of NIPAAm or PNIPAAm with poly(vinyl alcohol)-graft-(maleic anhydride) (PVA-MA) grafts were performed in aqueous solution by irradiation techniques. The irradiation experiments were completed using a linear electron acceleration EL-V-2 (Budker Institute for Nuclear Physics Novosibirsk, Russia) having acceleration voltage of 1.0 MeV. Irradiation dose 80 kGy was accomplished by varying the irradiation time. In this respect, PVA-MA having different percentages of MA were mixed with equivalent mole ratios of NIPAAm or PNIPAAm and dissolved in water with concentration of 50 wt %. The reaction mixture was then deaerated with oxygen free nitrogen for 3 h. These solutions were transferred into Petri-dishes of 8 cm diameter at a liquid level of approximately 3 mm, and the dishes were covered with parafilm<sup>®</sup>. At the end of irradiation, the prepared polymers were removed and the gel was dried in vacuum oven at 30°C for 7 days until constant weight.

Characterization of cross-linked polymers

Lower critical solution temperatures, LCST, of the cross-linked copolymers were measured using the differential scanning calorimetry (Du Pont 910 DSC).

### Measurement of swelling parameters

Soluble fractions in the cross-linked xerogel discs were extracted with deionized water at 100°C for 24 h. Technique of measurements as well as equations used for calculating the sol fractions (SF) and swelling parameters equilibrium water content (EWC), swelling capacity ( $q$ ), volume fraction at polymerization ( $\Phi_r$ ), and volume fraction ( $\Phi_p$ ) of the hydrogels are described in a previous article.<sup>12</sup> Equilibrium water content (EWC) and swelling capacities ( $q$ ) for cross-linked polymer were measured after removal SF from the network.

### Swelling and deswelling kinetics of gels

Discs having diameter 11–12 mm and the thickness 0.3–0.5 mm were used to measure the swelling and deswelling rate. The water uptake capacity ( $W_u$ ) at 25°C can be calculated from the equation,  $W_u = ((W_t - W_x)/W_e) \times 100$ , where  $W_t$ ,  $W_x$ , 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 pH reversibility and temperature sensitivity

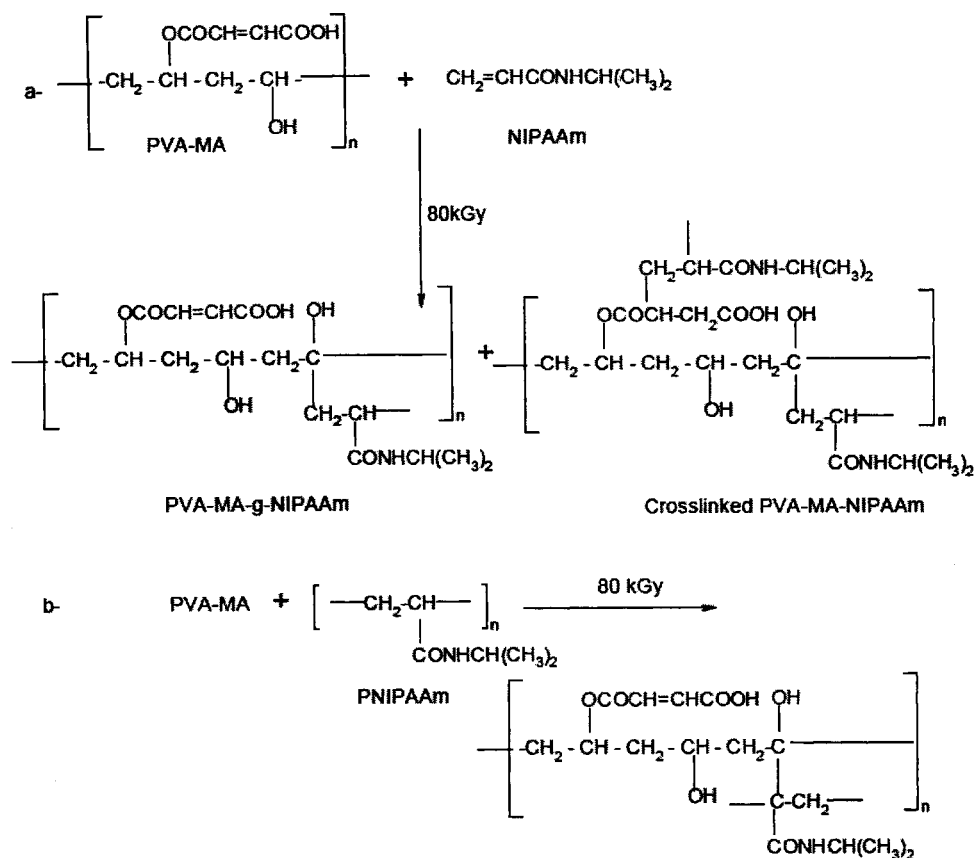
The swelling capacity,  $q$ , of gels at various pH solutions was measured as reported with deionized water. pH of solutions adjusted with aqueous solution of HCl and NaOH was measured with a pH meter (Radiometer pH M 95). The pH reversible experiments were carried out at pH 3 and pH 10 for 0.01M buffer solution at 40°C. The swelling equilibrium of cross-linked poly(vinyl alcohol)-graft-(*N*-isopropylacrylamide maleic anhydride) (PVA-MA-NIPAAm) gels was measured at different temperatures from 10 to 65°C. The swelling parameters were measured at fixed temperature as mentioned in the aforementioned method. The thermoreversibility is measured according to the following procedure: the dried discs were immersed in an excess of deionized water at 25°C for 24 h. Each swollen disc was removed to fresh deionized water at 50°C, and the gel was weighed at various time intervals. Finally, the gel was removed to deionized water at 25°C and weighted at various intervals. This operation was repeated for three cycles.

## RESULTS AND DISCUSSION

The irradiation of acrylate and methacrylate monomers with electron beams having energies between 120 and 300 KeV leads to nearly instantaneous curing by the formation of radicals starting both polymerization and cross-linking. However, a part from

these two main reactions, electron-induced side reactions such as chain scission, can occur simultaneously leading to radiolytic degradation processes in the polymer network.<sup>13</sup> Cross-linking and degradation of polymers are competing processes. It depends on the kinetic rate constants of both cross-linking and degradation reactions. The rate constants are influenced in a complex manner by several factors such as chemical structure of the polymer, the presence of sensitizing or desensitizing additives, and irradiation dose rates.<sup>14</sup> To find out the optimum irradiation conditions for achieving maximum conversion of the methacrylate functionalities and avoiding extensive radiolytic degradation, the dose dependence of the cross-linking process was studied. In our previous work,<sup>10,12,15</sup> the effect of dose rate of electron beam-irradiation on gelation of acrylate monomers was investigated. It was found that 80 kGy is the optimum dose rate to obtain cross-linked acrylate polymers without chain scission degradation. As has been briefly reviewed in previous publication,<sup>13</sup> experimental efforts have been reported to prepare ionic PVA gels. In a previous work,<sup>13</sup> we have reported the cross-linking of PVA-MA grafts with different cross-linkers. Graft copolymerization of MA onto partially and fully hydrolyzed PVA was carried out in the presence and absence of an initia-

tor. Two types of cross-linkers were used to cross-link PVA-MA grafts using 1,1,1-trimethylolpropane trimethacrylate (TPT) and methylene bisacrylamide (MBA) as hexa- and tetra-functional cross-linker, respectively. The effect of TPT and MBA cross-linkers on swelling properties were determined. On the other hand, grafting and cross-linking of NIPAAm onto PVA-MA in presence of different weight percentages of MBA cross-linker using chemical initiator was discussed in the previous investigation.<sup>16</sup> The temperature of cross-linking was carried out at 5 and 55°C. The cross-linked PVA-MA-NIPAAm polymers show different pH and temperature swelling sensitivities. The swelling behaviors were referred to formation of hydrogen bonding between amide and carboxylic groups and also to hydrophobic aggregation of PVA-MA-NIPAAm grafts. In the present article, we have decided to prepare cross-linked PVA-MA-NIPAAm hydrogels using electron beam irradiation at dose 80 kGy. A scheme of synthesis of PVA-MA-NIPAAm grafts is shown in Figure 1. The reaction conditions for grafting of NIPAAm and PNIPAAm onto both partially and fully hydrolyzed PVA-MA grafts are listed in Table I. The designations of the PVA-MA grafts are denoted as PPVA-MA (X) and FPVA-MA (X), where P and F represent the partially and fully hydrolyzed PVA respectively,



**Figure 1** Scheme of cross-linking of reactive PVA-MA-NIPAAm grafts.

**TABLE I**  
**Reaction Conditions and Composition Analysis**  
**for Preparation of Cross-Linked PVA-MA and**  
**PVA-MA-NIPAAm Grafts Using Electron Beam**  
**Irradiation at Dose 80 kGy**

Grafts	%MA grafting by $^1\text{H}$ NMR <sup>13</sup>	Weight of PVA-MA grafts (g)	Weight of NIPAAm or PNIPAAm (g)
FPVA-MA <sub>10</sub>	10.2	10	0.92
FPVA-MA <sub>33</sub>	33	10	3.1
FPVA-MA <sub>51</sub>	51.4	10	4.7
PPVA-MA <sub>25</sub> 25	25	10	2.3
PPVA-MA <sub>45</sub> 45	45	10	4.2
PPVA-MA <sub>75</sub> 75	75	10	6.9

and (X) denotes the percentage of grafting (i.e., MA grafted on PVA). More details on  $^1\text{H}$ NMR analysis and acid base titration and equations used to determine MA% were discussed in previous work.<sup>13,16–18</sup> The composition analysis of PVA-MA grafts is based on comparing the integration of mainly two signals, at 2.75 ppm (assigned to ungrafted —OH protons of PVA) and 13.3 ppm (assigned to —COOH protons of MA). On the other hand, grafting of NIPAAm and acrylic or methacrylic acid with PVA was discussed by Nonaka et al.<sup>19,20</sup> They report on chemical grafting of NIPAAm and acrylic acid onto PVA using chemical initiator and *N,N,N,N'*-tetramethylethylenediamine, TMEA, as accelerator. In the present study, the grafting of NIPAAm onto PVA-MA grafts is investigated. In this respect, data of MA percentage were calculated and listed in Table I. The data show that MA% for PPVA is higher than that for FPVA. This can be attributed to the higher solubility of PPVA in water than FPVA that enhances the probability for reaction of PPVA with MA.<sup>13</sup>

#### Cross-linked PVA-MA-NIPAAm grafts

High-energy electron beam has found numerous applications ranged from sterilization of medical equipment to curing of coating or composites.<sup>21</sup> The use of electron beam to initiate polymerization reactions is one area to which much interest has been focused. The curing of vinyl, acrylate, methacrylate, and maleimide monomers by means of high-energy electron beam irradiation normally proceeds via a free radical mechanism.<sup>22</sup> Numerous other reactions are occurred as side reactions to various extents during the polymerization. The high dose of irradiation produce heat, which can lead to degradation of polymer chains and the resulting release of short-chain fragment.<sup>23</sup> A radiation technique is promising for preparation of hydrogels because a polymer hydrogels is not contaminated with foreign additives and the cross-linking must composed of stable C—C bonds. In this study, ionizing irradiation technique

was used for the preparation of PVA-MA-NIPAAm hydrogels at dose 80 kGy. There are two possible ways to prepare hydrogels from aqueous solutions: initiating the polymerization reaction using radical initiators and thermal activation or radiation technique. Irradiation technique is done with gamma rays or electron beams. The latter methods lead to a cross-linked polymer and a real gel without cross-linkers. The chain initiating and cross-linking mechanism in dilute solution of NIPAAm and PNIPAAm by irradiation technique was studied using electron pulse radiolysis with optical detection at room temperature.<sup>24</sup> Several transients of NIPAAm generated by reactions with electrons, hydroxyl radicals, and hydrogen atoms were observed. Hydrogen abstraction was not observed in the case of NIPAAm monomer, but it was found for the reaction of OH radicals with PNIPAAm. The cross-linking mechanism of PVA-MA with NIPAAm and PNIPAAm can be illustrated in Figure 2. In electron pulse radiolysis, a dilute monomer solution is irradiated with short pulses of high energetic electrons. The radiolysis of water leads to the formation of hydrated electrons, hydroxyl radicals and hydrogen atoms as reactive species [Fig. 2(a)]. OH radicals can either abstract hydrogen from a monomer NIPAAm or add to double bond. If possible, the addition to the double bond is preferred. Therefore, we assume the formation of the more stable  $\alpha$ -carboxyalkyl radical in the reaction of OH radicals with NIPAAm [Fig. 2(b)]. There are two possible ways to cross-link the monofunctional NIPAAm during the irradiation. The first way is based on forming of mid-chain radicals (cross-link sites) during polymerization by intramolecular H-shift. The second way depends on formation of radicals by hydrogen abstraction from the growing polymer [Fig. 2(c)]. The mechanism of cross-linking indicates that the cross-linking degree increases when PNIPAAm used instead of NIPAAm monomer due to OH abstraction. On the other hand, PVA-MA grafts could be cross-linked the presence of —C=C— groups of MA grafts that can react with another monomers using electron beam irradiation technique. In this respect, NIPAAm and PNIPAAm were used at different concentrations (1–7 wt %) to react with PVA-MA grafts. The same molar ratios of NIPAAm, listed in Table I, were added to aqueous solution of PVA-MA grafts (25–30 wt %). The weight or number of moles of NIPAAm or PNIPAAm were calculated to equal weight or mole percentage of MA grafts. As example, 10 g of (—CH<sub>2</sub>—CH—OCOCH=CHCOOCH) equals 0.0704 mol or 0.00704 mol for PVA-MA having 10% of MA grafts. Accordingly, 0.00704 mol of 10%PVA-MA graft required to 0.92 g of NIPAAm or PNIPAAm that calculated on the basis; weight of NIPAAm = number of moles of PVA-MA grafts  $\times$  133 while, 133 is the molecular



TABLE II  
SF, Swelling Parameters, and LCST Values of Cross-Linked PVA-MANIPAAm and PVA-MA Hydrogels<sup>16</sup>

Grafts	Swelling parameters (cross-linked gels with NIPAAm)				Swelling parameters (cross-linked gels with PNIPAAm)				SF <sup>a</sup>	SF <sup>b</sup>	LCST (°C)	
	EWC	<i>q</i>	$\phi_p$	$\phi_r$	EWC	<i>q</i>	$\phi_p$	$\phi_r$			T <sup>a</sup>	T <sup>b</sup>
FPVA-MA <sub>10</sub> -NIPAAm	96.00	25	0.03	0.75	93.33	15	0.021	0.31	18	14	25.26	31.98
Chemical cross-linked <sup>16</sup>	84.62	6.5	0.100	0.65					8.4		22.6	
FPVA-MA <sub>33</sub> -NIPAAm	96.87	32	0.0244	0.78	95.65	23	0.014	0.32	15	17	30.18	30.18
Chemical cross-linked <sup>16</sup>	92.71	13.7	0.049	0.68					11.4		27.2	
FPVA-MA <sub>51</sub> -NIPAAm	97.92	48	0.017	0.81	97.22	36	0.009	0.34	10	20	33.16	29.7
Chemical cross-linked	95.05	20.2	0.035	0.71					17.8		32.7	
PPVA-MA <sub>25</sub> -NIPAAm	97.14	35	0.019	0.66	96.15	26	0.012	0.31	25	11	32.95	31.94
Chemical cross-linked	76.36	4.23	0.132	0.56					5.5		18.2	
PPVA-MA <sub>45</sub> -NIPAAm	97.61	42	0.017	0.71	96.55	29	0.012	0.35	22	20	33.14	31.72
Chemical cross-linked	92.06	12.6	0.048	0.61					13.2		19.5	
PPVA-MA <sub>75</sub> -NIPAAm	95.83	24	0.028	0.68	93.33	15	0.019	0.28	15	22	35.12	30.64
Chemical cross-linked	83.61	6.1	0.095	0.58					10.7		26.2	

<sup>a</sup> Cross-linked gels using NIPAAm.

<sup>b</sup> Cross-linked gels using PNIPAAm.

monomer. The data of cross-linked PVA-MA-NIPAAm in the presence of chemical initiator indicate that the SF values were lower than that cross-linked by using electron beam irradiation. This may be ascribed to the different cross-linking densities of such xerogels, which arises from chemical cross-linking by esterification of anhydride group with OH groups of PVA.<sup>16</sup> On the other hand, cross-linking in presence of PNIPAAm arises from radical polymerization of PNIPAAm radicals besides intercross-linking through the double bonds of the polymeric anhydride.<sup>29</sup> Careful inspection of SF data, Table II, indicates that the SF values were decreased with increasing MA content for both PPVA and FPVA when irradiated with NIPAAm. This behavior can be related to increasing of cross-link densities of cross-linked polymers with increasing of MA content. This behavior was not observed for cross-linked polymers with PNIPAAm. It was observed that the SF values were increased for irradiated FPVA-MA and PPVA-MA with PNIPAAm. This can be attributed to the presence of NIPAAm as side chain onto PVA-MA grafts, which creates less compact structure for PVA-MA-NIPAAm grafts. This can be referred to destabilization of hydrogen bonds between carboxyl and hydroxyl groups of PVA-MA due to the strong interaction between carboxylic groups of PVA-MA-NIPAAm grafts with water.<sup>16</sup> This indicates that the strong interaction between water and polymer increases on introducing NIPAAm, which increases probability for grafting of NIPAAm onto PVA-MA more than PNIPAAm onto PVA-MA grafts. Accordingly, we can conclude that the cross-linked PVA-MA-PNIPAAm have greater probability to form cross-linked polymers more than PVA-NIPAAm

when irradiated with electron beam irradiation at dose 80 kGy.

#### LCST values of irradiated polymers

It is well known that PNIPAAm molecules in aqueous solution exhibit a rapid and reversible hydration-dehydration change in response to small temperature change around its lower critical solution temperature (LCST; 32°C). Isopropyl groups in the PNIPAAm side chain play an important role in the temperature dependent hydrophobic aggregation in water, resulting in a phase separation above LCST. Accordingly, the factors that will increase the hydrophobicity of polymers will decrease LCST values. On the other hand, the factors that increase hydrophilicity of polymers, hydrogen bonds between polar groups of polymers, will increase LCST values. The hydrophobic interaction may arise from interaction between isopropyl groups of NIPAAm and hydrophobic sites of MA ( $-C=C-$ ) as represented in Figure 1. Although several types of hydrogen bonding are possible in PVA-MA-NIPAAm, hydrogen bonding between carboxyl groups in MA grafts and amide groups in NIPAAm residues may specifically be formed. Additionally, in the synthesis of cross-linked PVA-MA-NIPAAm grafts, electron beam is likely to lead to the formation of hydrogen bonding complexes between PNIPAAm and MA grafts.<sup>16</sup> Accordingly increasing MA and NIPAAm contents increases hydrogen bonding and consequently increases LCST values. In the present work, the phase transition temperatures of PVA-MA-NIPAAm films were determined by DSC (as described in the experimental section) and listed in Table II. The data

of LCST of the cross-linked PVA-MA-NIPAAm gels in the presence of chemical initiator, which represented in previous work,<sup>16</sup> were represented in Table II. Careful inspection of data indicates that the cross-linked of PVA-MA-NIPAAm in the presence of chemical initiator have lower LCST than that cross-linked by irradiation. This can be attributed to low hydrophilicity of cross-linked PVA-MA-NIPAAm in presence of chemical initiator, which arises from high cross-linking densities of these gels.<sup>16</sup> The data of LCST for irradiation of NIPAAm with PVA-MA grafts data agree with previous speculation on hydrogen bonding. While the data of LCST, for PVA-MAPNIPAAm, indicate that their values were decreased with MA and PNIPAAm contents. This behavior indicates that electron beam irradiation affects the hydrophobicity of PNIPAAm and PVA-MA-PNIPAAm grafts.

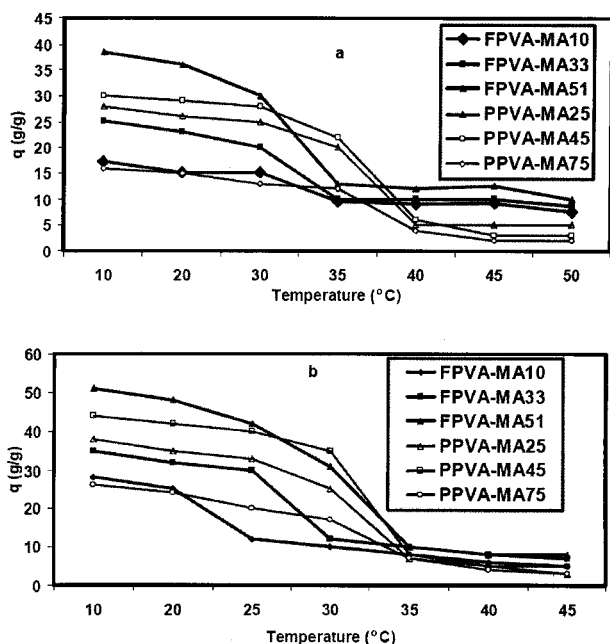
### Swelling behavior

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>30</sup> reported that the polyacid hydrogels swelled abruptly when the pH of medium is raised above the pKa value of the acid. In this respect, the cross-linked PVA-MA-NIPAAm and PVA-MA-PNIPAAm have two ionic moieties based on maleic and succinic acids. It is well known that the first pKa value of maleic and succinic acid lie between 3 and 4. On the other hand, the prepared gels were fully swelled in deionized water (pH 5.5) at 25°C. In this respect, the swelling parameters EWC,  $q$ ,  $\Phi_p$ , and  $\Phi_r$  values of PVA-MA-NIPAAm and PVA-MA-PNIPAAm gels in deionized water at 25°C were determined and listed in Table II. It was found that the water content of cross-linked PVA-MA-PNIPAAm gels was less than cross-linked PVA-MA-NIPAAm. It was also noted that cross-linked PVA-MA-NIPAAm have higher  $\Phi_p$  than that cross-linked PVA-MA-PNIPAAm. This can be referred to formation of high cross-link density network due to inter-cross-linking with PVA-MAPNIPAAm. On the basis of the study of Flory and Rehner,<sup>31</sup> the cross-link density of polymers decreases when polymer volume fraction at cross-linking  $\Phi_p$  increases. On the other hand, the high cross-link density of polymer networks increases the interaction between ionic carboxyl groups that decreases the swelling capacity. The data of the swelling capacities, listed in Table II, reveal that the swelling degree of PVA-MA-PNIPAAm gels increases with increment of the cross-linking sites of the polymer network (MA contents). This behavior contradicts the data published in literature that indicate that the swelling degree decreases with increas-

ing cross-link density of network. It is proved from the previous work<sup>16</sup> that PVA-MA grafts have helicoidally structure. Maleic acid groups stabilize the helicoidally structure through formation hydrogen bonds. The structure is destroyed by cross-linking during the incorporation of NIPAAm.<sup>16,31</sup> This distortion increases the interaction of —COOH or —OH groups of PVA-MA with water in the swelling process. On the other hand, grafting of NIPAAm onto PVA-MA backbone decreases the interaction between —COOH and —OH groups of PVA-MA as described in previous work.<sup>13,16</sup> This allows networks to absorb unbounded water.<sup>31</sup> This behavior is observed for all grafts except PPVA-MA75 that shows lower swelling capacities as compared with PPVA-MA45. This can be explained on the basis that PPVA-MA75 possesses high compact structures. Also, the possibility for grafting PNIPAAm onto the PVA backbone was decreased due to increasing of MA contents. So, we can conclude that the cross-linking reaction produces more compact network that decreases the maximum swelling degree.

### Effect of temperature on swelling parameters

The swelling degree of the hydrogels depends on the balance between the repulsive and attractive specific intermolecular interactions, i.e., 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 and PNIPAAm are among the most widely studied materials.<sup>33</sup> The coil-to-globule transition of aqueous solutions of PNIPAAm and their gels are referred to various types of interactions.<sup>34</sup> In this respect, PVA-MA-NIPAAm grafts contain NIPAAm as side chain which can be cross-linked when irradiated with electron beam. The driving forces for swelling of these gels are referred to formation of hydrogen bonds between —COOH of MA, O=C—NH of NIPAAm and —OH of PVA with water. While hydrophobic interaction may arise from interaction between isopropyl groups of NIPAAm and hydrophobic sites of MA (—C=C—). The phase transition temperatures of PVA-MA-NIPAAm films were determined by DSC (as described in the experimental section) and listed in Table II. The relations between swelling ratio of gels,  $q$ , and temperature of swelling medium in deionized water are shown in Figure 3(a,b). It was observed that the swelling ratios for all PVA-MA-NIPAAm and PVA-MAPNIPAAm gels were decreased with increasing temperature near their LCSTs. However, PVA-MA-NIPAAm gels show different swelling

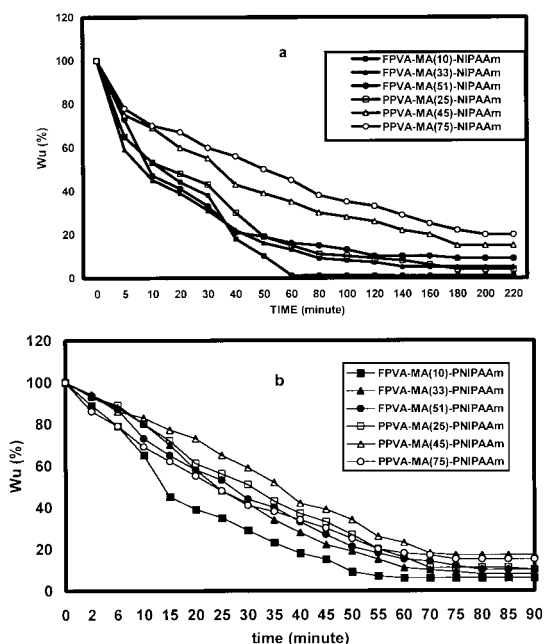


**Figure 3** Swelling capacities of cross-linked (a) PVA-MA-PNIPAAm and (b) PVA-MA-NIPAAm gels at different temperatures.

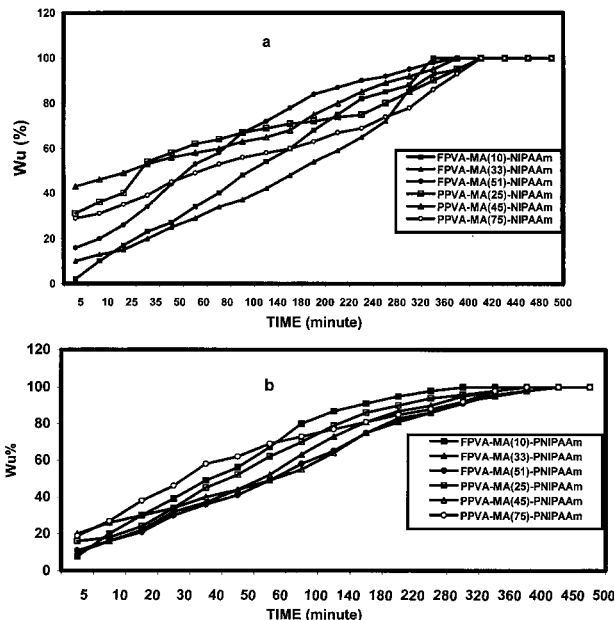
ratios depending on MA contents. The phase transition temperature of the grafts was shifted to higher temperature with increasing MA content. At the same time, the phase transition of PVA-MA-NIPAAm was shifted to higher value. It was also observed that the swelling ratio increases with increasing the temperature up to LCST. This can be

referred to the formation of hydrogen bonding between amide groups of NIPAAm and  $-COOH$  groups of MA grafts. This behavior was reversed in PVA-MA-PNIPAAm gels, which indicate that their LCST values were decreased when MA content increased. This behavior agrees with the data reported from DSC and SF measurements. This indicates that the presence of high weight percentages of PNIPAAm, Table I, during irradiation of PVA-NIPAAm decreases from incorporation of PNIPAAm as grafts onto PVA-MA chains. Accordingly, the hydrophilicity and LCST of irradiated networks were decreased. Perhaps, the effect of MA content with the critical value 51% providing the highest swelling degrees ( $q$ ) (Fig. 3) in combination with the lowest SF1 and LCST ( $T_2$ ) (and highest SF1 for chemical cross-linking) should be considered in terms of the differences between chemical and radiation cross-linking.

The swelling ratios of PVA-MA-NIPAAm grafts were measured at different temperatures of swelling media. Stepwise swelling behavior of the prepared gels in deionized water with alternating temperature between 25 and 50°C was investigated to confirm the reversibility of the swelling process with temperature. Deswelling kinetics of irradiated PVA-MA-NIPAAm and PVA-MA-PNIPAAm gels were measured every hour at 50°C and represented in Figure 4(a,b). While Figure 5(a,b) show reswelling data of the samples at 25°C. It was noted that the cross-linked grafts with PNIPAAm swells and deswells much faster than that cross-linked with NIPAAm.

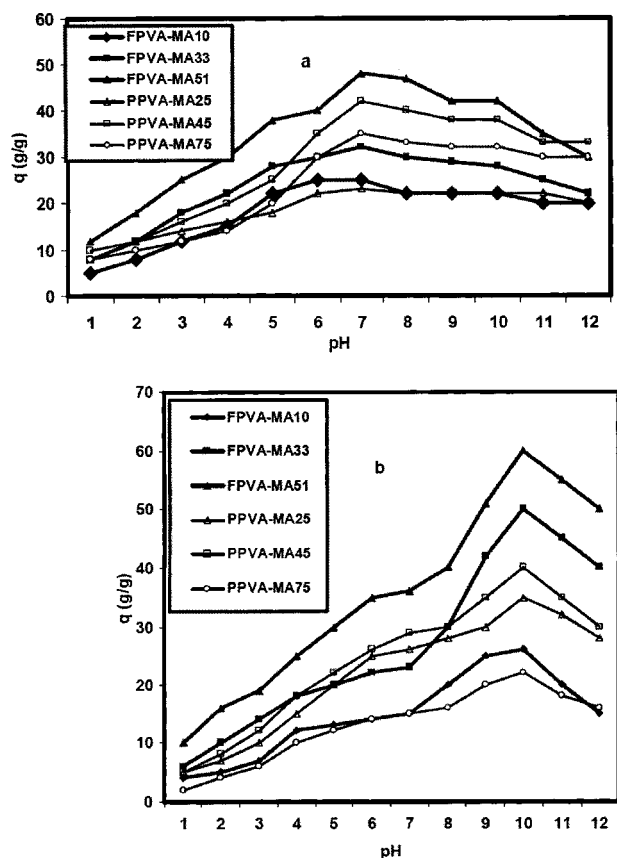


**Figure 4** Deswelling kinetics of (a) PVA-MA-NIPAAm and (b) PVA-MA-PNIPAAm in aqueous solution at 50°C.



**Figure 5** Reswelling kinetics of (a) PVA-MA-NIPAAm and (b) PVA-MA-PNIPAAm in aqueous solution at 25°C (pH = 5).





**Figure 6** Relation between swelling capacity and pH of aqueous solution of cross-linked (a) PVA-MA-NIPAAm and (b) PVA-MA-PNIPAAm.

This can be attributed to regular arrangement of polymer chain that arises from the irradiation of PVA-MA chains with PNIPAAm. This arrangement leads to a fast deswelling rate that shrinks or dehydrates quickly.<sup>35</sup> The same behavior was reported for hydrogels composed of cross-linked acrylamide-acrylic acid copolymer.<sup>36,37</sup> This behavior was referred to formation of hydrogen bonding between amide groups in acrylamide and acrylic acid at 30°C.

#### Effect of pH on swelling parameters

pH sensitive gels may be synthesized by cross-linking 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 PVA-MA-NIPAAm and PVA-MAPNIPAAm gels were determined at different pH to study the effect of pH on swelling parameters. The swelling ratios of PVA-MA-NIPAAm and PVA-MA-PNIPAAm gels, irradiated with electron-beam, were measured at different pH of the swelling medium in aqueous solutions and represented in Figure 6(a,b). The data show that

PVA-MA-NIPAAm gels cross-linked at 55°C attain maximum swelling ratios at pH 7 and remains constant thereafter up to pH 12 in deionized solution. However, the swelling ratio of gels was remained unchanged at pH about 3. This value was found between the first pKa values of maleic acid (= 2) and succinic acid (= 4.1).<sup>19</sup> While, the cross-linked PVA-MA-PNIPAAm gels were fully swelled from pH 9–10. This stepwise swelling is probably due to the delayed acid dissociation of the pendant maleic acid of PVA-MA-PNIPAAm gels.<sup>19</sup> The dissociation of the first few maleic and succinic acids shields the residual acid units of the same polymer.<sup>38</sup> These observations may be explained on the basis that PVA-MA-PNIPAAm gels have dangling chains and possess more flexible network than that cross-linked with NIPAAm monomer. 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 pKa of the residual maleic acid of PVA-MA-PNIPAAm.<sup>38</sup>

#### CONCLUSIONS

Temperature- and pH-sensitive hydrogels based on reactive PVA-MA-NIPAAm grafts have been successfully prepared by electron beam irradiation at 80 kGy. The SF measurements show that the grafting of NIPAAm onto PVA-MA polymers modifies the highly coiled structure of grafts. The swelling measurements of PVA-MA- show that the polymers cross-linked with NIPAAm have higher swelling ratios than that cross-linked with PNIPAAm. The cross-linked PVA-MA-NIPAAm gel attains maximum swelling ratios at pH 7. While the cross-linked PVA-MA-PNIPAAm swells step wisely at pH 2–7 and attains their maximum swelling ratios at pH 9–10. The swelling behaviors of PVA-MA-NIPAAm gels are closely correlated with the dissociation of the pendant maleic acid. Swelling behavior of FPVA-MA-NIPAAm was explained on the basis that incorporation of NIPAAm onto PVA-MA grafts modifies polymer–polymer interaction of these grafts. Sensitivity of PVA-MA-NIPAAm and PVA-MA-PNIPAAm gels to pH variations was referred the delayed acid dissociation of the pendant maleic acid.

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