

# Thermoreversible Hydrogel. V. Synthesis and Swelling Behavior of the *N*-Isopropylacrylamide-*co*-Trimethyl Methacryloyloxyethyl Ammonium Iodide Copolymeric Hydrogels

WEN-FU LEE, CHENG-HAWN HSU

Department of Chemical Engineering, Tatung Institute of Technology, Taipei, Taiwan, Republic of China

Received 9 September 1997; accepted 17 October 1997

**ABSTRACT:** A series of *N*-isopropylacrylamide/trimethyl methacryloyloxyethyl ammonium iodide (NIPAAm/TMMAI) copolymeric gels are prepared from the various molar ratios of NIPAAm, cationic monomer TMMAI, and *N,N'*-methylene bisacrylamide (NMBA) in this article. The influences of the amount of the cationic monomer in the copolymeric gels on the swelling behavior in water, various saline solutions, and various temperatures are investigated. Results show that the swelling ratios of copolymeric gels are significantly larger than those of pure homopolymer NIPAAm gel, and the more the TMMAI content, the higher the gel transition temperature. In the saline solution, results show that the swelling ratio of pure NIPAAm gel has not significantly changed with an increase of the salt concentration until the salt concentration is larger than 0.1M. The swelling ratios for the copolymeric gels NIPAAm/TMMAI decrease with increasing salt concentration. In various saline solutions, results show that the anionic effects are greater than cationic effects in the presence of common anion, different cations and common cation, and different anions for these hydrogels. Finally, we also tested the reversibility of the NIPAAm/TMMAI copolymeric gels. The deswelling and reswelling kinetics are dependent on the temperature, which is below or above the gel transition temperature. The gel with little TMMAI content has a good reversibility.

© 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1793–1803, 1998

**Key words:** cationic; thermosensitive; hydrogel; thermoreversible

## INTRODUCTION

Hydrogel is a kind of polymer that can be swollen but cannot be dissolved in water. There are some hydrogels that can modulate the swelling ratio in response to environmental stimuli such as temperature,<sup>1,2</sup> pH,<sup>3,4</sup> chemicals,<sup>5</sup> photoirradiation,<sup>6</sup> electric field,<sup>7</sup> etc. The collapse of a gel in response to environmental changes was predicted by Dusek and Patterson<sup>8</sup> and intensively investigated by Tanaka and co-workers.<sup>9–13</sup> Thermosensitive hy-

drogel, one of the environmental stimuli response hydrogels, collapses at elevated temperature through the lower critical solution temperature (LCST). The volume change occurs within a quite narrow temperature range. Permeability of water through the gel can be changed by an “on–off” switch according to the environmental temperature. Therefore, such materials can be used in many fields such as drug delivery system,<sup>14,15</sup> extraction,<sup>16</sup> and enzyme activity control.<sup>17</sup>

*N*-Isopropylacrylamide (NIPAAm) hydrogels demonstrate a nearly continuous volume transition and associated phase transition from low temperature, a highly swollen gel network, to high temperature, a collapsed phase near its criti-

Correspondence to: W.-F. Lee.

cal point between 31–35°C.<sup>18</sup> Recently, Hirotsu<sup>19</sup> investigated the phase behavior of the NIPAAm gel/water/alcohol system and explained their thermoshinking by the destruction of hydrogen bonds between water molecules and NH or CO of NIPAAm.

NIPAAm gels containing sodium acrylate (SA) in pure water have been studied previously by Tanaka and co-workers.<sup>12,13,20</sup> Their results indicated that incorporation of small amount of anionic SA into NIPAAm networks produced continuous swelling transition in macroscopic gels at the critical temperature. Moreover, the gel transition temperature increased monotonically as a function of SA content. Some NIPAAm gels containing cationic comonomer have been reported by Beltran et al.<sup>21,22</sup> They reported on the behavior and properties of NIPAAm gels containing cationic comonomer methacrylamidopropyl trimethylammonium chloride (MAPTAC). Their results showed that the swelling ratio of the gel in water and in salt solution at low ionic strength was highly dependent on the degree of gel ionization, and the temperature range increased strongly with gel ionization. In addition, the volume change appeared to become less dramatic as the percentage of cationic monomer increased.

A series of cationic monomers and their corresponding polymers were prepared and the aqueous salt solution properties were investigated in our previous report.<sup>23</sup> In our previous study, a series of NIPAAm/trimethyl acrylamido propyl ammonium iodide (TMAAI) copolymeric gels were prepared. The influence of the amount of TMAAI in the copolymeric gels on the swelling behaviors in water and various saline solutions were investigated.<sup>24</sup> Hence, a series of *N*-isopropylacrylamide/trimethyl methacryloyloxyethyl ammonium iodide (NIPAAm/TMMAI) copolymeric gels were prepared in an attempt to investigate the influence of molar ratio of NIPAAm/TMMAI and the effect of various salt solutions on swelling behaviors for these copolymeric gels. The results obtained from this study will be compared with those obtained from previous studies.

## EXPERIMENTAL

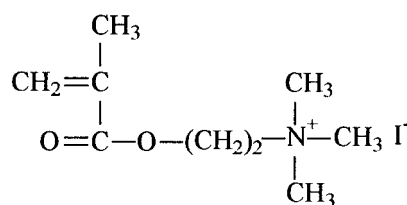
### Materials

Dimethylaminoethyl methacrylate (TCI Co.) was further purified by vacuum distillation at 160°C/16 KPa. *N*-isopropylacrylamide (NIPAAm) (Fluka

Chemical Co.) was recrystallized in *n*-hexane before use to remove an inhibitor. Methyl iodide (TCI Co.), *N,N'*-methylene bisacrylamide (NMBA) (Sigma Chemical Co., St. Louis, MO) as a crosslinker, and *N,N,N',N'*-tetramethylethylenediamine (TEMED) (Fluka Chemical Co.) as an accelerator were used as received. Ammonium peroxodisulfate (APS) (Wako Pure Chemical Co. Ltd.) as an initiator was further purified by recrystallization.

### Synthesis of Monomer

The monomer trimethyl methacryloyloxyethyl ammonium iodide (TMMAI) was prepared as described previously.<sup>25</sup> Yield 97%; m.p. 178°C. The structure is given below.



### Preparation of Hydrogels

Various ratios of NIPAAm, TMMAI, and 3 mol % NMBA based on total monomer content were dissolved in 10 mL of deionized water. To this solution, 3 wt % APS and 3 wt % TEMED as redox initiator were added, and the mixture was immediately injected into the space between two glass plates. The gel membrane thickness was adjusted with a silicone spacer between the two glass plates. Polymerization was carried out at room temperature for 1 day. After the gelation was completed, the gel membrane was cut into disks, 10 mm in diameter, and then immersed in an excess amount of deionized water for 7 days to remove the residual unreacted monomer. Swollen polymeric gels were dried at room temperature for 1 day, and these samples were further dried in a vacuum oven for two days at 60°C.

### Measurement of Swelling Ratio

The dried gels were immersed in an excess amount of deionized water or various saline solutions with different concentrations at 25°C until swelling equilibrium was attained. Each sample was then removed from the water bath and its respective vial, tapped with filter paper to remove

**Table I** Characterization of NIPAAm/TMMAI Copolymer Gels

Sample No.	Feed Composition (%)		Cloud Point Effect <sup>a</sup>	Cloud Point Temperature	Swelling Ratio (g H <sub>2</sub> O/g Dry Gel)
	NIPAAm	TMMAI			
TMM0	100	0	st	30–35	14.1
TMM1	99	1	st	30–35	19.3
TMM2	98	2	st	40–50	24.1
TMM3	97	3	vw	40–50	31.9
TMM5	95	5	vw	50–60	44.5
TMM6	94	6	vw	50–60	53.2

<sup>a</sup> st, strong; vw, very weak.

excess surface water, and weighed as the wet weight ( $W_w$ ). Dry weight ( $W_d$ ) was determined after drying the gel in a vacuum oven for 2 days. Swelling ratio ( $Q$ ) was calculated from the following formula:

$$Q = \frac{W_w - W_d}{W_d} \quad (1)$$

### Dynamic Swelling

The dried gels were immersed in an excess amount of deionized water at different temperatures. The swelling ratio was obtained by weighing the initial and swollen samples at various time intervals. The amount of water sorbed,  $M_t$ , was reported as a function of time, and the equilibrium sorption at infinitely long time was designated  $M_\infty$ . The following equation can be used to calculate the diffusion coefficient  $D$  for  $M_t/M_\infty \leq 0.8$ .<sup>26</sup>

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \times \left( \frac{D \times t}{L^2} \right)^{1/2} \quad (2)$$

where  $t$  is the time and  $L$  is the initial thickness of the dried gel.

## RESULTS AND DISCUSSION

The swelling behavior of the hydrogels depends on the nature of the polymer and the environment conditions. The polymer's nature involves the nature of the charge, ionic content, and crosslinking agent content.

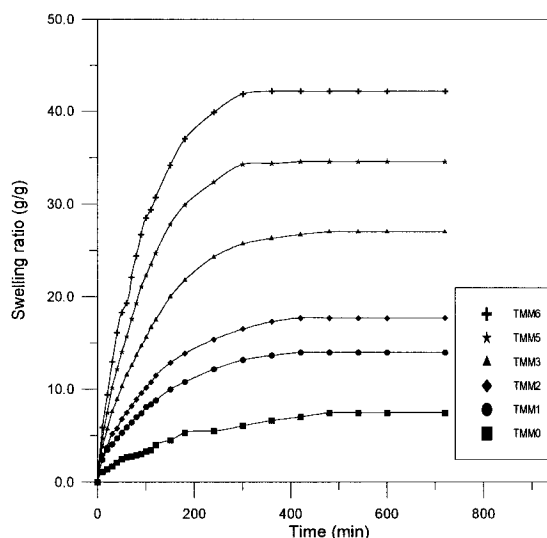
### Characterization of NIPAAm/TMMAI Copolymeric Gels

Some characteristics of the NIPAAm/TMMAI copolymeric gels for various feed compositions are shown in Table I. The results, in Table I, show

that the cloud point effect of the copolymeric gels is weaker with increasing content of TMMAI monomer. The gel transition temperatures are increased with an increase of the content of TMMAI in the copolymeric composition; i.e., from 30 to 60°C for TMM0–TMM6, respectively. The reason is that addition of TMMAI monomer into gel composition made the gel become more hydrophilic. Moreover, the gel intensity here was stronger than for that which was prepared in our previous work.<sup>24</sup> The equilibrium swelling ratios of the copolymeric gels also increased with increasing content of TMMAI (also see Fig. 1).

### Effect of TMMAI Content on Swelling Ratio

The swelling ratios as a function of time for NIPAAm/TMMAI copolymeric gels at 30°C in deionized water are shown in Figure 1. The results



**Figure 1** Swelling ratio as a function of time for NIPAAm/TMMAI copolymeric gels at 30°C.

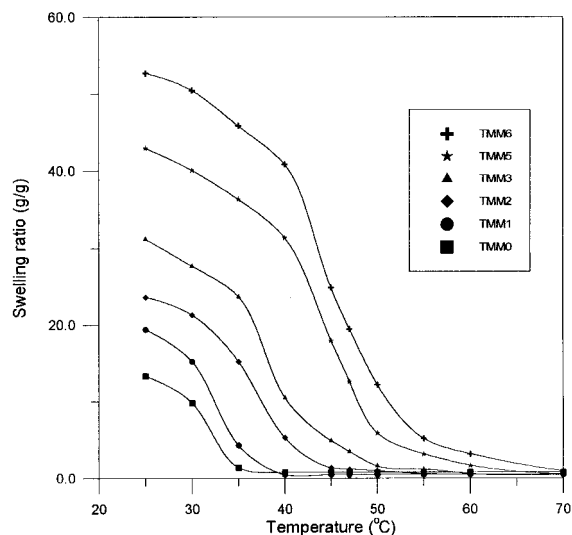
shown in Figure 1 indicate that the swelling ratios increase with TMMAI content. According to Flory's swelling theory,<sup>27</sup> the following equation was given:

$$Q^{5/3} = [(i/2V_\mu S^{1/2})^{1/2} + (\frac{1}{2} - \chi_1)/v_1]/(\nu_e/V_0) \quad (3)$$

where  $i/V_\mu$  is the concentration of fixed charge referred to unswollen network,  $S$  is the ionic concentration in the external solution,  $(\frac{1}{2} - \chi_1)/v_1$  is the affinity of the hydrogel for water, and  $\nu_e/V_0$  is the crosslinked density of the hydrogel. It is well known that the swelling ratio has a relation to ionic osmotic pressure, crosslinked density, and the affinity of the hydrogel for water from the above equation. The crosslinked density was fixed in a series of different compositions of NIPAAm/TMMAI copolymeric hydrogels, so the influence of the swelling ratio of the hydrogels is the affinity of hydrogel for water and total charges inside the gel. Because the TMMAI monomer is a hydrophilic cationic monomer, the greater the TMMAI content, the larger the affinity of the gel for water, and the higher the swelling ratio of the hydrogel. In other words, the TMMAI monomer is ionized in aqueous solution and the mutual repulsion of their charges causes expansion of the polymeric chain. This occurrence leads to a higher swelling ratio of the hydrogel with more content of TMMAI.

#### Effect of Temperature on Swelling Ratio for NIPAAm/TMMAI Copolymeric Gels

The effect of temperature on the equilibrium swelling ratio for a series of NIPAAm/TMMAI copolymeric gels is shown in Figure 2. The results shown in Figure 2 indicate that the higher the temperature the lower the swelling ratio; and the more the TMMAI content the higher the gel transition temperature. For the NIPAAm gel, the hydrophilic group (amido —NHCO—) in the polymer structure would form an intermolecular hydrogen bond with surrounding water at low temperature (below gel transition temperature). Hence, water penetrated into the NIPAAm gels is in a bound state at low temperature. The water molecule would gain an enthalpy during the temperature increase, and the hydrophilic groups (amido) in the NIPAAm gels would be turned into intramolecular hydrogen bonds in this condition. This occurrence leads to the hydration force of the gel decrease. At the same time, the hydrophobic

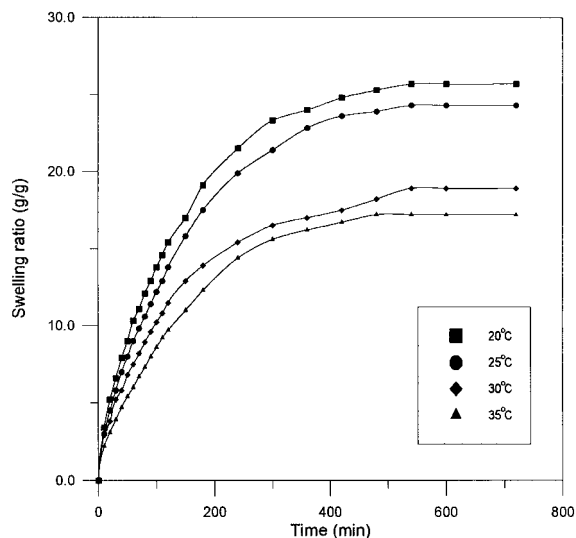


**Figure 2** Swelling ratio as a function of temperature for NIPAAm/TMMAI copolymeric gels.

force of isopropyl group of NIPAAm gel increases. These two results make the water molecules inside the gel change from bound state to free state and are released out of the gel network. This phenomenon makes the swelling ratio of the gel rapidly decrease at the gel transition temperature. The results shown in Figure 2 also indicate that the greater the TMMAI content, the higher the hydrophilic ability of the gel, and the stronger the affinity of the hydrogel for water. Therefore, the gel transition temperature becomes higher as the TMMAI content in these copolymeric gels increases. These results conform to our previous studies for NEPAAm/AAm or NTHFAAm/AAm hydrogels.<sup>28,29</sup> The increase of the gel transition temperature was lower in the NIPAAm/TMMAI gel system, so the hydrophilicity of the monomer TMMAI was lower than that of the TMAAI monomer.

#### Investigation of Water Diffusion in Xerogels

Typical swelling ratios as a function of time, for sample TMM2 copolymeric gel at various temperatures, are shown in Figure 3. The results shown in Figure 3 indicate that the swelling ratio decreases with increasing temperature. As more cationic groups are incorporated into the gel, the equilibrium swelling can be reached more quickly. This is related to the LCST as well as the amount of ionic charged group in the individual gel matrix. As the charge density rises, the driving force for swelling also increases. Swelling kinetic can



**Figure 3** A typical swelling ratio as a function of time for TMM2 at different temperatures.

be generally described in two terms: the diffusion rate of imbibing solvent into the gel, and the relaxation rate of the polymer network.

To obtain a more quantitative understanding of the nature of the sorption kinetic in TMM series gels, the initial swelling data were fitted to the exponential heuristic equation<sup>30,31</sup>:

$$\frac{M_t}{M_\infty} = kt^n$$

where  $k$  is a characteristic constant of the gel, and  $n$  is a characteristic exponent of the mode transport of the penetrate. “ $n$ ” and “ $k$ ” were calculated from the slopes and intercepts of the plot of  $\log(M_t/M_\infty)$  against  $\log(t)$  at various temperatures, respectively. For Fickian kinetics in which the rate of penetrate diffusion is rate limiting,  $n = 0.5$ , whereas values of  $n$  between 0.5 and 1 indicate the contribution of non-Fickian processes such as polymer relaxation. The results are shown in Table II, we see that the swelling exponent “ $n$ ” for all NIPAAm/TMMAI copolymeric gels at various temperatures are between 0.5 and 1.0. These results indicate that the swelling transport mechanism is a non-Fickian transport.

The measurement techniques of diffusion coefficient in polymers have been fully discussed by Crank and Park.<sup>32</sup> The measurement technique used in their experiment is based on the use of initial rates of sorption.<sup>33</sup> It is possible to deduce an average diffusion coefficient from the initial gradient of the sorption curve when plotted

against the square root of time. Equation (2) was used to calculate the diffusion coefficient ( $D$ ). The data shown in Table II indicate that the diffusion coefficients for various NIPAAm/TMMAI copolymeric gels are increased with an increase of temperature. Because TMM0 gel is unswollen at 35°C, due to the temperature being higher than the LCST of the gel, the values of  $n$ ,  $K$ , and  $D$  are not shown in Table II. The equilibrium swelling ratio and equilibrium time are decreased with an increase of temperature. The initial absorption rates (at the initial 3 h) decrease with increasing temperature for TMM0–TMM3, but increased with increasing of temperature for TMM5–TMM6, respectively. Hence, it is apparently show that the initial water absorption rate is affected by the TMMAI content in the copolymeric composition.

### Effect of Various Salt Solutions on the Swelling Ratio

We investigated the influence of TMMAI component in the copolymeric gel on the swelling behavior for the NIPAAm gel in the presence of various salt solutions. From the above results it seems that the more the TMMAI content, the more apparent the ionic effect. Samples TMM6 and TMM0 were chosen to compare and discuss in subsequent sections.

### The Influence of Different Monovalent Cations with a Common Anion ( $\text{Cl}^-$ ) on the Swelling Ratio

Figure 4 shows the swelling ratios of sample TMM0 and TMM6 as a function of the salt concentration for LiCl, NaCl, and KCl solutions, respectively. The results shown in Figure 4 indicate that the swelling ratios of sample TMM0 keep an approximately constant value in the range of the salt concentration from  $1 \times 10^{-5}$  to  $0.5M$  and then rapidly decrease with concentration of the salts over  $0.5M$ . Because the total fixed charge for pure NIPAAm gel is zero, the concentration of fixed charge referred to unswollen network,  $1/V_\mu$ , is zero according to Flory’s swelling theory.<sup>27</sup> This implies that the swelling ratio of TMM0 gel could not be affected by the external dilute salt solution. But the swelling ratio of the NIPAAm gel rapidly decreases while the concentration of salt solutions is over  $0.1M$ , in the order of  $\text{LiCl} > \text{NaCl} = \text{KCl}$  (contract to zero swelling ratio). This can be explained as that the hydration force of  $\text{Li}^+$  is larger than that of  $\text{Na}^+$  and  $\text{K}^+$ , so the hydrated lithium

**Table II** Initial Diffusion Coefficient of Water,  $D$ , Kinetic Exponent,  $n$ , and Characteristic Constant,  $K$ , of Water Penetrated Through NIPAAm/TMMAI Copolymeric Gels at Various Temperature

Sample No.	Temp. (°C)	$n$	$K \times 10^3$	$D \times 10^8$ (cm <sup>2</sup> /s)	$SR_{eq}^a$ (g/g)	$T_{eq}$ (h)	Initial Rate (g/min)
TMM0	20°C	0.545	4.5	6.44	14	16	0.061
	25°C	0.510	6.2	6.51	12	12	0.044
	30°C	0.507	6.6	9.21	6	6	0.029
	35°C	—	—	—	0.6	1	0
TMM1	20°C	0.543	5.16	4.95	18.8	10	0.079
	25°C	0.552	4.4	7.14	17.0	9	0.069
	30°C	0.519	6.1	7.62	14.0	8	0.060
	35°C	0.533	4.2	7.69	9.7	7	0.034
TMM2	20°C	0.608	2.7	9.76	25.7	11	0.106
	25°C	0.611	2.5	9.81	24.2	9	0.097
	30°C	0.568	3.8	9.98	18.9	9	0.077
	35°C	0.610	2.4	10.2	17.2	8	0.068
TMM3	20°C	0.610	2.6	8.07	32.9	10	0.132
	25°C	0.600	3.1	9.90	29.8	9	0.117
	30°C	0.619	2.7	10.1	27.1	9	0.116
	35°C	0.610	4.8	13.6	25.8	8	0.097
TMM5	20°C	0.734	1.0	11.0	40.3	10	0.161
	25°C	0.713	1.1	11.6	38.9	9	0.166
	30°C	0.678	1.8	14.8	36.2	7	0.172
	35°C	0.740	1.1	15.9	34.5	6	0.174
TMM6	20°C	0.712	1.2	10.6	47.5	9	0.201
	25°C	0.775	0.8	11.2	46.2	8	0.206
	30°C	0.684	1.7	13.1	43.5	6	0.211
	35°C	0.798	0.8	16.2	41.9	6	0.222

<sup>a</sup>  $SR_{eq}$ , equilibrium swelling ratio;  $T_{eq}$ , equilibrium time.

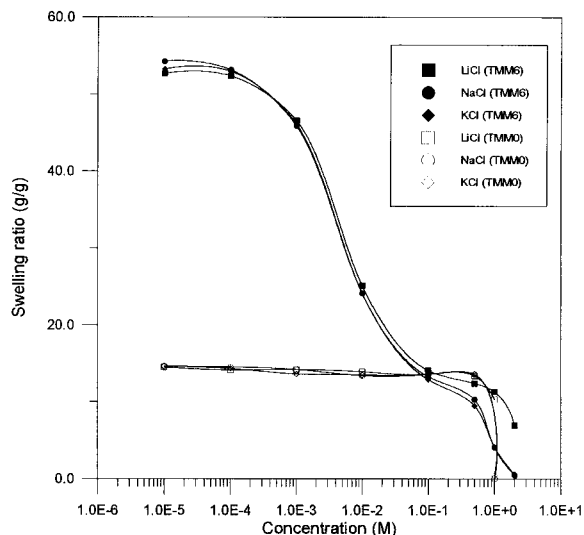
ion can easily hydrogen bond onto the amido group of the NIPAAm gel. Hence, the swelling ratio of poly(NIPAAm) gel has a higher value in the concentrated LiCl solution. The swelling ratio of sample TMM6, however, was influenced by the affinity of water and the fixed charge of gel, because the side chain of TMMAI would bear a positive charge as the iodide ion became ionized in an aqueous solution.

The swelling ratios for TMM6 shown in Figure 4 show that the swelling ratios keep constant at salt concentrations from  $10^{-5}M$  to  $10^{-4}M$ , then gradually decrease with an increase of salt concentration. This behavior can be readily explained on the basis of simple physical argument. At low ionic strength, the concentration of bound charges within the gel exceeds the concentration of salt in the external solution; a large ion-swelling pressure causes the gel to expand, thereby lowering the concentration of co-ions within the gel. As the external salt concentration rises, the difference between the internal and external ion concentration decreases and the gel deswells; the gel contin-

ues to deswell with rising external salt concentration until the mobile-ion concentrations inside and outside the gel are approximately equal. These phenomena, shown in Figure 4, can also be explained on the basis of repulsion between fixed charged groups on the gel. At low ionic strength, repulsion is long range and the gel expands to minimize the repulsive free energy; as ionic strength rises, repulsion is shielded and the gel deswells (shielding effect).

#### The Influence of Different Divalent Cations with a Common Anion ( $Cl^-$ ) on the Swelling Ratio

Figure 5 shows the swelling ratios for TMM0 and TMM6 xerogels in salt solutions of  $MgCl_2$ ,  $CaCl_2$ , and  $SrCl_2$ , respectively. The swelling behaviors for TMM0 in these salt solutions have the same tendency as those in the salt solutions of LiCl, NaCl, and KCl, respectively. But the swelling behavior for TMM6 gradually decreases with increasing content of these divalent salts from the concentration of  $10^{-5}M$  to  $2M$ , and the swelling

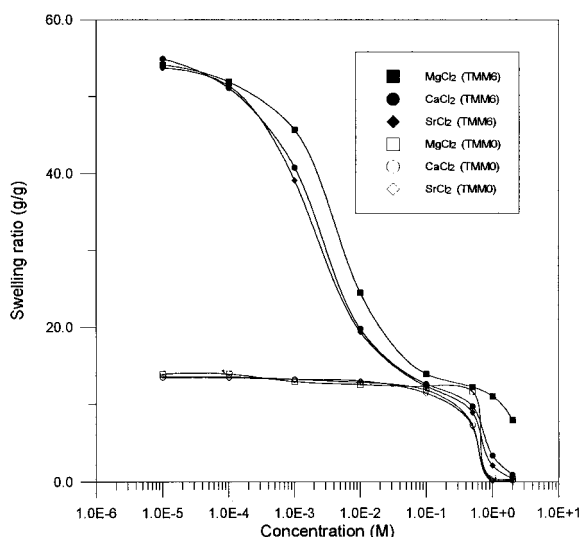


**Figure 4** Swelling ratio for TMM0 and TMM6 in the various salt solutions with different monovalent cations at 25°C.

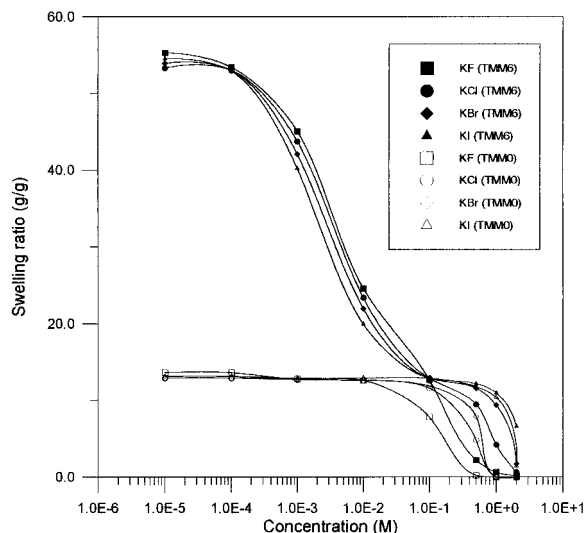
ratios for these two gels show a trend in the order of  $\text{MgCl}_2 > \text{CaCl}_2 > \text{SrCl}_2$ . These results imply that the swelling ratios for these gels are influenced by the fixed charges inside the gels.

#### The Influence of Different Halide Ions with a Common Cation ( $\text{K}^+$ ) on the Swelling Ratio

The influence of different halide ions with a common cation ( $\text{K}^+$ ) on the swelling ratio for TMM0



**Figure 5** Swelling ratio for TMM0 and TMM6 in various salt solutions with different divalent cations at 25°C.



**Figure 6** Swelling ratio for TMM0 and TMM6 in various salt solutions with different halide ions at 25°C.

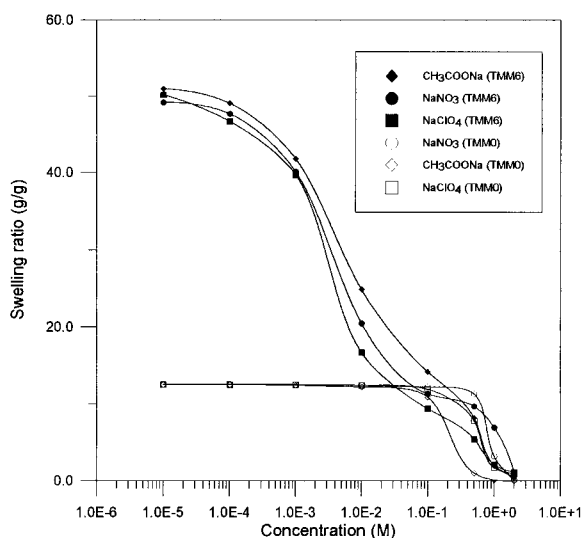
and TMM6 was investigated. The results shown in Figure 6 indicate that the swelling ratio for TMM6 decreases with an increase of the salt concentration from  $10^{-5}$  to  $0.1\text{M}$ . The results also show that the deswelling curves are divided into two parts. The swelling ratio of the gels in different salt solutions is in the order of  $\text{KF} > \text{KCl} > \text{KBr} > \text{KI}$  when the salt concentration is below  $0.1\text{M}$ . This is because the larger anion with common positive charge (charge density is smaller) is easily polarized and bound to quaternary ammonium group ( $\text{R}_4\text{N}^+$ ) on the chain. The positive charge on the polymeric side chain could, therefore, become effectively neutralized by the larger anion ( $\text{I}^-$ ) and decrease the swelling ratio. When the salt concentration is larger than  $0.1\text{M}$ , the trend of the swelling ratio is in the order of  $\text{KF} < \text{KCl} < \text{KBr} < \text{KI}$ , due to the polyelectrolyte behavior of the gels being shielded by the salt effect (screen effect). Therefore, the behavior of the gels is like the uncharged gels. This deswelling behavior in this condition is similar to the deswelling behavior of the poly(NIPAAm) gel (TMM0). Figure 6 also shows the swelling ratio of sample TMM0 as a function of the salt concentration for KF, KCl, KBr, and KI solutions, respectively. The results indicate that the swelling ratios of sample TMM0 keep constant values at low concentration ( $<0.1\text{M}$ ), but decrease in the order of  $\text{KF} < \text{KCl} < \text{KBr} < \text{KI}$ , respectively. The result is the same as the behavior of sample TMM6 at high concentration ( $>0.1\text{M}$ ). From the above results, it is also found that the anionic effect is

greater than the cationic effect for the copolymeric gels. The effect of different acidic ions with common cation on the swelling ratio will be discussed in the next section.

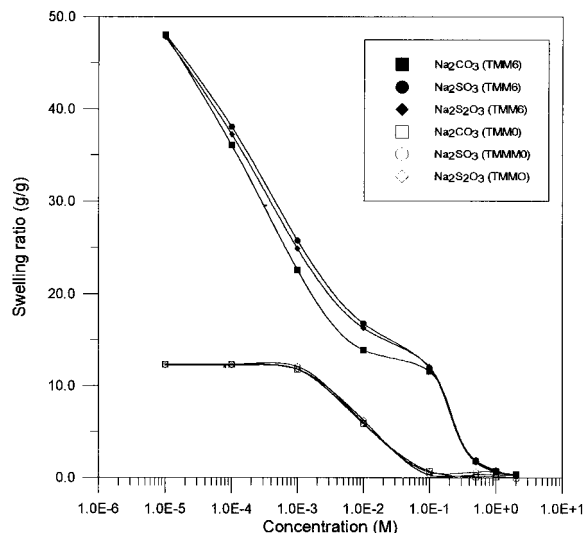
### The Influence of Different Acidic Ions with a Common Cation ( $\text{Na}^+$ ) on the Swelling Ratio

The influence of different acidic ions ( $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ , and  $\text{CH}_3\text{COO}^-$ ) with a common cation ( $\text{Na}^+$ ) on the swelling ratio for TMM0 and TMM6 copolymeric gel was investigated. The results shown in Figure 7 indicate that the trend of the swelling ratio for TMM6 gel is in the order of  $\text{CH}_3\text{COO}^- > \text{NO}_3^- > \text{ClO}_4^-$  for  $\text{CH}_3\text{COONa}$ ,  $\text{NaNO}_3$ , and  $\text{NaClO}_4$  solutions, respectively, as the concentration of salts is lower than  $0.2\text{M}$ . This is because the acetate ion ( $\text{CH}_3\text{COO}^-$ ) is a weak acidic group and easily associates to form acetic acid in aqueous solution. The  $\text{ClO}_4^-$  ion is attracted to the polymeric side chain and this attraction causes the polymeric chain not to expand and agglomerate in this situation. The results shown in Figure 7 also show that the trend of the swelling ratio for TMM6 gel is in the order of  $\text{NO}_3^- > \text{CH}_3\text{COO}^- = \text{ClO}_4^-$  for high concentrations ( $>0.2\text{M}$ ) of  $\text{NaNO}_3$ ,  $\text{CH}_3\text{COONa}$ , and  $\text{NaClO}_4$  solutions, respectively.

From Figure 7, the results indicate that the swelling ratio of TMM0 keeps a constant value at low concentration ( $<0.01\text{M}$ ), but decreases rapidly at high concentration. The trend for swelling ratio is in the order of  $\text{CH}_3\text{COO}^- < \text{ClO}_4^- < \text{NO}_3^-$



**Figure 7** Swelling ratio for TMM0 and TMM6 in various salt solutions with different acidic ions at  $25^\circ\text{C}$ .



**Figure 8** Swelling ratio for TMM0 and TMM6 in various salt solutions with different diacidic ions at  $25^\circ\text{C}$ .

for  $\text{CH}_3\text{COONa}$ ,  $\text{NaClO}_4$ , and  $\text{NaNO}_3$  solutions, respectively. From the above results, we know that the swelling behavior of sample TMM6 is like an uncharged hydrogel in high concentration of salt solutions and is similar to sample TMM0.

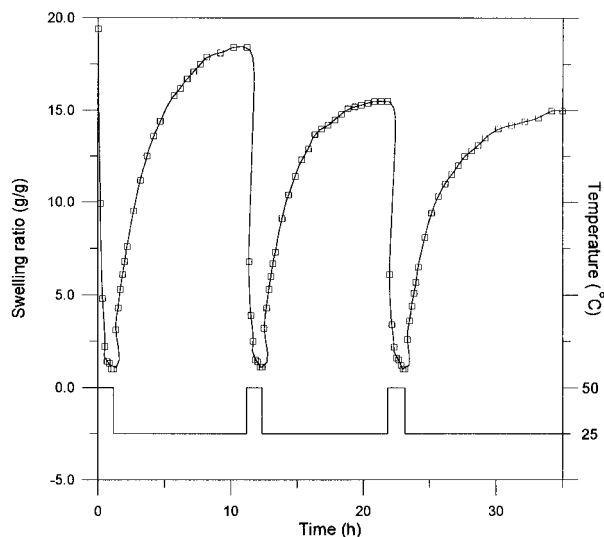
For the various divalent acidic groups, the data (see Fig. 8) show that the swelling ratios decrease with an increase of concentration of salt solution. For Figure 8, the swelling ratio for TMM0 rapidly decreases from 12 at  $10^{-3}\text{M}$  to zero at  $10^{-1}\text{M}$  at various salt solution concentrations. The swelling ratio for TMM6 shows a two-stage decrease; i.e. the first stage is from  $10^{-5}$  to  $10^{-1}\text{M}$ , and the second stage is from  $10^{-1}$  to  $1\text{M}$  for various divalent acidic salt solutions. Comparing these two gels, it is known that the first stage deswelling behavior for TMM6 is mainly attributed to the TMMAI component, and their swelling ratios show a decrease in the order of  $\text{SO}_3^{2-} > \text{S}_2\text{O}_3^{2-} > \text{CO}_3^{2-}$  for  $\text{Na}_2\text{SO}_3$ ,  $\text{Na}_2\text{S}_2\text{O}_3$ , and  $\text{Na}_2\text{CO}_3$  solutions, respectively. This phenomenon was explained by Pearson's theory.<sup>23,34</sup> The second stage deswelling behavior for the TMM6 gel is consistent with the deswelling behavior of TMM0.

### Swelling and Deswelling Kinetics of NIPAAm/TMMAI Copolymeric Gels and Its Reversibility

The swelling–deswelling kinetics of NIPAAm/TMMAI copolymeric gels (TMM1, TMM3, and TMM6) with temperature modulation between  $25$  and  $50^\circ\text{C}$  are shown in Figures 9, 10, and 11.

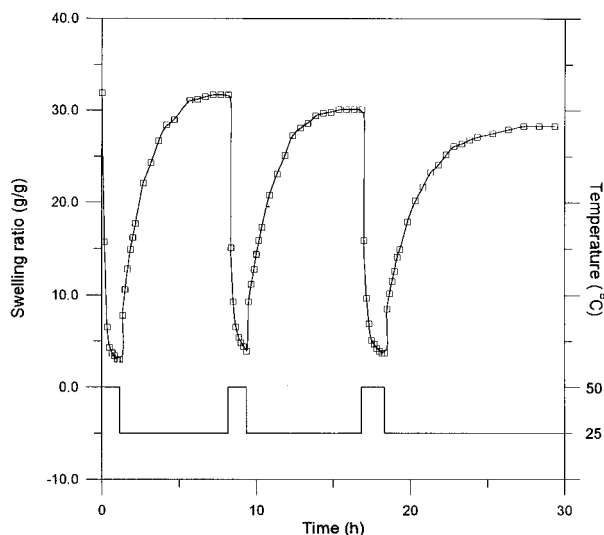
As seen from Figure 9, the swelling kinetics,



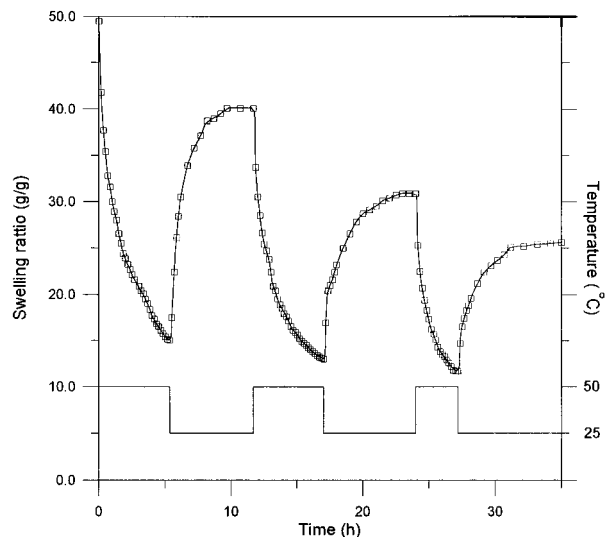


**Figure 9** Swelling-deswelling kinetics of TMM1 by temperature modulation from 25 to 50°C.

when the temperature is modulated from 25 to 50°C, took only 30 min to squeeze 90% of the water out. Reswelling kinetics took almost 10 h to attain the next equilibrium stage. Mukae and Colleagues<sup>35</sup> reported a poly(NIPAAm) gel took about 3 h to extrude the 70% water from 25 to 40°C. In reswelling, 12 h was needed to absorb 80% of the water. Concerning the rate of the swelling rate change, it is supposed that the TMM1 gel is more thermosensitive than the poly(NIPAAm) gel. The reason is that when the temperature is raised to the gel shrinking temperature, the out-



**Figure 10** Swelling-deswelling kinetics of TMM3 by temperature modulation from 25 to 50°C.



**Figure 11** Swelling-deswelling kinetics of TMM6 by temperature modulation from 25 to 50°C.

layer of the disk is the first area to be affected. Skin is formed, which retards the flux of water out of the gel. So the deswelling rate is slow. In contrast, the TMM1 gel is more hydrophilic than poly(NIPAAm) gel. No skin is formed as the temperature increases through the LCST. The water in the gel layer easily passes through when it shrinks. Hence, the more hydrophilic monomer is contained in the copolymeric gel, the affinity of the gel with water is stronger, and a response to the temperature is faster.

The result shown in Figure 10 is the same as that shown in Figure 9. But the reswelling time for TMM3 gel is shorter than that for TMM1 gel shown in Figure 9. This is because the higher the TMMAI content, the more hydrophilic is the gel, and the shorter the response time.

The result for TMM6 shown in Figure 11 indicates a large difference from those shown in Figures 9 and 10. It took 5 h to reach the next equilibrium when the temperature is modulated from 25 to 50°C, and reswelling kinetics took 7 h to attain the next equilibrium stage. From our previous results, the gel transition temperature for TMM6 is about 50 to 60°C, and the process of the gel shrinking is not clear. The response time in deswelling kinetics is longer than that for TMM1 and TMM3 gels, yet, the response time for reswelling kinetics is only taking 7 h. The reason is the same as before. So from our previous discussion, the gel deswelling and reswelling kinetics are very much dependent on whether the temperature is below or above the gel transition temperature.

Comparing the first swelling ratio at 25°C and the last swelling ratio at 25°C, there is no significant decrease in the experiments for TMM1 and TMM3. But the swelling ratio for TMM6 decreases from 50 g H<sub>2</sub>O/g sample to 26 g H<sub>2</sub>O/g sample. This is because, during the process of measurement, pieces of TMM6 gel fragments were found in the solution, so the new equilibrium swelling ratio was decreased.

The samples of NIPAAm/TMMAI gels were swollen in deionized water at 25 and 50°C, and weighed several times. In this way, we can test the reversibility of the sample, as also shown in Figures 9, 10, and 11. The result indicates that the thermosensitive gels of TMM1 and TMM3 have very good reversibility.

We compared the effect of the TMMAI (in this article) and TMAAI (in the previous study)<sup>24</sup> on the swelling behavior. The difference between the poly(NIPAAm) gels with cationic comonomers TMMAI or TMAAI was only the ability to be hydrophilic. Monomer TMAAI has an amido structure, and the hydrophilic group (amido) would easily form an intermolecular hydrogen bond with surrounding water. So the swelling ratio of NIPAAm/TMAAI gels were larger than those of NIPAAm/TMMAI gels. The greater the hydrophilicity, the higher the gel transition temperature, and the water easily penetrated into the gels. Relatively, the diffusion coefficient constant ( $D$ ) was larger.

The effects of various salt solutions on the swelling ratio were the same in both series of gels. The effect of various salt solutions on the swelling ratio was only due to the fixed charges of the gel networks that were cationic, anionic, or neutral. Both these gels would bear a positive charge as the iodide ion became ionized in an aqueous solution, they had the same swelling behaviors in various salt solutions.

## CONCLUSION

The swelling ratios of NIPAAm/TMMAI copolymeric gels are increased with an increase of TMMAI content, and the equilibrium absorption time of hydrogels is shorter. In addition, the higher the TMMAI content, the larger the affinity of the hydrogels for water. The gel transition temperature is increased as TMMAI content is increased.

In diffusion transport mechanism, the results indicate that the swelling exponents " $n$ " of all NI-

PAAm/TMMAI copolymeric gels at various temperatures have values between 0.5 and 1.0. This implies that the swelling transport mechanism is a non-Fickian transport. The diffusion coefficients ( $D$ ) for various copolymeric gels are increased with an increase of temperature. So the water easily diffuses into hydrogels at the high temperature.

The effect of salt solution on the swelling ratio for these series of gels shows special behavior. The swelling ratios of various copolymeric gels decrease with an increase of salt concentration. When the salt concentration is between 0.1 and 2M, various copolymeric gels exhibit uncharged swelling behavior. In other words, the swelling behavior may be changed at higher concentration. The anionic effect is greater than cationic effect in the presence of common anion ( $\text{Cl}^-$ ), different cations and common cation ( $\text{K}^+$ ), and different anions for the hydrogels.

Finally, the temperature is the important role affecting the reversibility of the gel, and TMM1 and TMM3 have good reversibilities.

## REFERENCES

1. Y. H. Bae, T. Okano, and S. W. Kim, *J. Polym. Sci., Polym. Phys.*, **28**, 923 (1990).
2. J. Ricka and T. Tanaka, *Macromolecules*, **17**, 2916 (1984).
3. E. Hirokawa and T. Tanaka, *J. Chem. Phys.*, **81**, 6379 (1984).
4. A. S. Hoffman, *J. Control. Release*, **6**, 297 (1987).
5. K. Ishihara, N. Muramoto, and I. Shinohara, *J. Appl. Polym. Sci.*, **29**, 211 (1984).
6. D. Kungwachakun and M. Irie, *Makromol. Chem. Rapid Commun.*, **9**, 243 (1988).
7. S. R. Eisenberg and A. J. Grodzinski, *J. Membr. Sci.*, **19**, 173 (1984).
8. K. Dusek and D. Patterson, *J. Polym. Sci., Part A-2*, **6**, 1209 (1968).
9. T. Tanaka, *Physiol. Rev. Lett.*, **40**, 820 (1978).
10. T. Tanaka, T. Nishio, S. Sun, and S. U. Nishio, *Science*, **218**, 467 (1982).
11. T. Tanaka, D. Fillmore, S. Sun, I. Nishio, G. Swislow, and A. Shah, *Physiol. Rev. Lett.*, **45**, 1637 (1980).
12. S. Hirotsu, Y. Hirokawa, and T. Tanaka, *J. Chem. Phys.*, **87**, 1392 (1987).
13. E. S. Matsuo and T. Tanaka, *J. Chem. Phys.*, **89**, 1696 (1988).
14. A. S. Hoffman, A. Afrassiabi, and L. C. Dong, *J. Control. Release*, **4**, 213 (1986).
15. Y. H. Bea, T. Okano, and S. W. Kim, *Makromol. Chem. Rapid Commun.*, **8**, 481 (1987).

16. R. F. S. Freltas and E. L. Cussler, *Sep. Sci. Technol.*, **22**, 911 (1987).
17. L. C. Dong and A. S. Hoffman, *J. Control. Release*, **4**, 223 (1986).
18. M. Heskins and J. E. Guillet, *J. Macromol. Sci. Chem.*, **A2**, 1441 (1968).
19. S. Hirotsu, *J. Physiol. Soc. Jpn.*, **56**, 233 (1987).
20. Y. Hirose, T. Amiya, Y. Hirokawa, and T. Tanaka, *Macromolecules*, **20**, 1342 (1987).
21. S. Beltran, J. P. Baker, H. H. Hooper, H. W. Blanch, and J. M. Prausnitz, *Macromolecules*, **24**, 549 (1991).
22. S. Beltran, H. H. Hooper, H. W. Blanch, and J. M. Prausnitz, *J. Chem. Phys.*, **92**, 2061 (1990).
23. W. F. Lee and C. C. Tsai, *J. Appl. Polym. Sci.*, **52**, 1447 (1994).
24. W. F. Lee and C. H. Hsu, *Polymer*, to appear.
25. W. F. Lee and C. C. Tsai, *Polymer*, **35**, 2210 (1994).
26. B. G. Kabra, S. H. Gehrke, and S. T. Hwang, *J. Appl. Polym. Sci.*, **42**, 2409 (1991).
27. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
28. G. C. Hung, MS Thesis, Tatung Institute of Technology, Taipei, Taiwan (1995).
29. W. F. Lee and P. L. Yeh, *J. Appl. Polym. Sci.*, to appear.
30. N. M. Franson and N. A. Peppas, *J. Appl. Polym. Sci.*, **28**, 1299 (1983).
31. R. W. Kormeyer, E. W. Merrwall, and N. A. Peppas, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 409 (1986).
32. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, London, 1968.
33. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Caledon Press, Oxford, (1975).
34. J. E. Huheey, *Inorganic Chemistry*, Harper and Row, New York, 1984, p. 218.
35. K. Mukae, Y. H. Bae, T. Okano, and S. W. Kim, *Polym. J.*, **22**, 206 (1990).