PII: S0032-3861(97)10234-8

Thermoreversible hydrogels: 3. Synthesis and swelling behavior of the (*N*-isopropylacrylamide-co-trimethylacrylamidopropyl ammonium iodide) copolymeric hydrogels

Wen-Fu Lee* and Cheng-Hawn Hsu

Department of Chemical Engineering, Tatung Institute of Technology, Taipei, Taiwan 10451, ROC
(Received 2 June 1997; revised 29 September 1997; accepted 20 October 1997)

In this study, a series of *N*-isopropylacrylamide/trimethyl acrylamidopropyl ammonium iodide (NIPAAm/TMAAI) copolymeric gels were prepared from the various molar ratios of NIPAAm, cationic monomer TMAAI, and *N,N'*-methylene bisacrylamide (NMBA). The influences of the amount of the cationic monomer in the copolymeric gels on the swelling behaviors in water, various saline solutions, and various temperatures were investigated. Results showed that the swelling ratios of copolymeric gels were significantly larger than those of pure homopolymer NIPAAm gels, and the more the TMAAI content, the higher the gel transition temperature. In the saline solution, results showed that the swelling ratio of pure NIPAAm gel did not significantly change with an increase of the salt concentration until the salt concentration was greater than 0.1 M. The swelling ratios for the copolymeric gels NIPAAm/TMAAI were decreased with increasing of the salt concentration. In various saline solutions, results showed that the anionic effects were greater than cationic effects in the presence of common anion, different cations and common cation, different anions for these hydrogels © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: thermoreversible hydrogels; *N*-isopropylacrylamide; cationic copolymeric hydrogels)

INTRODUCTION

Hydrogel is a kind of polymer which can be swollen but cannot be dissolved in water. There are some hydrogels which can modulate the swelling ratio in response to environmental stimuli, such as temperature[1,2], pH[3,4], chemicals[5], photoirradiation[6], electric field[7], etc. The collapse of a gel in response to environmental changes was predicted by Dusek and Patterson[8] and intensively investigated by Tanaka and co-workers[9–13]. The thermosensitive hydrogel, one type of 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 systems[14,15], extraction[16], and enzyme activity control[17].

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 critical point between 31 and 35°C[18]. Recently, Hirotsu[19] investigated the phase behaviors of NIPAAm gel/water/alcohol systems and explained their thermoshrinking 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[12,13]. Their results indicated that incorporation of small amounts of anionic SA into NIPAAm networks produced continuous swelling transition in macroscopic gels at 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.[21,22]. They reported the behaviors 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 of poly(TMAAI) were investigated in our previous report[23]. Hence, a series of *N*-isopropylacrylamide/trimethyl acrylamidopropyl ammonium iodide (NIPAAm/TMAAI) copolymeric gels are prepared in an attempt to investigate the influence of molar ratio of NIPAAm/TMAAI and the effect of various salt solutions on swelling behaviors for these copolymeric gels.

* To whom correspondence should be addressed

EXPERIMENTAL

Materials

Dimethyl amino propylacrylamide (TCI Co.) was further purified by vacuum distillation at 174°C/60 mmHg. *N*-Isopropylacrylamide (NIPAAm) (Fluka Chemical Co.) was recrystallized in *n*-hexane before use in order to remove an inhibitor. Methyl iodide (TCI Co.), *N,N'*-Methylene bisacrylamide (NMBA) (Sigma Chemical Co.) as a crosslinker, and *N,N,N',N'*-tetramethylethylene diamine (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 acrylamidopropyl ammonium iodide (TMAAI) was prepared as described previously[24]. Yield 96%; m.p. 148°C. The structure is given as:

$$CH_2{=}CH$$
$$|$$
$$O{=}C-NH-(CH_2)_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^+}}-CH_3 \; I^-$$
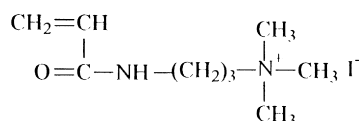
Preparation of hydrogels

Various ratios of NIPAAm, TMAAI, 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 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 2 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 dabbed with filter paper to remove 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:

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

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_∞. The following equation can be used to calculate the diffusion coefficient D for $M_t/M_\infty \leq 0.8$[25].

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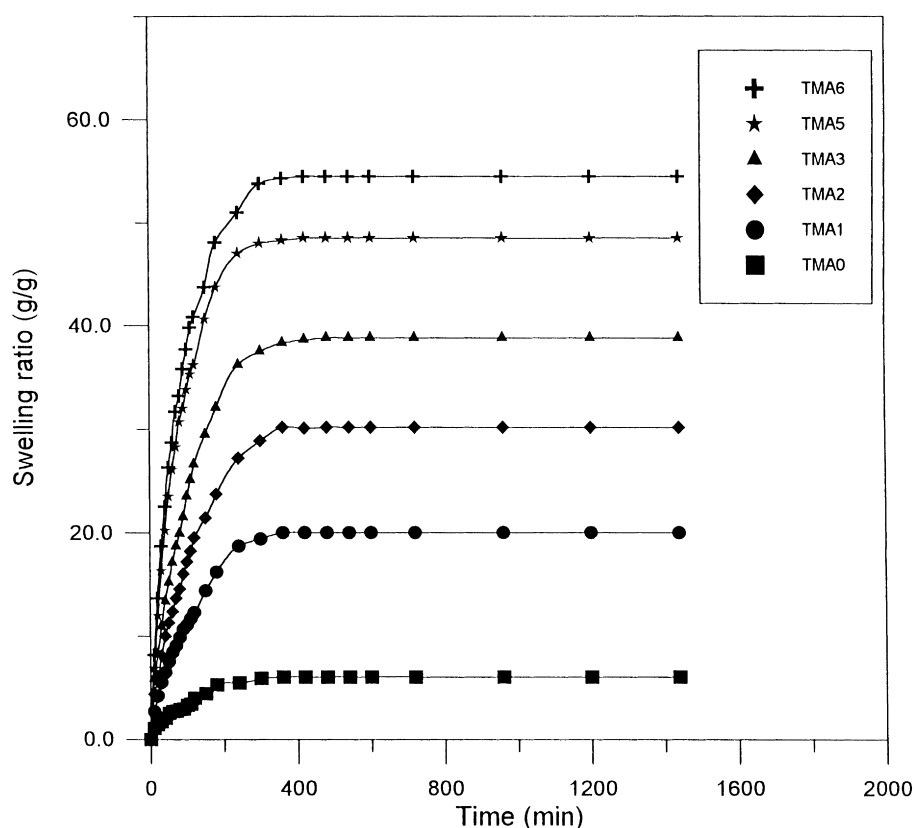

Figure 1 Swelling ratio as a function of time for NIPAAm/TMAAI copolymeric gels at 30°C

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

RESULT 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 NIPPAm/TMAAI copolymeric gels

Some characteristics of the NIPAAm/TMAAI copolymeric gels for various feed compositions are shown in *Table 1*. The results observed from *Table 1* show that the cloud point effects of the copolymeric gels are weaker with increasing content of TMAAI monomer. The gel transition temperatures are increased with increase of the content of TMAAI in the copolymeric composition; i.e. from 30 to 60°C for TMA0–TMA3. But the gel transition temperatures of TMA5 and TMA6 were not observed in the experiment

(also see *Figure 2*). The reason is that addition of TMAAI monomer into the gel composition made the gel become more hydrophilic. We also observed that the gel becomes easily collapsed. The equilibrium swelling ratios of the copolymeric gels are also increased with increasing content of TMAAI (see also *Figure 1*).

Effect of TMAAI content on swelling ratio

The swelling ratios as a function of time for NIPAAm/TMAAI copolymeric gels at 30°C in deionized water are shown in *Figure 1*. The results shown in *Figure 1* indicate that the swelling ratios increase with TMAAI content. According to Flory's swelling theory[26], the following equation was given:

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

where i/V_μ is the concentration of fixed charge referred to unswollen network, S is the ionic concentration in the external solution, $(1/2 - \chi_1)/v_1$ is the affinity of the hydrogel for water, v_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/TMAAI 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 TMAAI monomer is a hydrophilic cationic monomer, the more the TMAAI content the larger the affinity of the gel for water, and the higher the swelling ratio of the hydrogel. In other words, the TMAAI monomer is ionized in aqueous solution, the mutual repulsion of their charges causes the expansion of the polymeric chain. This occurrence leads to a higher swelling ratio of the hydrogel with higher content of TMAAI.
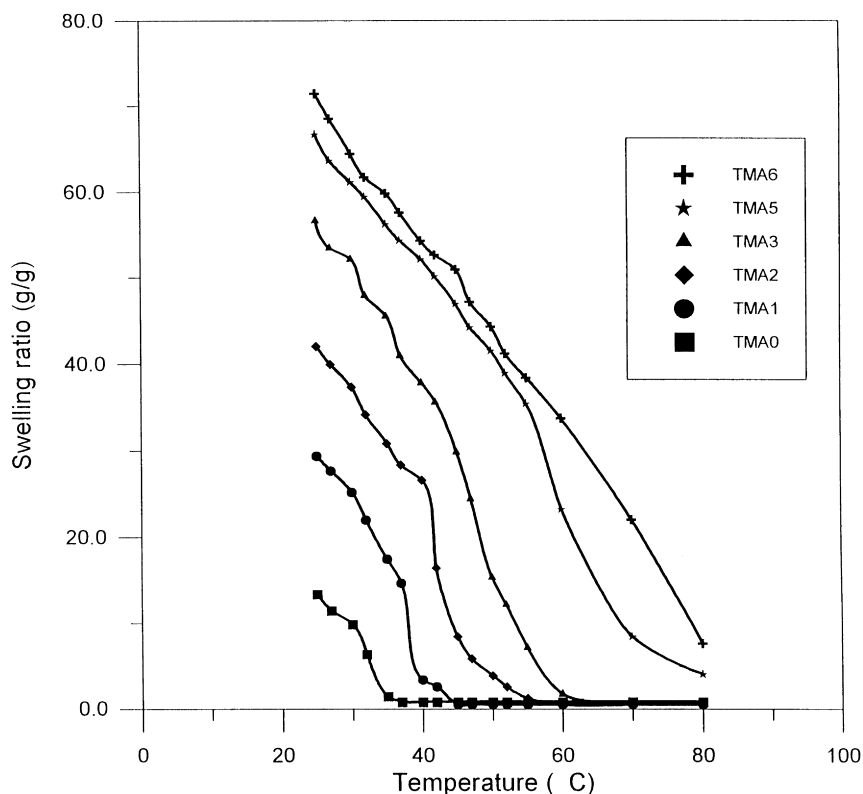
Table 1 Characterization of NIPAAm/TMAAI copolymeric gels

Sample no.	Feed composition (%)		Cloud point effect*	Cloud point temperature	Swelling ratio (g H$_2$O/g dry gel)
	NIPAAm	TMAAI			
TMA0	100	0	st	30–35	14.1
TMA1	99	1	st	35–40	28.5
TMA2	98	2	st	45–50	42
TMA3	97	3	vw	55–60	56.6
TMA5	95	5	no	no	66.6
TMA6	94	6	no	no	71.4

st, strong; vw, very weak; no, not observed

Figure 2 Swelling ratio as a function of temperature for NIPAAm/TMAAI copolymeric gels

Effect of temperature on swelling ratio for NIPAAm/TMAAI copolymeric gels

The effect of temperature on the equilibrium swelling ratio for a series of NIPAAm/TMAAI 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 greater the TMAAI content the higher the gel transition temperature. For NIPAAm gel, the hydrophilic group (amido-NHCO–) in the polymer structure would form an intermolecular hydrogen bond with surrounding water at low temperature (below the gel transition temperature). Hence, the water penetrated into the NIPAAm gels is a bound state under low temperature conditions. The water molecule would gain an enthalpy

Table 2 Initial diffusion coefficient of water, D, and kinetic exponent, n, and characteristic constant, K, of water penetrated through NIPAAm/TMAAI copolymeric gels at various temperatures

| Sample no.	Temp. (°C)	n	$K \times 10^3$	$D \times 10^8$ (cm^2/s)	SR_{eq} (g/g)	T_{eq} (h)	Initial rate (g/min)
TMA0	20	0.55	4.5	6.44	14	16	0.061
	25	0.51	6.2	6.51	12	12	0.044
	30	0.51	6.6	9.21	6	6	0.029
	35				0.6	1	0
TMA1	20	0.68	1.3	8.97	27	10	0.099
	25	0.63	2.2	9.95	24	9	0.101
	30	0.61	2.8	10.6	20	6	0.090
	35	0.55	7.6	12.8	13	5	0.076
TMA2	20	0.61	2.4	7.84	37	10	0.137
	25	0.60	2.8	9.56	35	9	0.151
	30	0.60	3.0	10.0	30	6	0.132
	35	0.57	6.6	13.9	26	5	0.123
TMA3	20	0.64	1.8	6.62	45	9	0.156
	25	0.56	4.0	6.83	40	9	0.162
	30	0.61	3.0	9.89	38	7	0.169
	35	0.51	5.4	11.4	36	6	0.178
TMA5	20	0.66	1.7	7.04	64	9	0.243
	25	0.68	2.0	9.48	54	8	0.247
	30	0.73	1.4	13.3	49	7	0.258
	35	0.54	4.2	14.3	44	6	0.27
TMA6	20	0.66	1.7	8.6	67	9	0.267
	25	0.71	1.5	12.1	60	7	0.268
	30	0.70	1.8	14.5	55	7	0.282
	35	0.53	4.5	17.9	53	6	0.305
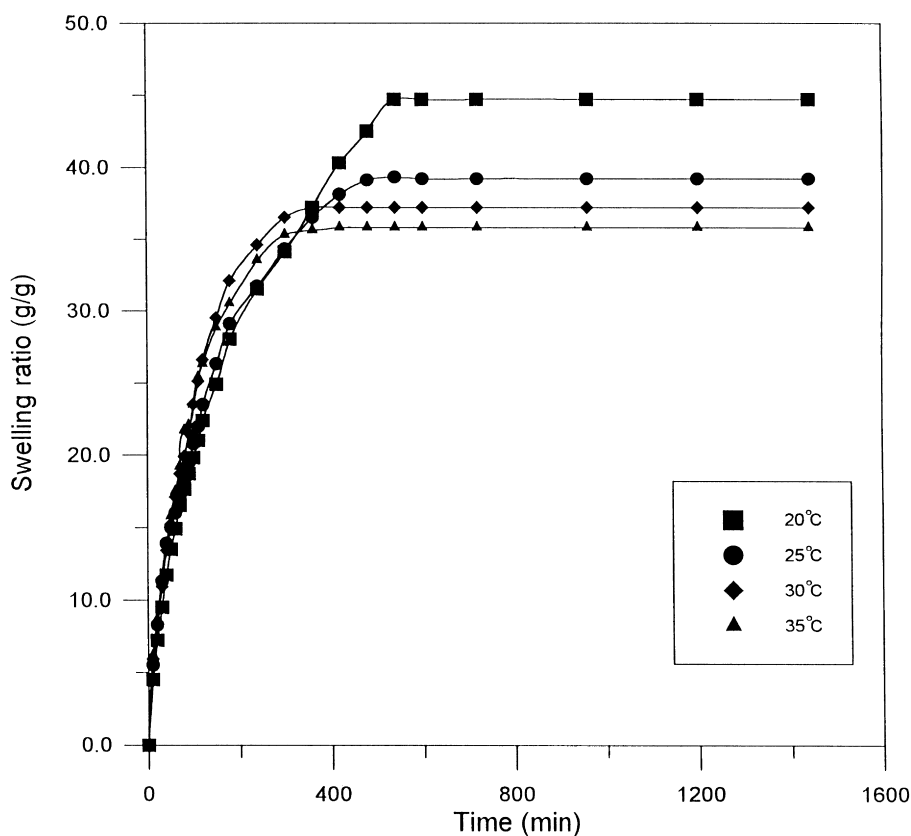
Figure 3 A typical swelling ratio as a function of time for TMA3 at different temperatures

during the temperature increase, and the hydrophilic group (amido) in the NIPAAm gels would become an intramolecular hydrogen bond under these conditions. This occurrence leads to a decrease in the hydration force of the gel. At the same time, the hydrophobic force of isopropyl group of NIPAAm gel increases. These two factors cause the water molecule inside the gel to change from bound state to free state and to be 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 higher the TMAAI content, the higher the hydrophilic ability of the gel, and the stronger the affinity of the hydrogel for water. Therefore, the curves of swelling ratio vs. temperature become smoother as the TMAAI content in these copolymeric gels increases. This result means that the gel does not shrink easily as the temperature increases. These results conform to our previous studies for NEPAAm/AAm or NTHFAAm/AAm hydrogels[27,28].

Investigation of water diffusion in xerogels

Typical swelling ratios, as a function of time for sample TMA3 copolymeric gel at various temperatures, are shown in *Figure 3*. The results observed in *Figure 3* indicate that the swelling ratio decreases with increasing temperature. The equilibrium absorption time decreases for TMAAI-containing hydrogels, as can be observed in *Table 2*. 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 to the amount of ionic charged group in the individual gel matrix. As the charge density rises, the driving force for swelling also increases. Swelling kinetics can 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 kinetics in TMA series gels, the initial swelling data were fitted to the exponential heuristic equation[29,30]:

$$\frac{M_t}{M_\infty} = kt^n \tag{4}$$

where k is a characteristic constant of the gel, and n is a characteristic exponent of the mode transport of the penetrate. Values of 'n' and 'k' were calculated from the slopes
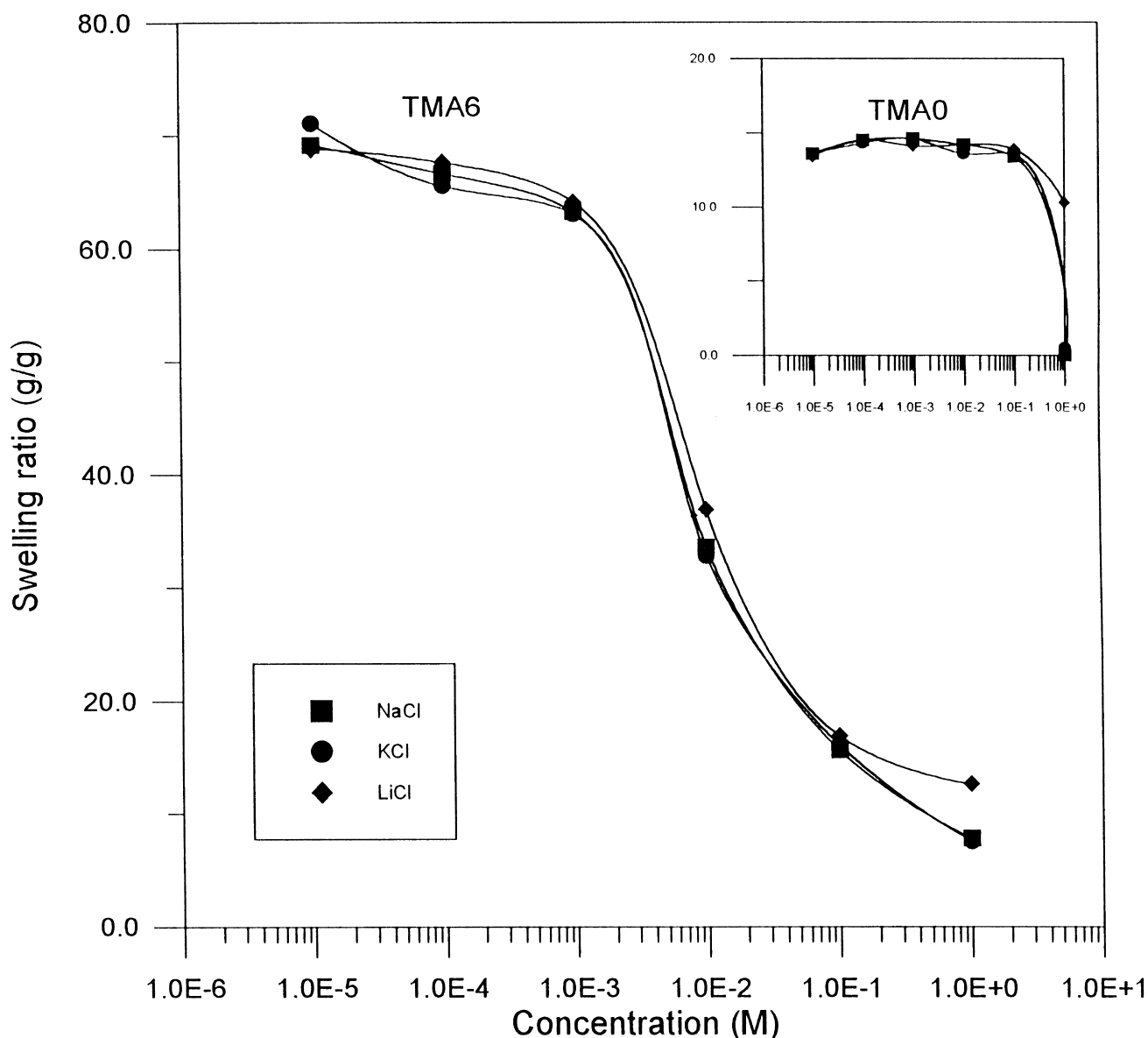

Figure 4 Swelling ratio for TMA0 and TMA6 in the various salt solutions with different monovalent cations at 25°C

and intercepts of the plot of $\log(M_t/M_\infty)$ against $\log(t)$ at various temperatures. 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 shown in *Table 2* show that the swelling exponents '*n*' for all NIPAAm/TMAAI 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 well discussed by Crank and Park[31]. The measurement technique used in this experiment is based on the use of initial rates of sorption[32]. 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 2* indicate that the diffusion coefficients for various NIPAAm/TMAAI copolymeric gels are increased with an increase of temperature. Because TMA0 gel is unswollen at 35°C, which is due to the fact that this temperature is higher than the LCST of the gel, the values of n, K, D are not shown in

Table 2. The equilibrium swelling ratio and equilibrium time decrease with increase of temperature. The initial absorption rates (at initial 3 h) are decreased with increasing of temperature for TMA0–TMA2, but increased with increasing temperature for TMA3–TMA6. It is apparently shown that the initial water absorption rate is affected by the TMAAI content in the copolymeric composition.

Effect of various salt solutions on the swelling ratio

Most of the theories on swelling of ionic gels tend to be quite complex, attempting to combine the description of the contractile force of the network (network swelling pressure) and the electrostatic interactions (ion swelling pressure). The simplest one of the theories attributes the ion swelling pressure to the difference between the osmotic pressure of freely mobile ions in the gel and in the outer solutions. The distribution of the ions between the gel and the outer solution is obtained from Donnan equilibrium. Within this theory the ionic force depends only on the ionic composition of the solvent and on the concentration of fixed ionizable groups in the gel, but not on the properties of the neutral network.
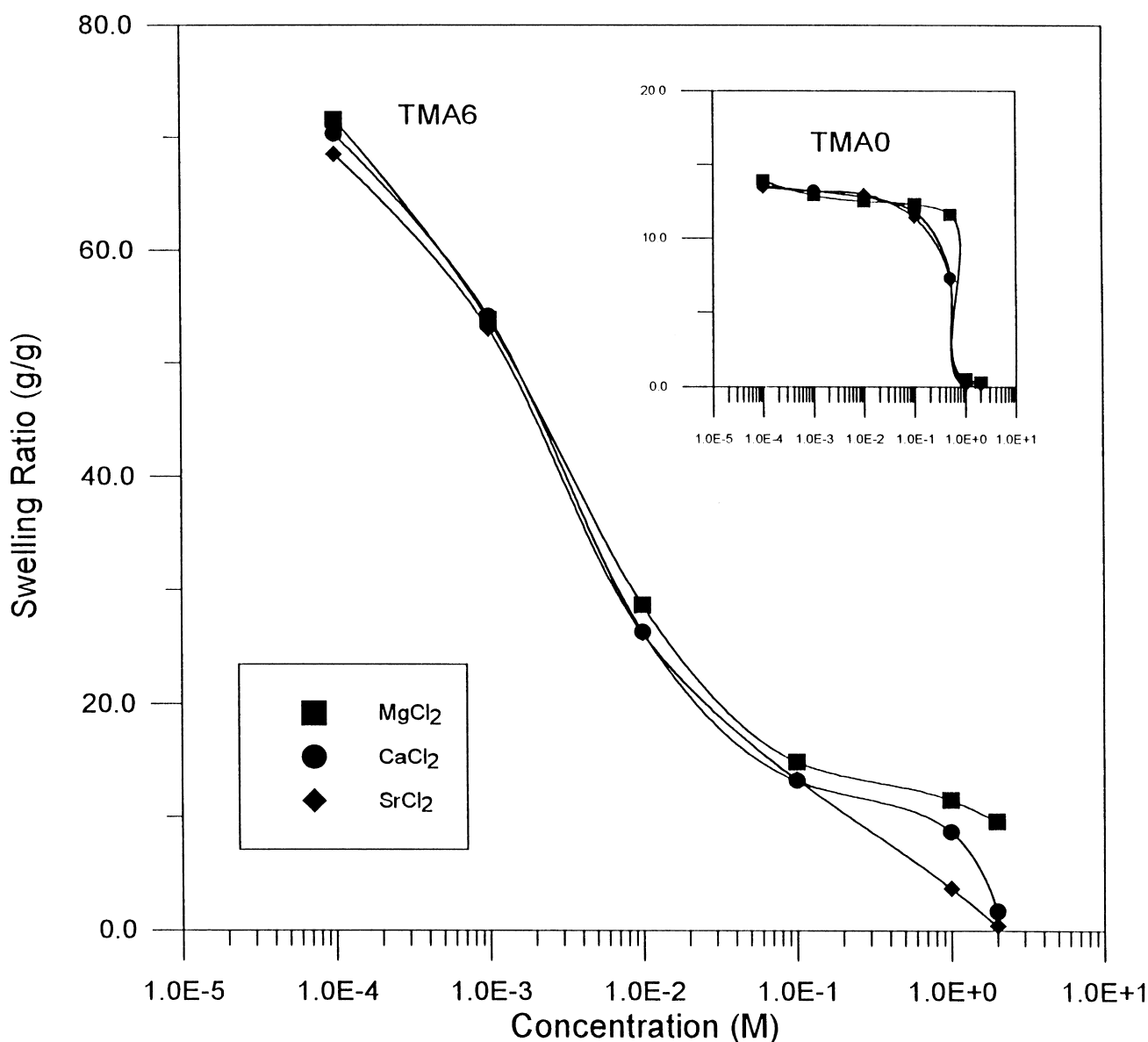

Figure 5 Swelling ratio for TMA0 and TMA6 in various salt solutions with different divalent cations at 25°C

To investigate the influence of the TMAAI component in the copolymeric gel on the swelling behavior for the NIPAAm gel in the presence of various salt solutions, samples TMA6 and TMA0 were chosen for comparison and discussed in subsequent sections.

The influence of different monovalent cations with a common anion (Cl⁻) on the swelling ratio

Figure 4 shows the swelling ratio of samples TMA0 and TMA6 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 TMA0 keep an approximately constant value at the range of salt concentration from 1×10^{-5} to 0.1 M, and then rapidly decrease at a salt concentration of over 0.1 M. 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 equation (3). This implies that the swelling ratio of TMA0 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 0.1 M, and shows the tendency in the

order of LiCl > NaCl = KCl (contract to zero swelling ratio). This can be explained by the fact that the hydration force of Li⁺ is larger than that of Na⁺ and K⁺, so the hydrated lithium ion can easily hydrogen-bind 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 TMA6, however, was influenced by the affinity of water and the fixed charge of gel, because the side chain of TMAAI would bear a positive charge as the iodide ion became ionized in an aqueous solution.

The swelling ratios for TMA6 shown in *Figure 4* show that the swelling ratios are constant at a salt concentration from 10^{-5} to 10^{-3} M, they 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
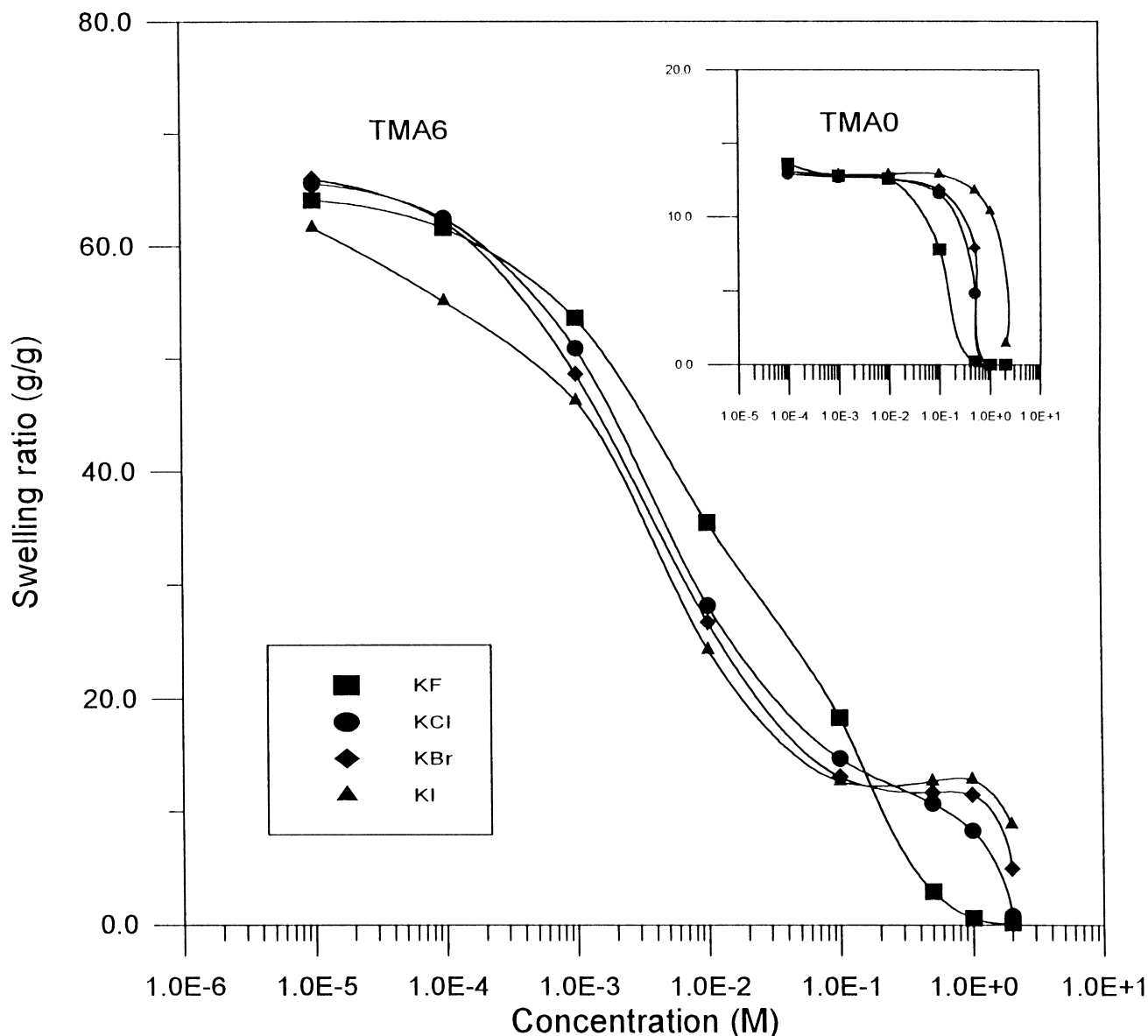

Figure 6 Swelling ratio for TMA0 and TMA6 in various salt solutions with different halide ions at 25°C

and external ion concentration decreases and the gel deswells; the gel continues 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 increases, 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 TMA0 and TMA6 xerogels in salt solutions of $MgCl_2$, $CaCl_2$, and $SrCl_2$, respectively. The swelling behaviors for TMA0 in these salt solutions have a similartendency as those in the salt solutions of LiCl, NaCl, and KCl, respectively. But the swelling behavior for TMA6 gradually decreases with increasing of these divalent salts from a concentration of 10^{-5} to 2 M and the swelling ratios for these two gels show a tendency in the order of $MgCl_2 > CaCl_2 > SrCl_2$.

These results imply that the swelling ratio exhibited in these gels is influenced by the fixed charges inside the gels.

The influence of different halide ions with a common cation (K^+) on the swelling ratio

The influence of different halide ions with a common cation (K^+) on the swelling ratio for TMA0 and TMA6 is investigated. The results shown in *Figure 6* indicate that the swelling ratio for TMA6 decreases with an increase of the salt concentration from 10^{-5} to 0.2 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 KF > KCl > KBr > KI when the salt concentration is below 0.2 M. This is because the larger anion with a common positive charge (charge density is smaller) is easily polarized and bound to a quaternary ammonium group (R_4N^+) on the chain. The positive charge on polymeric side chain could therefore become effectively neutralized by the larger anion (I^-) and decrease the swelling ratio. When the salt concentration is larger than 0.2 M, the tendency of the swelling ratio is in the order of KF < KCl < KBr < KI. This
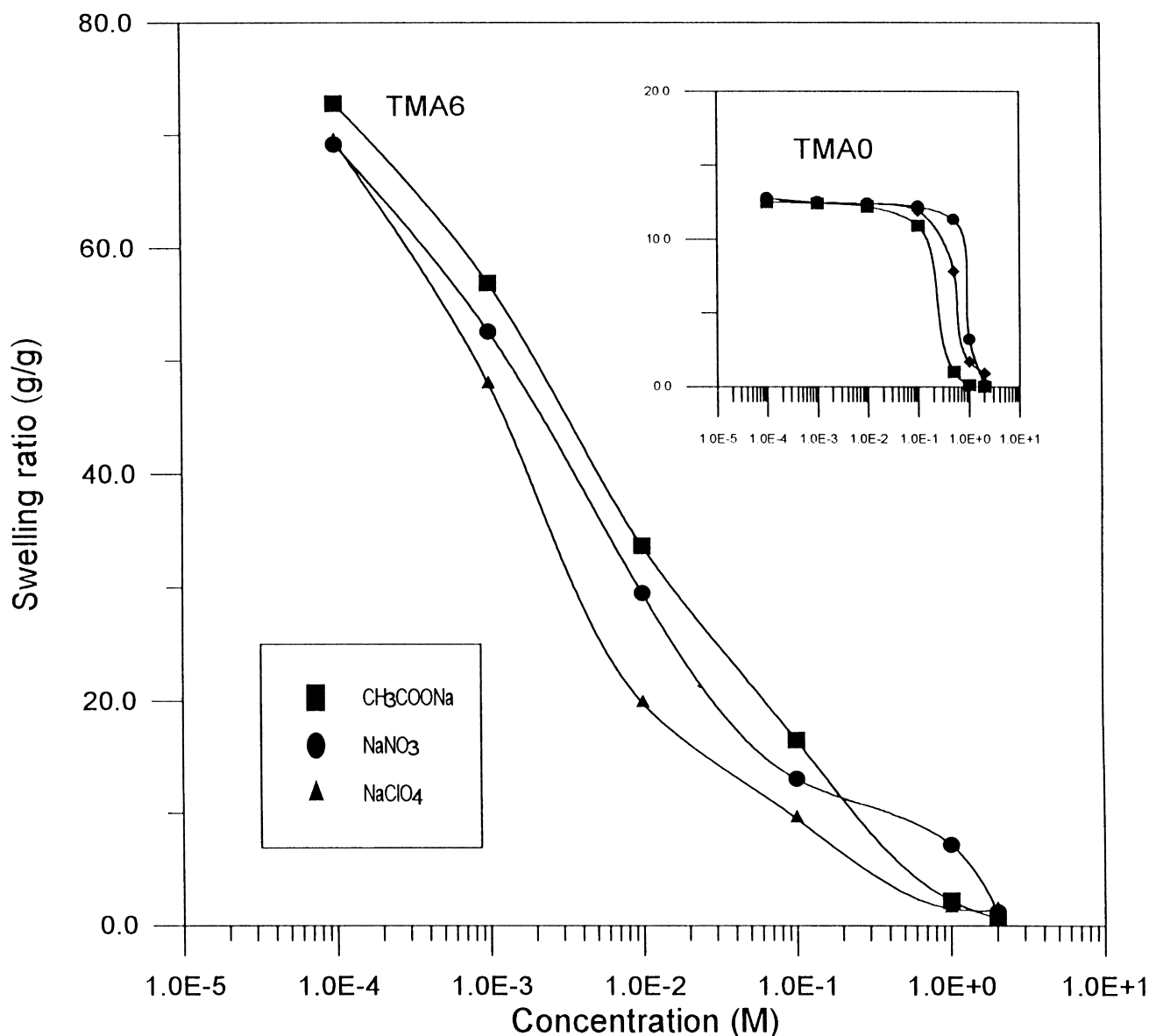

Figure 7 Swelling ratio for TMA0 and TMA6 in various salt solutions with different monovalent acidic ions at 25°C

is due to the fact that the polyelectrolyte behavior of the gels was shielded by the salt effect (screen effect). Therefore the behavior of the gels is like the uncharged gels. This deswelling behavior is similar to the deswelling behavior of the poly(NIPAAm) gel (TMA0). *Figure 6* also shows the swelling ratio of sample TMA0 as a function of the salt concentration for KF, KCl, KBr, and KI solutions, respectively. The results indicate that the swelling ratio of TMA0 keep a constant value at low concentration (<0.1 M), but decrease in the order of KF < KCl < KBr<KI. This result is similar to the behavior of sample TMA6 at high concentration (> 0.1 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 (Na^+) on the swelling ratio

The influence of different acidic ions (ClO_4^-, NO_3^-, and CH_3COO^-) with a common cation (Na^+) on the swelling ratio for TMA0 and TMA6 copolymeric gels is investigated.

The results, shown in *Figure 7*, indicate that the tendency of the swelling ratio for TMA6 gel is in the order of CH_3COO^- > NO_3^- > ClO_4^- for CH_3COONa, $NaNO_3$, and $NaClO_4$ solutions, respectively, as the concentration of salts is lower than 0.1 M. This tendency conforms to the aqueous salt solution properties of cationic poly(TMAAI) reported previously[23]. The results shown in *Figure 7* also show that the tendency of the swelling ratio for TMA6 gel is in the order of NO_3^- > CH_3COO^-=ClO_4^- for high concentrations (> 0.1 M) of $NaNO_3$, CH_3COONa, and $NaClO_4$ solutions, respectively.

From *Figure 7*, the swelling ratios of TMA0 keep a constant value at low concentration (< 0.01 M), but decrease rapidly at high concentration. The tendency of swelling ratio is in the order of CH_3COO^- < ClO_4^- < NO_3^- for CH_3COONa, $NaClO_4$, and $NaNO_3$ solutions, respectively. From the above result, we know that the swelling behaviors of sample TMA6 is like an uncharged hydrogel in high concentration salt solutions, and similar to sample TMA0.

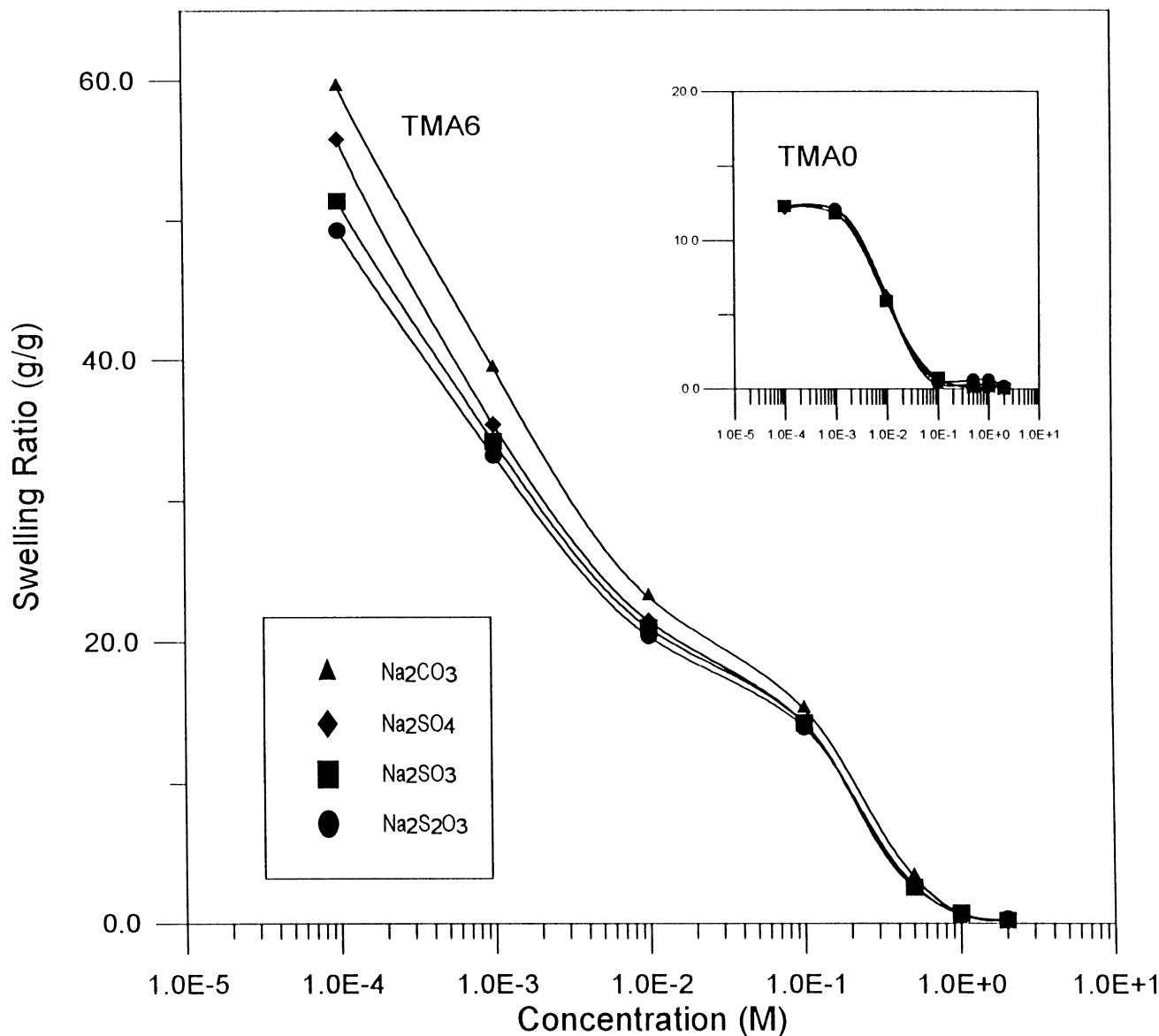For the various divalent acidic groups, the data (see *Figure 8*) show that the swelling ratios decrease with an

Figure 8 Swelling ratio for TMA0 and TMA6 in various salt solutions with different divalent acidic ions at 25°C
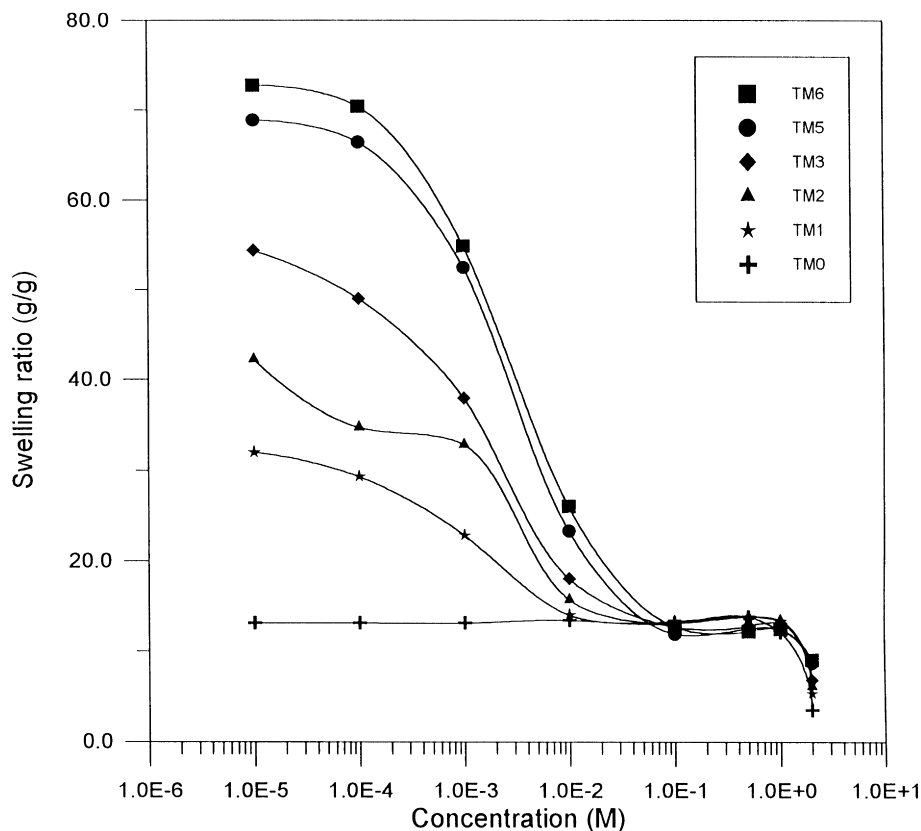
Figure 9 Swelling ratio for TMA series hydrogels in KI aqueous solutions at 25°C

increase of concentration of salt solution. For *Figure 8*, the swelling ratio for TMA0 rapidly decreased from 12 to zero at 10^{-3} to 10^{-1} M of various salt solutions. But the swelling ratio for TMA6 shows a two-stage decrease; i.e. the first stage is from 10^{-4} to 10^{-1} M, and the second stage is from 10^{-1} to 1 M for various divalent acidic salt solutions. Compare these two gels, it is known that the first-stage deswelling behavior for TMA6 contributes mainly to the TMAAI component, and their swelling ratios show an decrease in the order of $CO_3^{2-} > SO_4^{2-} > SO_3^{2-} > S_2O_3^{2-}$ for Na_2CO_3, Na_2SO_4, Na_2SO_3, and $Na_2S_2O_3$ solutions, respectively. The deswelling behavior corresponds to the aqueous behavior of the poly(TMAAI) in the presence of these salt solutions in our previous report[23]. This phenomenon was explained by Pearson's theory[23,33]. The second-stage deswelling behavior for the TMA6 gel is consistent with the deswelling behavior of TMA0.

Effect of TMAAI content on swelling ratio for salt effect

In order to check the second stage of deswelling behavior in the divalent acidic salt solution with a similar poly(NIPAAm) gel behavior, a series of TMAAI gel studies was conducted to examine their deswelling behavior in various concentrations of KI solution. The results shown in *Figure 9* indicate that the swelling ratios are increased with increase of TMAAI content in the copolymeric gels, and show a two-stage deswelling behavior between 10^{-5} to 10^{-1} M (first stage) and 10^{-1} to 2 M (second stage). The second-stage deswelling behavior corresponds to the TMA0 deswelling behavior. From the above results, we can confirm that the initial deswelling behavior of the cationic copolymeric gels results mainly from the cationic momoner

component in the copolymeric gel in the presence of various salt solutions. The deswelling behavior for uncharged NIPAAm gel only occurs in the higher salt solutions.

CONCLUSION

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

In the diffusion transport mechanism, the results indicate that the swelling exponents '*n*' of all NIPAAm/ TMAAI copolymeric gels at various temperatures are at 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 is easily diffused into hydrogels at high temperature.

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

REFERENCES

1. Bae, Y. H., Okano, T. and Kim, S. W., *J. Polym. Sci. Polym. Phys.*, 1990, **28**, 923.
2. Ricka, J. and Tanaka, T., *Macromolecules*, 1984, **17**, 2916.
3. Hirokawa, E. and Tanaka, T., *J. Chem. Phys.*, 1984, **81**, 6379–6380.
4. Hoffman, A. S., *J. Control. Release*, 1987, **6**, 297–305.
5. Ishihara, K., Muramoto, N. and Shinohara, I., *J. Appl. Polym. Sci.*, 1984, **29**, 211.
6. Kungwatchakun, D. and Irie, M., *Makromol. Chem. Rapid Commun.*, 1988, **9**, 243.
7. Eisenberg, S. R. and Grodzinski, A. J., *J. Membr. Sci.*, 1984, **19**, 173.
8. Dusek, K. and Patterson, D., *J. Polym. Sci.*, 1968, **Part A-2**(6), 1209.
9. Tanaka, T., *Phys. Rev. Lett.*, 1978, **40**, 820.
10. Tanaka, T., Nishio, T., Sun, S. and Nishio, S.U., *Science*, 1982, **218**, 467.
11. Tanaka, T., Fillmore, D., Sun, S., Nishio, I., Swislow, G. and Shah, A., *Phys. Rev. Lett.*, 1980, **45**, 1637.
12. Hirotsu, S., Hirokawa, Y. and Tanaka, T., *J. Chem. Phys.*, 1987, **87**, 1392.
13. Matsuo, E. S. and Tanaka, T., *J. Chem. Phys.*, 1988, **89**, 1696.
14. Hoffman, A. S., Afrassiabi, A. and Dong, L. C., *J. Control. Release*, 1986, **4**, 213.
15. Bea, Y. H., Okano, T. and Kim, S. W., *Makromol. Chem. Rapid Commun.*, 1987, **8**, 481.
16. Freltas, R. F. S. and Cussler, E. L., *Sep. Sci. Technol.*, 1987, **22**, 911.
17. Dong, L. C. and Hoffman, A. S., *J. Control. Release*, 1986, **4**, 223.
18. Heskins, M. and Guillet, J. E., *J. Macromol. Sci. Chem.*, 1968, **A2**, 1441.
19. Hirotsu, S., *J. Phys. Soc. Jpn.*, 1987, **56**, 233.
20. Hirose, Y., Amiya, T., Hirokawa, Y. and Tanaka, T., *Macromolecules*, 1987, **20**, 1342.
21. Beltran, S., Baker, J. P., Hooper, H. H., Blanch, H. W. and Prausnitz, J. M., *Macromolecules*, 1991, **24**, 549.
22. Beltran, S., Hooper, H. H., Blanch, H. W. and Prausnitz, J. M., *J. Chem. Phys.*, 1990, **92**, 2061.
23. Lee, W. F. and Tsai, C. C., *J. Appl. Polym. Sci.*, 1994, **52**, 1447.
24. Lee, W. F. and Tsai, C. C., *Polymer*, 1994, **35**, 2210.
25. Kabra, B.G., Gehrke, S.H. and Hwang, S. T., *J. Appl. Polym. Sci.*, 1991, **42**, 2409.
26. Flory, P. J., *Principles of Polymer Chemistry*, Ch. XIII, Cornell University Press, New York, 1953.
27. Hung, G. C., MS Thesis, Tatung Institute of Technology, Taipei, Taiwan, 1995.
28. Lee, F. W. and Yeh, P. L., *J. Appl. Polym. Sci.*, 1997, **65**, 909.
29. Franson, N. M. and Peppas, N. A., *J. Appl. Polym. Sci.*, 1983, **28**, 1299.
30. Korsmeyer, R. W., Merrwall, E. W. and Peppas, N. A., *J. Polym. Sci. Polym. Phys. Ed.*, 1986, **24**, 409.
31. Crank, J. and Park, G. S., *Diffusion in Polymers*, Ch. 1, Academic Press, London, 1968.
32. Crank, J., *The Mathematics of Diffusion*, 2nd ed., Ch. 10, Caledon Press, Oxford, 1975.
33. Huheey, J. E., *Inorganic Chemistry*, Harper and Row, New York, 1984, p. 218.