

Synthesis and Swelling Behavior of Thermosensitive Poly(*N*-isopropyl acrylamide-*co*-sodium-2-acrylamido-2-methyl propane sulfonate) and Poly(*N*-isopropyl acrylamide-*co*-sodium-2-acrylamido-2-methyl propane sulfonate-*co*-glycidyl methacrylate) Hydrogels

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ABSTRACT: The crosslinked copolymers and terpolymers of *N*-isopropyl acrylamide (NIPAm) with sodium-2-acrylamido-2-methyl propane sulfonate (NaAMPS) and glycidyl methacrylate (GMA) were prepared in the presence of *N,N'*-methylene bisacrylamide (NMBA) as crosslinker by free radical solution polymerization at 4°C. Potassium persulfate (KPS) and potassium bisulfide (KBS) were used as initiator and accelerator, respectively. While molar percentages of NaAMPS in copolymers feed were varied as 1, 2, and 3; NaAMPS and GMA were used in the molar percentages of 1 : 1, 2 : 2, and 3 : 3, respectively, for the terpolymer preparation. NMBA contents were kept constant as 1 or 1.5 mol % of total monomer moles in feed composition. The effects of the comonomer type, feed composition, and the crosslinker contents on the lower critical solution temperatures (LCST), equilibrium swelling values (*Q*) of polymers, swelling kinet-

ics in water at room temperature, and deswelling kinetics at 55°C were investigated. The results indicated that the higher the NaAMPS content in NIPAm/NaAMPS copolymer, the higher the *Q* and water uptake rate, but less the water release rate. However, the presence of hydrophobic GMA comonomer in the terpolymer of NIPAm/NaAMPS/GMA decreased the *Q* values, it increased both the water uptake and the water release rates. It was also observed that NIPAm/NaAMPS and NIPAm/NaAMPS/GMA polymers exhibit continuous phase transition behavior between 40 and 50°C. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 428–438, 2006

Key words: stimuli-sensitive hydrogels; swelling; hydrogels; hydrophilic polymers; nonlinear polymers

INTRODUCTION

Aqueous solutions of many smart polymers or their crosslinked and swollen counterparts exhibit reversible swelling changes in response to external stimuli, such as temperature, pH, solvent, ionic strength, and electric field. Thermosensitive hydrogels exhibit phase separation behavior in aqueous solution when the temperature is increased above a certain value. The temperature at which this phase separation occurs is called as lower critical solution temperature (LCST). One of the most studied thermosensitive hydrogels, poly (*N*-isopropylacrylamide) (pNIPAm) has a LCST of ~32°C.^{1–3} Below the LCST, pNIPAm hydrogel absorbs relatively high amount of water and exists in a swollen state. When the temperature is increased, pNIPAm hydrogel begins to shrink and a large volu-

metric change occurs at the LCST. Therefore, it exists in a collapsed state at the temperatures above LCST. This phase separation is reversible and as a result, these kinds of materials are finding applications in many fields such as drug delivery,^{4–7} separation processes,^{8–12} enzyme immobilization,^{13–15} etc.

The equilibrium swelling ratio of pNIPAm hydrogel is relatively low. To improve the swelling amount of polymer, hydrophilic comonomers like 2-acrylamido-2-methyl propane sulfonic acid (AMPS),^{16,17} 2-hydroxyethylmethacrylate (HEMA),¹⁸ and acrylic acid (AA)^{19,20} are reacted with NIPAm monomer. It is well known that hydrophilic and ionizable comonomers, for example AA, acrylamide (AAm), and AMPS, increase the LCST of pNIPAm hydrogel. Also, the higher the hydrophilic comonomer content of the polymer, the higher its LCST value is. However, in some cases, there is a restriction for the amount of comonomer, for example using 10% (mole) AA as a comonomer with NIPAm causes the disappearance of temperature sensitivity of the copolymer.²¹

The response rate of pNIPAm hydrogel to a stimulus is relatively slow and it puts restriction on some of

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its applications. There have been several successful studies to increase the response rate of pNIPAm hydrogels.^{22–25} Kabra and Gehrke²² prepared fast responsive pNIPAm hydrogels using a phase separation technique by starting the polymerization at 22°C, and then performing the polymerization at 38°C, which is above its LCST. Zhang and Zhuo²³ prepared fast responsive pNIPAm hydrogels by annealing the pNIPAm hydrogels at –11, –25, –33, and –40°C for 24 h and thawing them at 24°C after the polymerization. In another study by the same group,²⁴ the polymerization reaction was carried out in 1:1 (v:v) acetone–water mixture to obtain fast responsive hydrogels. Another method to increase the response rate of pNIPAm hydrogels is to use pore-forming agents like poly (ethylene glycol) (PEG) during the polymerization reaction.²⁵ Rathjen et al.²⁶ have reported that the polymerization of NIPAm at +4°C gives transparent and more homogenous hydrogels than those prepared at +20°C. The hydrogels prepared at 20°C are opaque and have inhomogeneities leading to the worsening of mechanical properties and a broad transition temperature range during phase transition of the hydrogels.

In this study, we copolymerized NIPAm with sodium 2-acrylamido-2-methylpropane sulfonate (NaAMPS) and glycidyl methacrylate (GMA) in the presence of a crosslinking agent, *N,N'*-methylene bis acrylamide (NMBA) to obtain polymers, (p(NIPAm-*co*-NaAMPS)), p(NIPAm-*co*-NaAMPS-*co*-GMA)), with high swelling ratios, and fast swelling/deswelling rates. Their swelling kinetics in distilled water and temperature sensitivity properties were studied.

EXPERIMENTAL

Materials

NIPAm was purchased from Aldrich Chemical Co. (Milwaukee, WI) and recrystallized from toluene before use. AMPS, GMA, NaOH, the crosslinker NMBA, the initiator potassium persulfate (KPS), and the accelerator potassium bisulfide (KBS) were all provided by Merck AG (Darmstadt, Germany) and used as received except GMA. GMA was purified by vacuum distillation (15 mmHg, 80°C). Double distilled water was used for the preparation of the hydrogels and distilled water was used in the swelling and deswelling experiments.

Preparation of NaAMPS

NaAMPS monomer solution was prepared by adding AMPS to 0.2*N* sodium hydroxide solution at room temperature, as given by Lee and Yuan.²⁷ The molar ratio of sodium hydroxide to AMPS was kept constant at 1:1 to approach complete neutralization. After neu-

tralization, NaAMPS was crystallized from its solution and dried under vacuum at 25°C before use.

Preparation of hydrogels

The hydrogels (NIPAm-*co*-NaAMPS copolymers and NIPAm-*co*-NaAMPS-*co*-GMA terpolymers) were prepared by free radical chain polymerization in aqueous solution. The monomers (NIPAm, NaAMPS, and GMA) and the crosslinking agent (NMBA) were dissolved in double distilled water in 12-cm-long glass tubes of 2 cm diameter. After sealing the tubes with rubber caps, the solution was degassed by oxygen-free nitrogen gas for 20 min, and the tubes were placed in a water bath at +4°C. Then, KPS and KBS were added as their solutions in water at the same concentration of 4.5 g/100 mL. The polymerization reactions were carried out for 24 h at 4°C. In all experiments, the total initial monomer concentration was fixed at 1*M*, the initiator concentration (KPS) was 1% (mole) with respect to total amount of monomers, and the amount of accelerator (KBS) was equal to the KPS in weight. At the end of the polymerization, the glass tubes were broken carefully without damaging the hydrogels. Afterwards, hydrogels were cut into discs in 5-mm length and put in distilled water. The discs were held in water at room temperature for 4 days and the water was replaced with fresh water twice in a day to remove the unreacted monomers. Swollen hydrogels obtained by immersion of polymers in distilled water at room temperature were used in swelling experiments at different temperatures. They were dried under vacuum at 40°C and these dry hydrogels were used in the experiments of swelling and deswelling kinetics.

The feed compositions of hydrogels were listed in Table I.

Swelling experiments

Temperature-dependent swelling experiments were performed by gravimetric method. The swollen hydrogel discs were held in distilled water at different temperatures (5, 20, 30, 40, 50, and 55°C) for 24 h to reach the swelling equilibrium, using a thermostated water bath (Grant LTD 6G) ($\pm 0.1^\circ\text{C}$). After wiping off the excess surface water of the swollen hydrogels with moistened filter paper, they were weighed (m_{eq}) and dried in a vacuum oven until a constant weight (m_d) is attained. The equilibrium-swelling values (in g H₂O/g polymer) of the hydrogels were calculated using the equation given below;

$$Q = (m_{\text{eq}} - m_d) / m_d \quad (1)$$

The experiment was done in triplicate to obtain three swelling values and the average was given as *Q*.

TABLE I
The Feed Compositions of the Hydrogels

Hydrogel	NIPAm (mole%)	NaAMPS (mole%)	GMA (mole%)	NMBA (mole%)
pNIPAm/1NMBA	100	0	0	1
pNIPAm/1.5NMBA	100	0	0	1.5
1NaAMPS/1NMBA	99	1	0	1
2NaAMPS/1NMBA	98	2	0	1
3NaAMPS/1NMBA	97	3	0	1
1NaAMPS/1.5NMBA	99	1	0	1.5
2NaAMPS/1.5NMBA	98	2	0	1.5
3NaAMPS/1.5NMBA	97	3	0	1.5
1NaAMPS/1GMA/1NMBA	98	1	1	1
2NaAMPS/2GMA/1NMBA	96	2	2	1
3NaAMPS/3GMA/1NMBA	94	3	3	1
1NaAMPS/1GMA/1.5NMBA	98	1	1	1.5
2NaAMPS/2GMA/1.5NMBA	96	2	2	1.5
3NaAMPS/3GMA/1.5NMBA	94	3	3	1.5

Kinetics of swelling and deswelling

Swelling kinetics experiments were carried out at room temperature by “demand absorbency test” method using a swelling apparatus as shown in Figure 1 and described in the references.^{28–30} The apparatus consists of a burette connected with a glass tube enabling the insertion of air bubbles into the water in burette. The burette is filled with water and its top is closed with a plastic cap. The bottom of the burette is connected to a Buchner funnel with a rubber tubing, which has a diameter of 3 cm in filtering area. When the dry gel sample is placed on the wet filter paper in the Buchner funnel, the water level in the burette decreases since gel sample absorbs water. Water level versus time values is recorded. The change in water volume in the burette was converted to gravimetric data by multiplying volumetric data by the density of

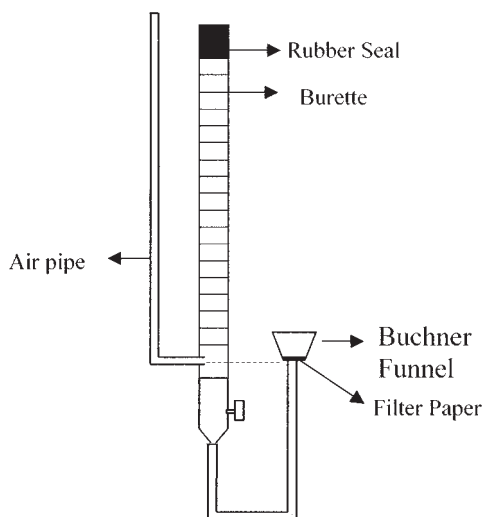


Figure 1 The apparatus for the measurements of swelling kinetics.

water at room temperature. The measurements were performed until the absorption equilibrium was reached. The water uptake percentage ($w_u\%$) was obtained by the following equation;

$$w_u\% = [(m_t - m_d)/m_d \times Q]100 \quad (2)$$

where m_t is the weight of swollen hydrogel at a given time obtained by using gravimetric data and m_d is the weight of dry hydrogel.

Deswelling kinetics experiments were carried out in a thermostated water-bath at 55°C by gravimetric method. A given amount of swollen-hydrogel at room temperature was immersed in water at 55°C. After a certain time (24 h), the hydrogels were freed from excess surface water and weighed. The weight changes versus time values of the hydrogels were recorded during the deswelling. The water retention percentage, ($w_r\%$), was calculated as follows:

$$w_r\% = (m_t - m_d) \times 100/m_d \quad (3)$$

LCST behavior

The LCST of the hydrogels was investigated by a SETARAM 131 differential scanning calorimeter (DSC). Swollen samples (50 mg) were heated from 20 to 90°C, with a heating rate of 0.5°C/min under air atmosphere.

Macroscopic observation

The morphologies of the hydrogel samples were observed using a scanning electron microscope (JSM 5600 Series, Jeol). Before SEM investigation, the hydrogels were dried by a vacuum freeze-dryer (Armfield SB4) (−45°C, 38×10^{-3} mmHg). The surfaces of the

TABLE II
The Equilibrium Swelling Values of the Hydrogels, at Room Temperature

NIPAm + comonomer (mole%)	Equilibrium swelling degree (g H ₂ O/g polymer)	
	NMBA (mole%)	
	1	1.5
—	43	33
NaAMPS		
1	120	65
2	224	105
3	270	134
NaAMPS + GMA		
1 + 1	51	45
2 + 1	90	81
3 + 3	140	118

freeze-dried hydrogels were sputter-coated with gold and observed with a magnification of 100 \times .

FTIR measurements

The FTIR spectra of dried hydrogels were obtained by Digilab, Excalibur-FTS 3000 MX model instrument. The dry hydrogel powder was thoroughly ground with KBr (IR grade, Merck-Germany) at a ratio of 1:200 and pressed into a pellet, and the spectrum was then recorded.

RESULTS AND DISCUSSION

Swelling results

The swelling mechanism is affected from several factors such as hydrophilic, hydrophobic and ionic character of the comonomer and comonomer content,³¹ dynamic volume³² and the molecular weight between the crosslinks, (Mc).^{33–35}

The equilibrium swelling ratios (Q) of the hydrogels at room temperature are given in Table II. The increase in NaAMPS content in feed composition of copolymers enhances Q values of the hydrogels because of the increases in the electrostatic free energy, repulsion between the same charged chains, and mobile counter ions. It is also observed that in the case of terpolymers, the increase in GMA content in feed composition decreases Q values of the hydrogels. Although it is not shown in Table II, the similar effect was observed for crosslinked p(NIPAm/GMA) copolymer and the equilibrium swelling values of p(NIPAm/GMA)/1NMBA copolymers with 1, 2, and 3 mol % GMA contents were found as 35, 30, and 29 g H₂O/g copolymer, respectively, (unpublished results). From the comparison of equilibrium swelling values of p(NIPAm)/1NMBA homopolymer and p(NIPAm/

3GMA)/1NMBA copolymer, the decreasing effect of GMA (from 43 to 29 g H₂O/g polymer) on the swelling values of hydrogels is evident. When terpolymers and copolymers with equal NaAMPS content prepared in this work are compared, it is observed that the equilibrium swelling ratios of terpolymers are approximately half of the copolymers. The Q value of the 1NaAMPS/1NMBA copolymer is 120 g H₂O/g polymer. However, the presence of 1% GMA comonomer decreased the water absorption of 1NaAMPS/1GMA/1NMBA terpolymer down to 51 g H₂O/g polymer due to hydrophobic character of GMA. The decreasing effect of GMA on the swelling values of polymers is more evident in case of terpolymers since the copolymers have higher swelling values due to the presence of ionizable NaAMPS comonomer in the hydrogel.

It is also seen that the Q values of the hydrogels decrease with the increase in crosslinker content in feed monomer composition because of the increase in the rigidity of hydrogel since the molecular weight between crosslinking points decreases.

Table III shows the values of dynamic swelling at different temperatures and water release at 55 $^{\circ}$ C of hydrogels. Percent water release was calculated according to the following equation:

$$\text{Water Release (\%)} = [(Q_{20} - Q_{55})/Q_{20}] \times 100 \quad (4)$$

where the indices indicate the temperature in $^{\circ}$ C.

All hydrogels release high amount of water at the temperatures between 40 and 50 $^{\circ}$ C. NIPAm/NaAMPS copolymers with 3% NaAMPS content containing 1

TABLE III
The Values of Equilibrium Swelling Ratio (Q) of NIPAm Copolymers and Terpolymers with two Different Crosslinker Contents at Different Temperatures

Feed composition of hydrogel			Equilibrium swelling degree (Q) (g H ₂ O/g polymer)						Water release (%)
			Temperature ($^{\circ}$ C)						
NaAMPS	GMA	NMBA	5	20	30	40	50	55	
1	—	1	130	120	116	110	19	4	97
2	—	1	300	240	238	230	50	12	95
3	—	1	310	270	267	265	61	45	83
1	—	1.5	69	65	62	46	2	1.5	98
2	—	1.5	110	105	89	63	19	4.4	96
3	—	1.5	135	134	132	100	20	17.5	87
1	1	1	55	51	46	26	3	2.8	95
2	2	1	97	90	85	70	23	4.7	95
3	3	1	148	140	127	86	54	10	93
1	1	1.5	46	45	39	21	2	2	96
2	2	1.5	86	81	75	61	20	3.7	95
3	3	1.5	121	118	112	99	60	7.2	94

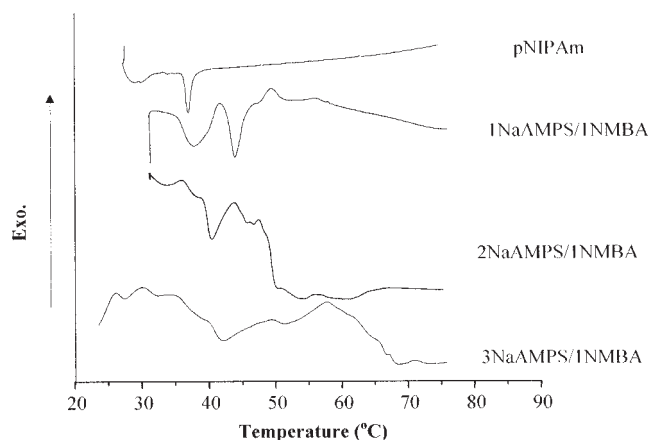


Figure 2 The DSC curves of pNIPAm and NIPAm-NaAMPS copolymers.

and 1.5% NMBA release minimum amount of water, 83 and 87%, respectively. Their water retention increases with the increase in NaAMPS content in copolymer as expected. On the other hand, the same release behavior was not exhibited by NIPAm/NaAMPS/GMA terpolymers due to dominant effect of hydrophobic GMA comonomer on the hydrophile/hydrophobe balance of whole network.

Since the other definition of LCST is the temperature at which swelling ratio decreased to half of its value at room temperature,³⁶ we can conclude that the LCST values of all hydrogels prepared in this work are between 40 and 50°C.

LCST behavior

It is known that the volume phase transition occurs continuously or discontinuously, according to copolymer composition and structure.^{37–43}

Thermosensitive linear NIPAm polymers dissolve in water at the temperatures below LCST, but they precipitate at the temperatures above LCST. While crosslinked counterparts of these polymers exist in the swollen state below LCST due to hydrogen bonding between water and amide groups of polymer, they collapse at higher temperatures than LCST, explained by increased affinity towards hydrophobic interaction as well as weakening of water-amide hydrogen bonding. When the temperature rises, NIPAm side chains tend to aggregate and the polymer deswells. However, hydrophilic side chains of hydrophilic comonomer interfere with the aggregation. To overcome this interference, higher energy is required for NIPAm side-chains to reach each other and aggregate. Thus, the presence of hydrophylic comonomer in NIPAm copolymer structure shifts LCST to a higher temperature. The other parameters affecting the phase transition are molecular weight (in linear polymers and

between crosslinking points in crosslinked polymers (M_c)), polydispersity, and crosslink density.^{44,45} It is known that the fraction with higher molecular weight of a polydispers polymer has lower LCST in comparison with that of lower molecular weight fraction.^{38,46} In case of crosslinked polymers, LCST increases with the increase in crosslink density. Low crosslinked pNIPAm or linear pNIPAm homopolymers exhibit a sharp and discontinuous phase transition.⁴⁴ However, continuous volume phase transition behavior was also observed for NIPAm and other hydrogels.^{43,47} Discontinuous phase transition occurs only in monodispers polymers.³⁸ But polydispers polymers exhibit a continuous volume phase transition behavior since each fraction of the polymer collapses at different temperatures.^{38,47,48} In other words, this continuous volume phase transition is ascribed to the inhomogeneity of the network.⁴⁹

The volume phase transition of the hydrogels that was observed by DSC occurs in several consecutive discontinuous stages, which can be taken into consideration as a continuous phase separation, with the increase in comonomer content (Figs. 2 and 3). The several endothermic peaks in the DSC curves correspond to the step by step release of water. All the DSC curves of the hydrogels prepared in this work are not presented and only two representative figures (Figs. 2 and 3) were given to show the effects of ionic and hydrophilic NaAMPS and nonionic and hydrophobic GMA comonomers on the LCST values; since the number of endothermic peaks and onset and offset points of the peaks ascribed to the start and end of the water release, the DSC curves are presented in Table IV. As it is seen in Figure 2, the incorporation of NaAMPS into the crosslinked pNIPAM hydrogel led to the observation of consecutive discontinuous endotherms and finally continuous phase transition with its further incorporation. In LCST study of p(NIPAm/GMA)/1NMBA with 1–3 mol % GMA content by DSC

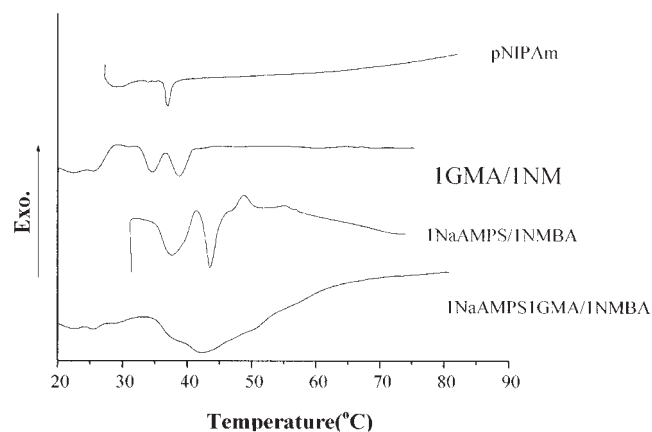


Figure 3 The DSC curves of pNIPAm, its copolymers and terpolymers.

TABLE IV
The On- and Off-Set Points of Endothermic Peaks in the DSC Curves of NIPAm Copolymer and Terpolymers Between 20 and 80°C

Hydrogels	Number of the endothermic peaks	On-set point (°C)	Off-set point (°C)
pNIPAm	1	35.72	38.55
1NaAMPS/1NMBA	2	35.25, 42.15	41.14, 49.14
2NaAMPS/1NMBA	3	36.29, 44.21, 47.82	43.81, 47.72, 50.99
3NaAMPS/1NMBA	3	35.29, 49.72, 57.63	49.69, 57.58, 68.44
1NaAMPS/1.5NMBA	2	31.51, 55.73	53.22, 63.9
2NaAMPS/1.5NMBA	2	41.00, 47.49	45.29, 54.98
3NaAMPS/1.5NMBA	1	43.10	60.93
1NaAMPS/1GMA/1NMBA	1	33.58	61.28
2NaAMPS/2GMA/1NMBA	3	36.36, 47.78, 61.70	43.84, 61.64, 65.20
3NaAMPS/3GMA/1NMBA	3	35.81, 48.10, 56.70	47.42, 56.60, 65.84
1NaAMPS/1GMA/1.5NMBA	3	41.83, 47.24, 56.00	47.16, 55.49, 59.99
2NaAMPS/2GMA/1.5NMBA	3	31.66, 42.21, 55.26	40.74, 48.00, 62.01
3NaAMPS/3GMA/1.5NMBA	2	38.39, 50.36	49.59, 59.97

(unpublished results), it was observed that GMA incorporation shifted endotherm peak temperatures to lower values. In addition, consecutive multiple endotherms were observed in DSC curves with the increase in GMA content. The decreasing effect of GMA and increasing effect of NaAMPS comonomers and their simultaneous effect on the LCST values of hydrogels were seen in Figure 3. In case of terpolymer with the lowest amount of comonomers, a continuous phase transition is observed, similar to the increase in NaAMPS content in case of p(NIPAm/NaAMPS) copolymer (Fig. 3).

DSC results given in Table IV and Figures 2 and 3 show that all hydrogels have a LCST in a range of 40–50°C, which confirms the dynamic swelling results.

In the preliminary experiments of this work, the polymerization experiments were performed at 20°C and the opaque polymers in appearance were obtained. It is known that the opaque appearance of the polymer is resulting from the inhomogeneities in the polymer structure.²⁶ To prepare structurally homogeneous polymer, the polymerization experiments were carried out at +4°C, and the transparent polymers were obtained. But, the multiple endothermic peaks in DSC curves of NIPAm copolymer and terpolymers (Table IV), which interacted with each other, indicated the continuous volume phase transition, namely polydispers polymer structure or the presence of inhomogeneities in network.

The copolymers with 5% NaAMPS content were also prepared. But these copolymers did not exhibit a volume phase transition up to 85°C. Since the LCSTs of the 3NaAMPS copolymers were in a range of 45–50°C, it was assumed that the copolymers with more than 3% NaAMPS content would not exhibit temperature sensitivity, practically. For that reason, the

NaAMPS content in copolymers and terpolymers was kept in the range of 1–3%.

Kinetic swelling and deswelling results

The initial swelling data were analyzed using the equation given below in the range of $m_t/m_\infty \leq 0.6$:

$$m_t/m_\infty = kt^n \quad (5)$$

where m_t and m_∞ is the weight of the swollen hydrogel at time t and infinite time, k , a characteristic constant of the gel; and n , a characteristic exponent depending on the mode of transport of the penetrating molecule.⁵⁰ For Fickian type kinetics (case I), diffusion rate of the penetrant is rate limiting and the exponent n is 0.5. For non-Fickian type (case II) diffusion processes, where contributions from other processes such as

TABLE V
Kinetic Parameters of the Swelling of Hydrogels with Different Compositions at Room Temperature

NaAMPS	Hydrogel		K	n
	GMA	NMBA		
1	—	1	0.016	0.51
2	—	1	0.015	0.53
3	—	1	0.007	0.73
1	—	1.5	0.012	0.51
2	—	1.5	0.011	0.54
3	—	1.5	0.010	0.61
1	1	1	0.018	0.59
2	2	1	0.010	0.70
3	3	1	0.016	0.94
1	1	1.5	0.022	0.51
2	2	1.5	0.034	0.58
3	3	1.5	0.022	0.79

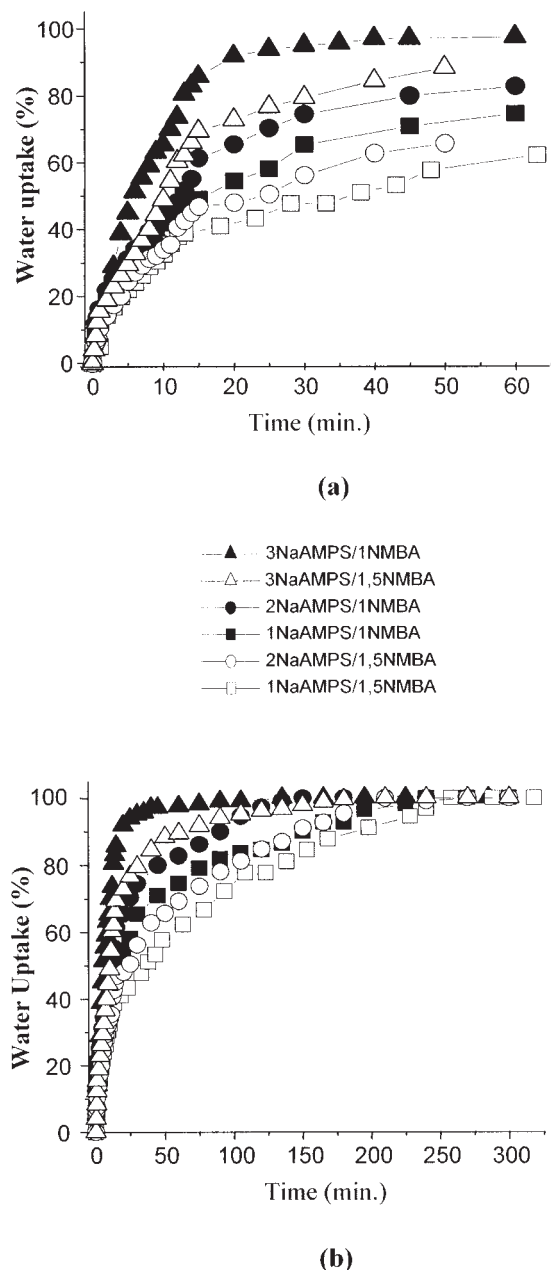


Figure 4 Swelling kinetics of NIPAm-NaAMPS copolymers. ((a) initial swelling, (b) overall swelling).

polymer relaxation are important, n is between 0.5 and 1.⁵¹ The values of k and n obtained from the plots (not given) of $\ln(m_t/m_\infty)$ versus $\ln(t)$ for all hydrogels are given in Table V. Also, it is observed that the increase in NaAMPS content of copolymer at both crosslinker contents (1 and 1.5% NMBA) changes the swelling mechanism from less non-Fickian to more non-Fickian. However, when the hydrogels with crosslinker contents of 1 and 1.5 mol % NMBA are compared, it is seen that the increase in NaAMPS content between 1 and 3 mol % changes the swelling mechanism of both copolymers and terpolymers from more non-Fickian

to less non-Fickian type. Thus, the n values of copolymers and terpolymers with 1% NaAMPS and 1.5% NMBA are nearly the same, 0.51 and 0.59. While the n values of copolymer and terpolymers with 1% NMBA and 3% NaAMPS are 0.73 and 0.94, respectively, they are 0.61 and 0.79, respectively, in the case of polymers with 1.5% NMBA and the same NaAMPS content.

Figure 4(a) and 4(b) shows the initial and overall swelling rates of NIPAm-NaAMPS copolymers with different NaAMPS and NMBA contents. As it is seen in Figure 4, when the hydrophilic comonomer of NaAMPS content increases, the swelling degree and rate values of polymers increase. Since the swelling exponents for six gels were all above 0.5, it can be concluded that the swelling mechanism is non-Fickian.

Table VI shows the time required to reach the swelling equilibrium for the hydrogels. All copolymers reach the swelling equilibrium in 120–260 min. But in case of terpolymers, the time required for swelling equilibrium is one or two orders of magnitude lower for the polymers with 1–2 and 3% NaAMPS contents, respectively, in comparison to those values of copolymers. The time to reach the swelling equilibrium also decreases with the increase in hydrophilic and ionizable comonomer content. It is also seen that the increase in NMBA content increases the time required to reach swelling equilibrium since the diffusion of water molecules into hydrogel becomes more difficult in this case.

Figure 5 shows swelling rates of NIPAm-NaAMPS-GMA terpolymers at room temperature. Similarly, the same behavior was observed in case of terpolymers' swelling kinetics; swelling exponents for six terpolymers were all above 0.5 and the swelling mechanism is non-Fickian type, too. In addition, all terpolymers swell faster than copolymers and reach equilibrium in 3–40 min, while for the copolymers it is between 120 and 260 min. (Table VI). This can possibly be attrib-

TABLE VI
The Time Values to Reach Swelling Equilibrium at Room Temperature

Hydrogel	Time to reach swelling equilibrium (min.)
1NaAMPS/1NMBA	240
2NaAMPS/1NMBA	150
3NaAMPS/1NMBA	120
1NaAMPS/1.5NMBA	258
2NaAMPS/1.5NMBA	240
3NaAMPS/1.5NMBA	180
1NaAMPS/1GMA/1NMBA	20
2NaAMPS/2GMA/1NMBA	16
3NaAMPS/3GMA/1NMBA	3
1NaAMPS/1GMA/1.5NMBA	40
2NaAMPS/2GMA/1.5NMBA	20
3NaAMPS/3GMA/1.5NMBA	5

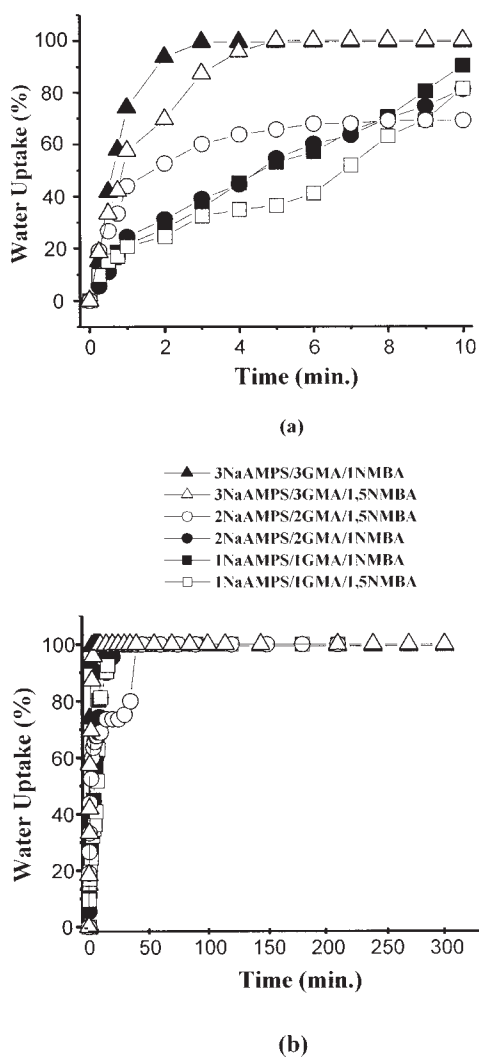


Figure 5 Swelling kinetics of NIPAm-NaAMPS-GMA terpolymers. ((a) initial swelling, (b) overall swelling).

uted to the formation of porous hydrogel structure, which enables diffusion of water molecules into the polymer network more easily.

In the SEM pictures of freeze-dried hydrogels (Fig. 6), it was seen that all hydrogels have porous structure. But in the case of terpolymers, they also have micropores, which can increase diffusion rate of water molecules into the gel structure. The hydrophobic GMA comonomer improved response rate of the terpolymers, in return, terpolymers have faster swelling and deswelling rates than the copolymers.

The deswelling rates of hydrogels at 55°C are shown in Figures 7 and 8. Figure 7 shows that the deswelling of copolymers with NaAMPS contents of 1 and 2% is much faster than that of the copolymers containing 3% NaAMPS. The copolymers with 1NaAMPS and 2NaAMPS (NMBA = 1 and 1.5%) release 90% of their water contents in 20–25 min. Copolymers with 3% NaAMPS content release 85% of their water contents

in 60 min. Deswelling of terpolymer gels is slightly faster than that of the copolymer gels. Figures 8(a) and 8(b) show that all swollen terpolymers lose 90–95% of their water contents in 20 min at 55°C. During the deswelling above the LCST values of hydrogels, the hydrogen bonds between water and the hydrophilic groups of polymers are broken, and the hydrophobic effects become dominant, and finally the shrinking of swollen hydrogels occurs. In case of terpolymers, the presence of hydrophobic GMA units makes extra contribution to the deswelling in addition to that of NIPAm units and favors the deswelling rates of terpolymers in comparison to those of copolymers.

FTIR studies

The FTIR spectra of pNIPAm, p(NIPAm-co-NaAMPS), and p(NIPAm-co-NaAMPS-co-GMA) were given in Figure 9. All three spectra display the characteristic absorption bands at about 1648 cm^{-1} (amide I), about 1542 cm^{-1} (amide II), about 1173 cm^{-1} (amide III) due to stretching of C=O bonds, vibration of N—H bonds, and bending of N—H bonds/stretching of C—N bonds, respectively.^{52–55} The bands related to $-\text{SO}_3^-$ groups (asymmetric and symmetric stretching of S—O bonds) are seen in two regions; 1250 and 1150 cm^{-1} , and 1100 and 1000 cm^{-1} .^{56–58} One of the peaks ascribed to the S—O bond was observed as a single band at 1041 cm^{-1} in the spectra of p(NIPAm-co-NaAMPS) and p(NIPAm-co-NaAMPS-co-GMA) polymers. However, the second band because of S—O bond at higher wave number region interacted with the bands of amide III band, its wave number could not be determined exactly. The band seen at about 1250 cm^{-1}

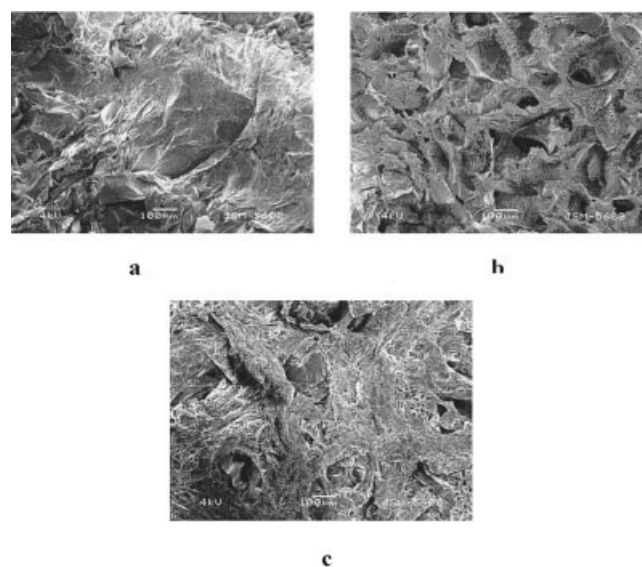
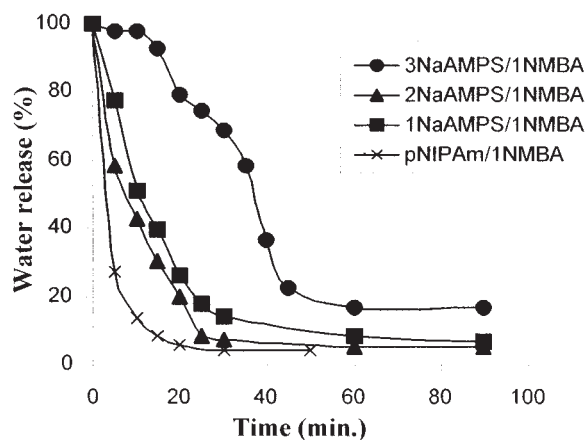
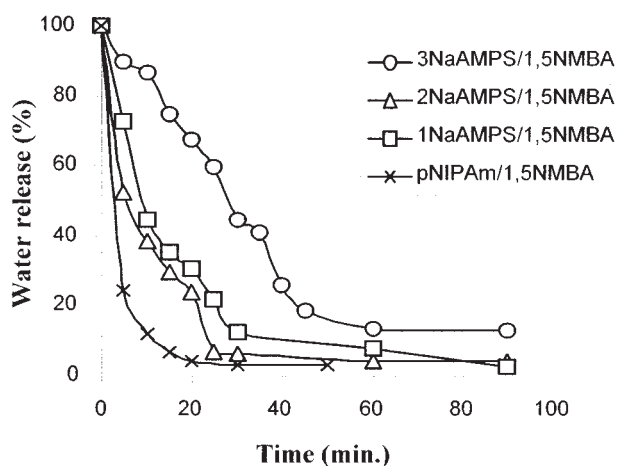


Figure 6 Scanning electron micrographs of polymers (magnification $\times 100$): (a) pNIPAm/1NMBA, (b) 3NaAMPS/1NMBA, (c) 3NaAMPS/3GMA/1NMBA.



(a)



(b)

Figure 7 Deswelling kinetics of NIPAm-NaAMPS copolymers, (a) NMBA = 1%, (b) NMBA = 1.5%.

ascribed to symmetric stretching of epoxy ring in GMA,⁵⁹ interacting with the amide III and S—O bonds is not seen as a single sharp peak. Even so, the presence of GMA in terpolymer structure can be understood because of the relative increase in the intensity and broadening of the so-called band.

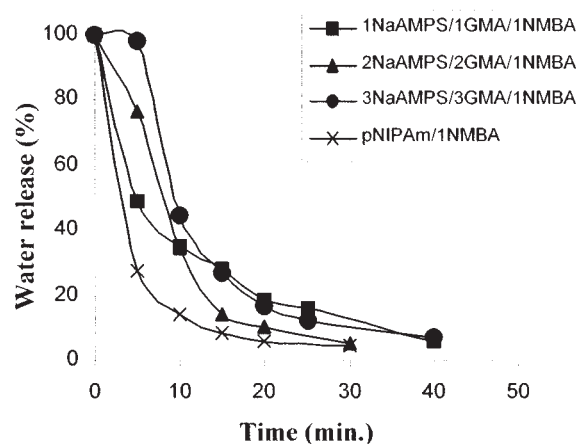
SEM studies

The structural morphology of polymers in the swollen state was studied by scanning electron microscopy. A cross-sectional surface area of the gels swollen at room temperature and freeze dried at -45°C was examined. The SEM images of NIPAm/NaAMPS or NIPAm/NaAMPS/GMA hydrogels are presented in Figure 6. The ionizable 3NaAMPS/1NMBA and 3NaAMPS/3GMA/1NMBA hydrogels display a more open struc-

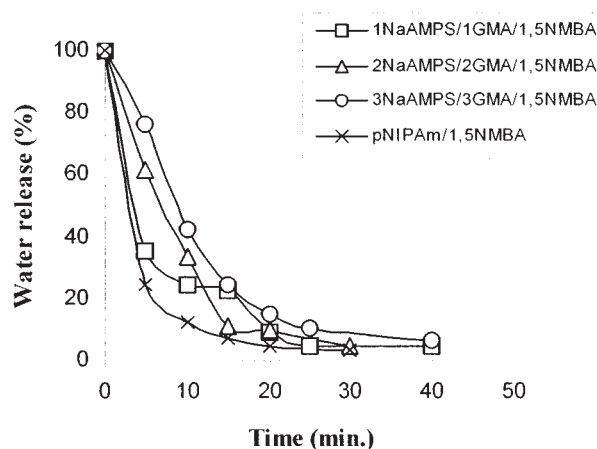
ture than the NIPAm/1NMBA displays. 3NaAMPS/1NMBA has a macro porous structure in addition to its ionic structure. Therefore, ionizable NIPAm/NaAMPS copolymers display fast swelling and deswelling response rate. 3NaAMPS/3GMA/1NMBA has both micro and macro porous structure on the surface. Therefore, terpolymers have faster swelling rates than the copolymers. As the SEM pictures of other copolymers and terpolymers are similar in appearance, only one representative SEM picture for each type of polymer was given.

CONCLUSIONS

Fast responsive temperature sensitive p(NIPAm-co-NaAMPS) and p(NIPAm-co-NaAMPS-co-GMA) hy-



(a)



(b)

Figure 8 Deswelling kinetics of NIPAm-NaAMPS-GMA terpolymers, (a) NMBA = 1%, (b) NMBA = 1.5%.

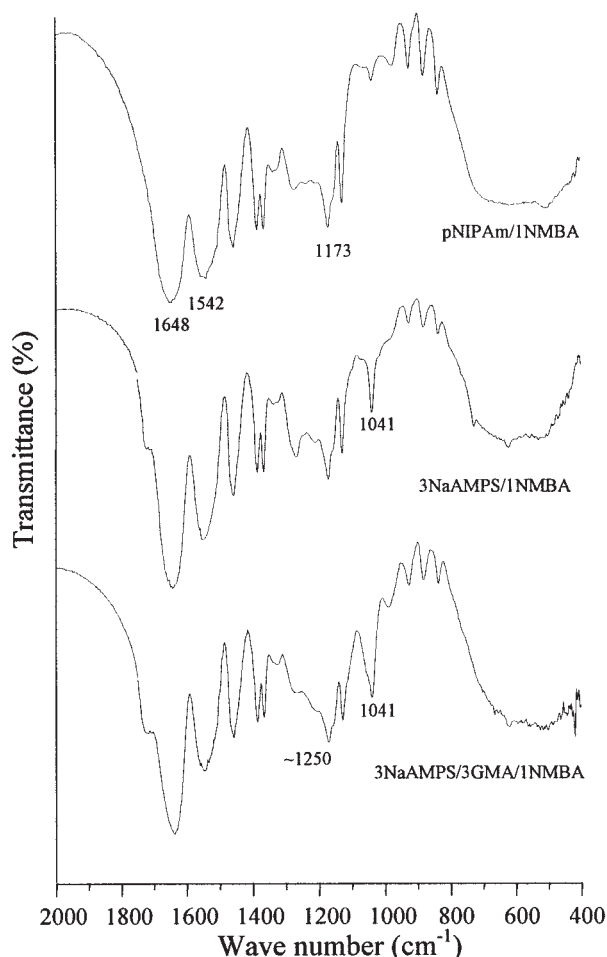


Figure 9 FTIR spectra of hydrogels.

drogels were prepared by free radical chain polymerization in aqueous solution at 4°C. The results show that the use of NaAMPS as a comonomer with NIPAm increases the swelling ratio of the hydrogel. In addition, the use of GMA as a second comonomer with NaAMPS to prepare NIPAm terpolymers led to the formation of hydrogels with faster swelling and deswelling rates than the copolymers prepared using only NaAMPS as comonomer. It is also concluded that NaAMPS content in feed composition more than 3% leads to the disappearance of temperature sensitivity.

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