Thermoreversible Hydrogels. VIII. Effect of a Zwitterionic Monomer on Swelling Behaviors of Thermosensitive Hydrogels Copolymerized by *N*-Isopropylacrylamide with *N,N'*-Dimethyl (Acrylamidopropyl) Ammonium Propane Sulfonate

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ABSTRACT: A series of thermosensitive hydrogels were prepared from the various molar ratios of *N*-isopropylacrylamide, zwitterionic monomer, *N,N'*-dimethyl (acrylamidopropyl) ammonium propane sulfonate (DMAAPS), and *N,N'*-methylene-bis-acrylamide. The influence of the amount of DMAAPS in the copolymeric gels on the swelling behaviors in water, various saline solutions, and various temperatures was investigated. Results indicated that the higher the DMAAPS content in the hydrogel system, the higher the swelling ratio and the gel transition temperature. In the saline solution results showed that, when the salt concentration was greater than the minimum salt concentration (MSC) of poly(DMAAPS), the deswelling behavior of the *N*-isopropylacrylamide gel was suppressed more effectively when more DMAAPS was added into the copolymeric gels; but the swelling ratios of the present copolymeric gels did not significantly change while the salt concentration was lower than the MSC of poly(DMAAPS). In addition, only the sample containing 12 mol % DMAAPS (D4) exhibited an antipolyelectrolyte's swelling behavior when the salt concentration was greater than the MSC of poly(DMAAPS). In other words, only when the amount of DMAAPS added into the gel is over some proportion, can the hydrogel show an antipolyelectrolyte's swelling behavior in concentrated salt solution. In saline solutions, the anion effects were greater than the cation effects in the presence of common anion (Cl⁻) with different cations and common cation (K⁺) with different cations for these gels. Finally, the more DMAAPS content in the hydrogel, the higher the diffusion coefficient in dynamic swelling. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 2170–2180, 1999

Key words: hydrogels; DMAAPS; MSC

INTRODUCTION

Hydrogels are crosslinked hydrophilic polymer networks that can be swollen but cannot be dissolved in water. Hydrogels sometimes undergo a volume change in response to a change in surrounding conditions, such as pH,[1] temperature,[2,3] ionic strength,[4] and electric field.[5,6] Therefore, they are applied in biochemistry systems extensively.

Poly (*N*-isopropylacrylamide) [poly(NIPAAm)] hydrogel is a thermoreversible hydrogel and exhibits a lower critical solution temperature approximately 33°C in aqueous solution; that is, the

hydrogel exhibits swelling or deswelling in temperatures below or above lower critical solution temperature.[7–9] Poly(NIPAAm) hydrogels have been reported recently in the field of controlled drug delivery,[10,11] immobilization of enzymes[12] and cells,[13] and dewatering of protein solutions.[14] However, only a few hydrogels containing zwitterionic monomer or sulfobetaine's monomer have been reported in the literature.[15–18] For example, Rego and Huglin[15–17] reported on copolymeric gels prepared from the copolymerization of 2-hydroxyethyl methacrylate and a zwitterionic monomer, N,N-dimethyl-N-methacryloyloxyethyl-N-(3-sulphopropyl)ammonium betaine to survey their swelling behavior in the presence of the salt potassium thiocyanate. In addition, Baker et al.[18] reported the ampholytic hydrogels prepared from the copolymerization of acrylamide with a zwitterionic monomer [N-(3-sulphopropyl)-N-methacrylamido-propyl-N,N-dimethylammonium betaine] (SB1) (AAm/SB1), or [N-(3-sulphopropyl)-N-methacroyloxyethyl-N,N-dimethylammonium betaine] (SB2) (AAm/SB2), and a cationic monomer, [(methacrylamido)propyl] trimethylammonium chloride (MAPTAC), and an anionic monomer, sodium styrene sulfonate (SSS) (AAm/MAPTAC/SSS). They investigated the swelling behavior of these three xerogels in water and in the various concentrations (10^{-5} to $5M$) of sodium chloride aqueous solution. Their results showed that antipolyelectrolyte behavior was observed for the ampholytic hydrogels. The ampholytic hydrogel reswelled as the sodium chloride concentration increased to over $0.1M$.

The thermoreversible hydrogels based on NIPAAm and zwitterionic monomer or sulfobetaine's monomer were not found in the literature. A series of sulfobetaine monomers were prepared and the aqueous salt behavior of their polymers was also investigated in our previous reports.[19–23] Hence, a series of crosslinked NIPAAm-co-N,N'-dimethyl (acrylamido propyl) ammonium propane sulfonate (DMAAPS) hydrogels were prepared in an attempt to survey the influence of the molar ratio of NIPAAm/DMAAPS and the effect of various salt solutions on swelling behavior for these copolymeric gels.
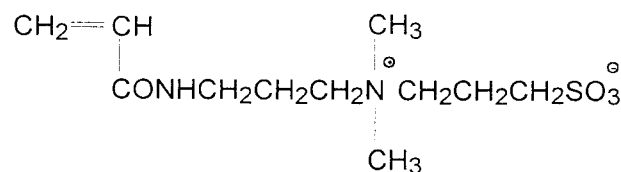
EXPERIMENTAL

Materials

Dimethyl amino propyl acrylamide (TCI Co.) was further purified by vacuum distillation at 174°C and 60 mmHg. Propane sultone (TCI Co.) was used as received. NIPAAm (Fluka Chemical Co.) was recrystallized in n-hexane before use to remove an inhibitor. N,N'-methylene-bisacrylamide (Sigma Chemical Co.) as a crosslinker was used as received. N,N,N',N'-tetramethylethylenediamine (Fluka Chemical Co.) as an accelerator was used as received. Ammonium peroxodisulfate (Wako Pure Chemical Co., Ltd.) as an initiator was further purified by recrystallization.

Synthesis of Monomer

The monomer, DMAAPS, was prepared as described previously.[21] The structure is given as:

$$CH_2{=}CH \quad\quad CH_3$$
$$\underset{}{|}$$
$$CONHCH_2CH_2CH_2\overset{\oplus}{N} CH_2CH_2CH_2SO_3^{\ominus}$$
$$\underset{}{|}$$
$$CH_3$$

Preparation of Hydrogels

Various ratios of NIPAAm and DMAAPS and 4 mol % N,N'-methylene-bisacrylamide were dissolved in 10 mL of deionized water. To this solution, 0.2 wt % ammonium peroxodisulfate and 1 wt % of tetramethylethylenediamine were added as redox initiators, 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 performed at room temperature for 1 day. After the gelation was completed, the gel membrane was cut into disks, 10 mm in diameter, and immersed in an excess amount of deionized water for 7 days to remove the residual unreacted monomer. Swollen polymer 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. The weight of wet sample (Ww) was determined after removing the surface water by blotting with filter paper. Dry weight (Wd) was determined after drying the gel in a vacuum oven for 2 days. Swelling ratio (Q)

Table I   Characterization of the NIPAAm/DMAAPS Copolymeric Gels

Sample No.	Feed Composition (%)		Actual Composition (%)		Cloud Point Effect[a]	Cloud Point Temperature	Swelling Ratio (g H$_2$O/g Dry Sample)
	NIPAAm	DMAAPS	NIPAAm	DMAAPS			
D0	100	0	100	0	st	30 ~ 35	14.07
D1	97	3	97.07	2.93	st	35 ~ 40	16.10
D2	94	6	94.44	5.56	w	50 ~ 60	17.45
D3	91	9	91.37	8.63	w	60 ~ 70	18.09
D4	88	12	88.75	11.25	vw	>80	20.56

[a] w, weak; vw, very weak; st, strong.

based on Ww and Wd was then calculated as the following relationship:

$$Q = \frac{Ww - Wd}{Wd} \tag{1}$$

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 absorbed, M_t, was reported as a function of time, and the equilibrium absorption at infinitely long time was designated as M_∞. The following equation can be used to calculate the diffusion coefficient D for $M_t/M_\infty \leq 0.8$.[24]

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

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

RESULTS AND DISCUSSION

The swelling behavior of the hydrogels depends on the nature of the polymer and the environmental conditions. The polymer's nature involves the charge, the ionic concentration, and the crosslinking agent concentration. The environmental conditions include the pH, temperature, or various salt solutions.

The swelling behavior of NIPAAm hydrogels has been widely studied by many researchers. A series of copolymeric NIPAAm/DMAAPS hydrogels have not been investigated in the literature.

The effect of DMAAPS on the swelling ratio of NIPAAm/DMAAPS copolymeric gels is studied.

Characterization of NIPAAm/DMAAPS Copolymeric Gels

The characteristics of the NIPAAm/DMAAPS copolymeric gels for various feed compositions shown in Table I indicate that the cloud point effect of the copolymeric gels is gradually weakened with the increase in the concentration of DMAAPS monomer and the gel transition temperatures increase with an increase of the concentration of DMAAPS in the copolymeric composition. The equilibrium swelling ratios of the copolymeric gels are also increased with increasing of the concentration of DMAAPS (see Fig. 1). The actual compositions which are almost equal to the feed composition were analyzed by elemental analysis.
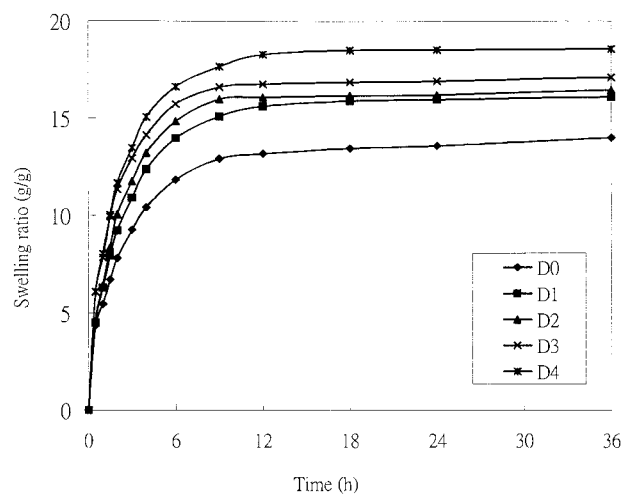

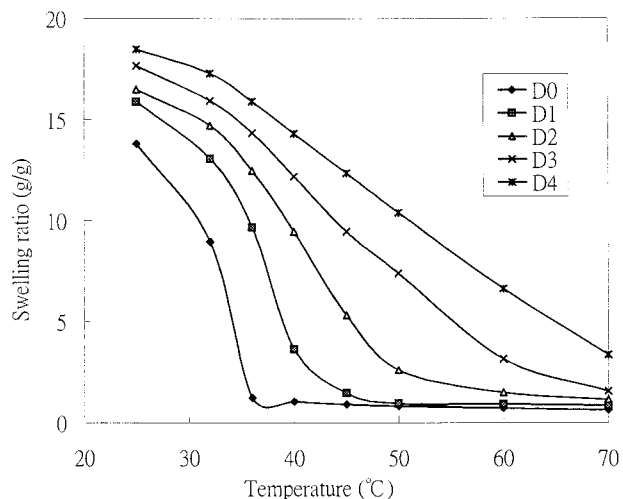**Figure 1**   Swelling ratios as a function of time for NIPAAm/DMAAPS copolymeric gels at 25°C.

Figure 2 Swelling ratios as a function of temperature for NIPAAm/DMAAPS copolymeric gels.

Effect of DMAAPS Content on Swelling Ratio

The swelling ratios as a function of time for NIPAAm/DMAAPS copolymeric hydrogels in deionized water, shown in Figure 1, indicate that the swelling ratio increases with increasing DMAAPS content. According to Flory's swelling theory,[25] the swelling ratio is related to ionic osmotic pressure, crosslinked density, and affinity of the hydrogel with water. Because the poly-(DMAAPS) is a zwitterionic polymer with a zero net charge in deionized water, the total fixed charge was zero and the crosslinked density was fixed in a series of different compositions of NIPAAm/DMAAPS hydrogels; the influence of the swelling ratio of the hydrogel is only the affinity of the gels for water. Because DMAAPS is a hydrophilic monomer, the higher the DMAAPS content, the larger the affinity of the gel for water, and the higher the swelling ratio of the hydrogel. In addition, the equilibrium absorption time (about 12 h for these copolymeric gels) has not been affected significantly by the addition of DMAAPS in the NIPAAm gel.

Effect of Temperature on Swelling Ratio for NIPAAm/DMAAPS Copolymeric Gels

The effect of temperature on the swelling ratio for the present copolymeric gels is shown in Figure 2. The results indicate that the higher the temperature the lower the swelling ratio, and the more the DMAAPS the higher the gel transition temperature. For NIPAAm gel (D0), the amide group

in the polymer structure would form an intermolecular hydrogen bond with surrounding water at lower temperatures (below the gel transition temperature) and turn into an intramolecular hydrogen bond at higher temperature.[7–9] This occurrence makes the state of the water molecule in the gel change from bound water to free water and releases it from the gel network. This phenomenon makes the swelling ratio of the gel rapidly decrease at the gel transition temperature. But the results in Figure 2 indicate that, the higher the DMAAPS content, the higher the swelling ratio for the copolymeric gels. This result is because the DMAAPS is a hydrophilic zwitterionic monomer. The larger the hydrophilicity of the gel, the stronger the affinity of the hydrogel for water. Therefore, the swelling curves become smoother as the DMAAPS concentration is increased. This evidence indicates that the gel does not shrink easily as the temperature increases. These results are compared to our previous studies for NEPAAm/AAm or NTHFAAm/AAm hydrogels.[26]

Investigation of Water Diffusion in Xerogels

The effect of temperature on the swelling ratio for sample D4, shown in Figure 3, indicates that the swelling ratio is decreased with increasing temperature. To elucidate the transport mechanism, the initial swelling data are fitted to the exponential heuristic equation[27,28]

$$\frac{M_t}{M_\infty} = Kt^n \tag{3}$$

where K is a characteristic constant of the gel, and n is a characteristic exponent of the mode
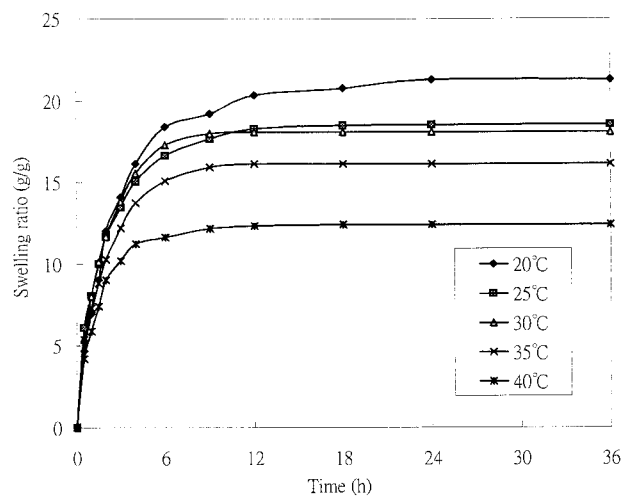

Figure 3 Swelling ratios as a function of time for sample D4 at various temperatures.

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

Sample No.	T (°C)	n	K	$D \times 10^7$ (cm²/sec)	Equilibrium Swelling Time (h)
D0	20	0.52	0.28	0.59	24
	25	0.53	0.35	0.61	18
	30	0.58	0.37	1.18	18
	35	0.59	0.47	1.27	4
	40	0.60	0.47	1.27	3
D1	20	0.56	0.34	0.60	24
	25	0.57	0.36	0.84	18
	30	0.59	0.38	1.00	12
	35	0.65	0.39	1.14	9
	40	0.67	0.42	1.29	4
D2	20	0.57	0.35	0.65	24
	25	0.58	0.40	0.87	18
	30	0.61	0.41	1.01	12
	35	0.64	0.43	1.15	9
	40	0.68	0.44	1.30	9
D3	20	0.60	0.35	0.66	24
	25	0.62	0.42	0.88	18
	30	0.63	0.43	1.01	12
	35	0.65	0.44	1.15	9
	40	0.69	0.45	1.30	9
D4	20	0.63	0.36	0.72	24
	25	0.64	0.44	0.98	18
	30	0.65	0.45	1.06	12
	35	0.67	0.46	1.16	10
	40	0.69	0.48	1.31	9

transport of the penetrant. "*n*" and "*K*" were calculated from the slope and intercepts of the plot of $\log(M_t/M_\infty)$ against $\log(t)$ at various temperatures, respectively. In addition, eq. (2) was used to calculate the diffusion coefficient D from the slope, $4\sqrt{D}/\sqrt{\pi}$, of the plot of (M_t/M_∞) against $(t/L^2)^{1/2}$ at different temperatures. Table II shows the values of D, n, and K for the present copolymeric gels at various temperatures. The results indicate that the swelling exponents "*n*" for all the copolymeric hydrogels at various temperatures are between 0.5 and 1.0. This result shows that the swelling transport mechanism is non-Fickian transport. In addition, the data shown in Table II also indicate that the swelling exponent "*n*" increases as the temperature is increased. This tendency indicates that the hydrogel swelling transport mechanism is affected by temperature.

The data shown in Table II indicate that the diffusion coefficients for various NIPAAm/DMAAPS copolymeric gels are increased with increase in temperature. According to the Arrhenius equation

$$D = D_0 \cdot \exp(-E_a/RT) \qquad (4)$$

the activation energies (E_a), for diffusion into glassy polymer for the present copolymeric gels, are calculated from the plot of the logarithm of the diffusion coefficient D against the reciprocal of temperature. The activation energies of the hydrogels shown in Table III indicate that the activation energies for various copolymeric gels are in the order D0 > D1 > D2 > D3 > D4. In other words, the higher the DMAAPS content, the

Table III   Activation Energies for NIPAAm/DMAAPS Copolymeric Gels

Sample No.	Ea (kJ/mol)
D0	34.79
D1	28.95
D2	24.98
D3	21.55
D4	21.17

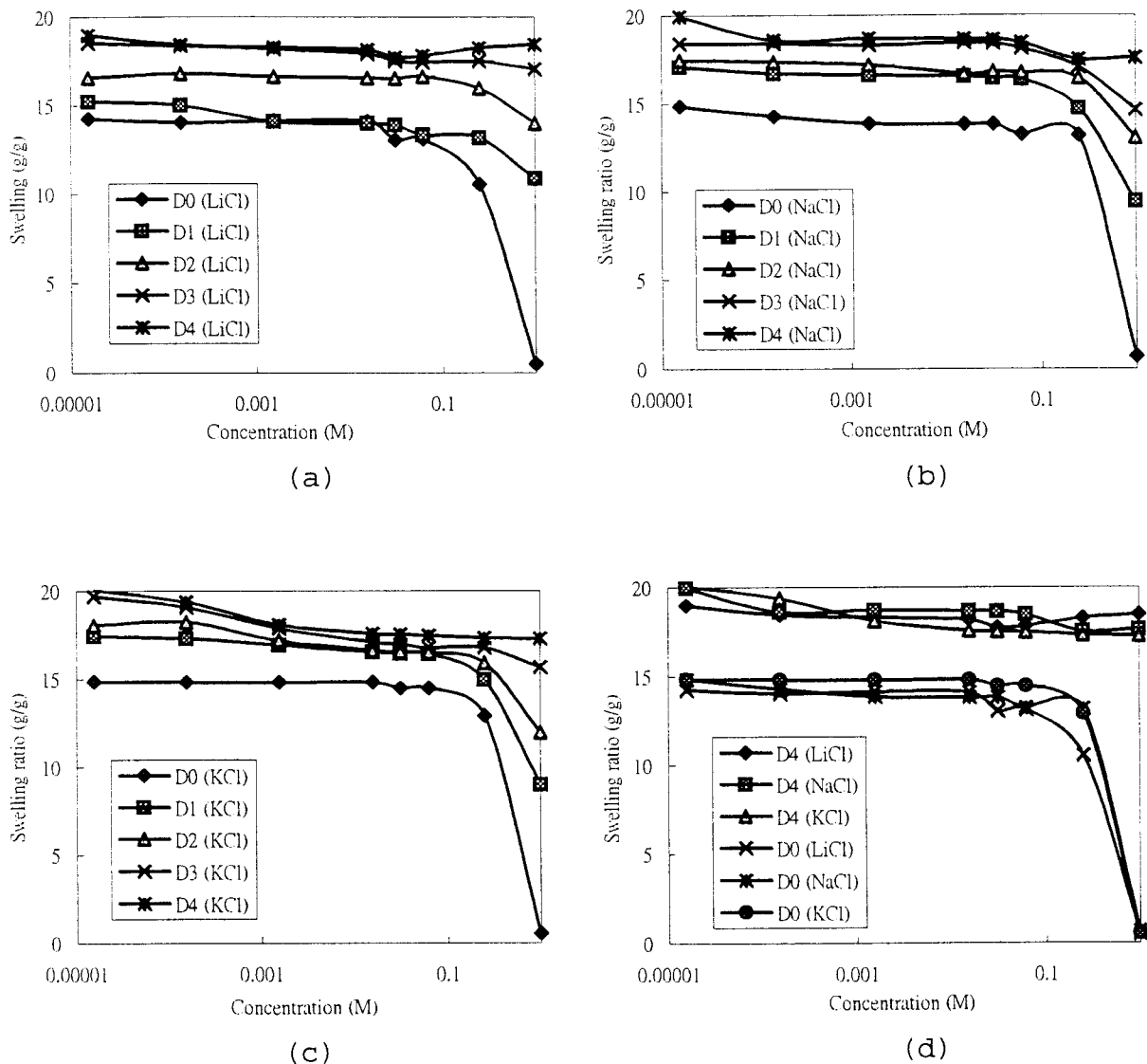**Figure 4** Swelling ratios as a function of aqueous salt solutions for NIPAAm/ DMAAPS copolymeric gels at 25°C. (a) $LiCl_{(aq)}$; (b) $NaCl_{(aq)}$; (c) $KCl_{(aq)}$; and (d) D0 and D4.

smaller the activation energy of diffusion of water into the dry gel, i.e., the water is easily diffused into hydrogel. This result leads to higher water uptake rate and shorter equilibrium swelling time (see Table II).

Effect of Salt Solution on the Swelling Ratio

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

Figure 4 shows the swelling ratios of five gels, D0, D1, D2, D3, and D4, in salt solutions of LiCl, NaCl, and KCl, respectively. The results, shown

in Figure 4, indicate that in the range of salt concentration from $1.56 \times 10^{-5}M$ to $1.56 \times 10^{-2}M$, the swelling ratios for the present co-polymeric gels maintain approximately constant values. According to the Flory's swelling theory,[25] the total fixed charge is zero at all hydrogels. In other words, the concentration of fixed charge referred to unswollen network is zero, meaning that the swelling ratio of hydrogels could not be affected by external dilute salt solution. But the poly(NIPAAm) gel, D0, rapidly contracts during the range of salt concentration from $1.56 \times 10^{-2}M$ to $1.0M$. Because the poly(NIPAAm)

had no fixed charge, the swelling ratio could only be affected by the affinity of water. This affinity makes the polymer-solvent interaction parameter, χ, increase. This result implies that the higher concentration of salt solution is a "poor solvent" for the hydrogel (also called salt effect). Therefore, the swelling ratio of poly(NIPAAm) hydrogel would rapidly decrease at the range of salt concentration from $1.56 \times 10^{-2}M$ to $1.0M$.

The results shown in Figure 4 also indicate that the rapid decrease of the swelling ratio is suppressed by the addition of DMAAPS monomer into NIPAAm gels at the range of the salt concentration from $1.56 \times 10^{-2}M$ to $1.0M$. This phenomenon can be accounted for the nature of poly(DMAAPS).[22] We have reported that the poly(DMAAPS) was insoluble in deionized water, because the collective positive charges on the polyampholyte attracted the collective negative charges to form an inner ionically crosslinked network. When the salt concentration was larger than its minimum salt concentration (MSC), the poly(DMAAPS) could be dissolved in aqueous solution. For this reason, when the salt concentration is increased, a part of the positive charges and negative charges of salt would site-bind on the sulphonate group (SO_3^-) and quaternary ammonium group (R_4N^+) on DMAAPS. The DMAAPS charges will be neutralized by counterion in the aqueous salt solution. This occurrence will reduce the degree of ionically crosslinked network of DMAAPS and remove the entanglement of molecular chain and expand the molecular chain. According to the aforesaid reason, the MSC of poly(DMAAPS) in LiCl aqueous solution is $0.043M$. When the salt concentration is less than $0.043M$, the inner ionic ring of DMAAPS could not be ruptured and the net charge of the copolymeric gel is still zero. The swelling ratios for a series of NIPAAm/DMAAPS copolymeric gels, therefore, do not change significantly when the salt concentration, $LiCl_{(aq)}$, is changed. On the other hand, the inner ring of DMAAPS would be opened when the salt concentration is greater than $0.043M$, and the molecular side chain of DMAAPS would be expanded and the polymer-solvent interaction parameter would be reduced. This behavior implies that the tendency of the rapidly decreased swelling ratio in concentrated salt solution would be effectively suppressed as the DMAAPS was introduced.

Figure 4(b) and (c) also show the same result for the respective gel in NaCl and KCl solutions. Figure 4(d) shows the swelling ratios for samples D4 and D0 as a function of the salt concentrations for LiCl, NaCl, and KCl solutions, respectively. The results indicate that the influence of different cations $(Li^+, Na^+, and K^+)$ with a common anion (Cl^-) on the swelling ratio of D4 and D0 is not significantly changed.

The Influence of Different Divalent Cations with a Common Anion (Cl⁻) on the Swelling Ratio

The swelling behavior of these five xerogels in $MgCl_2$, $CaCl_2$, and $BaCl_2$ solutions show an increase in swelling ratio with the increase of DMAAPS concentration (Fig. 5). Based on the reason presented above, the swelling ratios for these copolymeric gels have the same tendency as those in salt solutions of LiCl, NaCl, and KCl, respectively; i.e., when the salt concentration is greater than the MSC of poly(DMAAPS), the rapidly shrunk swelling ratio for these gels at the higher salt concentration will be more effectively suppressed as more DMAAPS is copolymerized into the copolymeric gels.

The results shown in Figure 5(d) exhibit that the influence of different divalent cations with a common anion (Cl^-) on the swelling ratio of samples D4 and D0 is relatively small. But there is a significant difference for sample D0 at high concentration. It is found that the swelling ratio for sample D0 is higher in $MgCl_2$ solution than that in $CaCl_2$ and $BaCl_2$ solutions. This result is due to the effect of cationic radius or hydration forces. The hydration radius grows as a result of the small cation surrounded with a large amount of water. Therefore, the swelling ratio for sample D0 is higher in $MgCl_2$ solution than that in $CaCl_2$ and $BaCl_2$ solutions.

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 the mentioned hydrogels, which is shown in Figure 6, is investigated. The swelling ratios of these hydrogels in the KF solutions exhibit a decrease with increase in the salt concentration [Fig. 6(a)]. This is because the poly(DMAAPS) is insoluble in KF solution[21]; KF is a poor solvent for poly(NIPAAm-co-DMAAPS) hydrogels and makes the polymer-solvent interaction parameter increase. Hence, the swelling ratio of hydrogels decreases with an increase of the salt concentration. However, Figures 6(b) and (c) do not show this phenomenon.
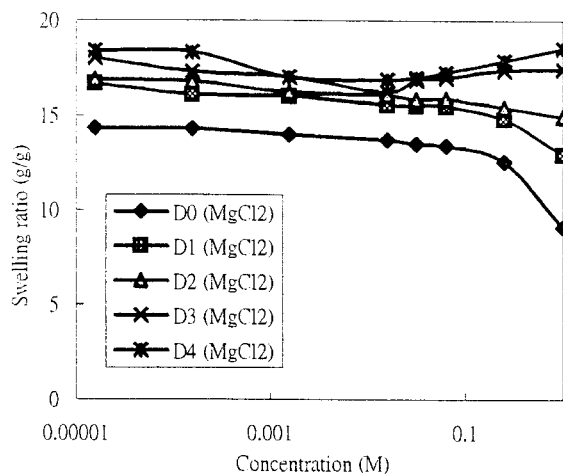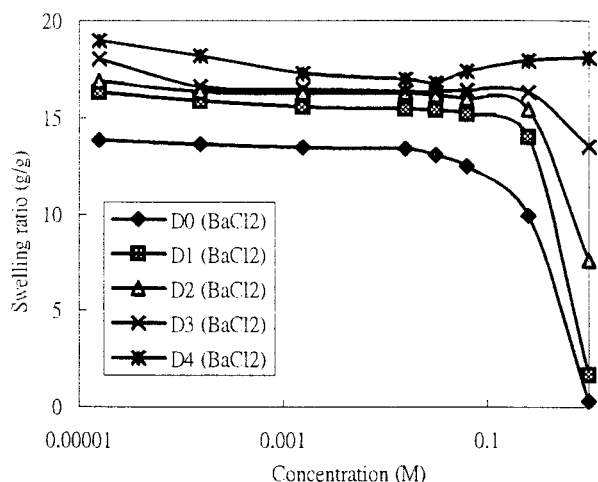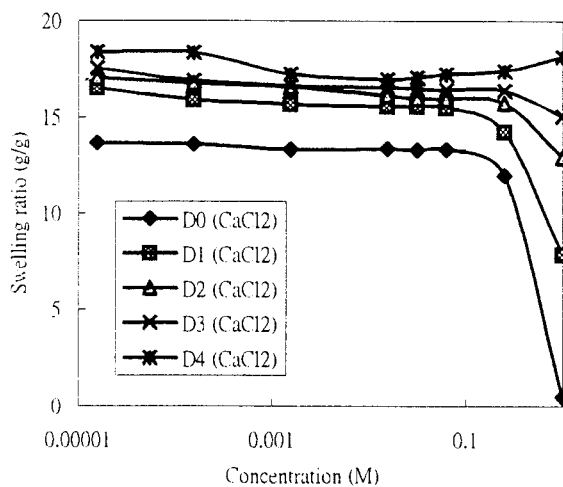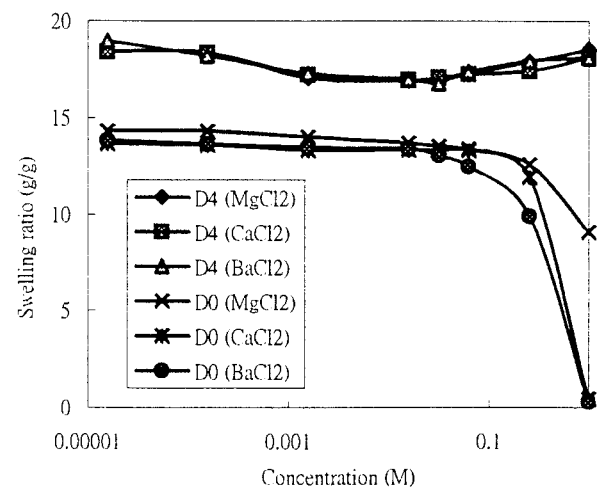
Figure 5 Swelling ratios as a function of aqueous salt solutions $MgCl_{2(aq)}$ for NIPAAm/DMAAPS copolymeric gels at 25°C. (a) $MgCl_{2(aq)}$; (b) $CaCl_{2(aq)}$; (c) $BaCl_{2(aq)}$; and (d) D0 and D4.

Figures 6(b) and (c) show the swelling ratios of poly(NIPAAm-co-DMAAPS) hydrogels in salt solutions of KBr and KI, respectively. The MSCs of poly(DMAAPS) in KBr and KI aqueous solution which are $0.021M$ and $0.0094M$, respectively, are reported in our previous studies.[22] When the salt concentration is greater than the MSC of poly-(DMAAPS), the hydrogels will have an antipolyelectrolyte's swelling behavior. The swelling ratio increases as salt concentration increases. However, the swelling ratios for these copolymeric gels have only a small change with increasing salt concentration when the salt concentration is under the MSC.

Figure 6(d) shows the swelling ratio of samples D4 and D0 as a function of the salt concentration for KF, KCl, KBr, and KI solutions, respectively. The results indicate that the swelling curves have a large difference for these four salt solutions. For the potassium salts, Figure 6(d) indicates an increase in the swelling ratio of hydrogels in the order of $F^- < Cl^- < Br^- < I^-$ for KF, KCl, KBr, and KI, respectively. Anion with a small charge density was easily bound on the quaternary am-
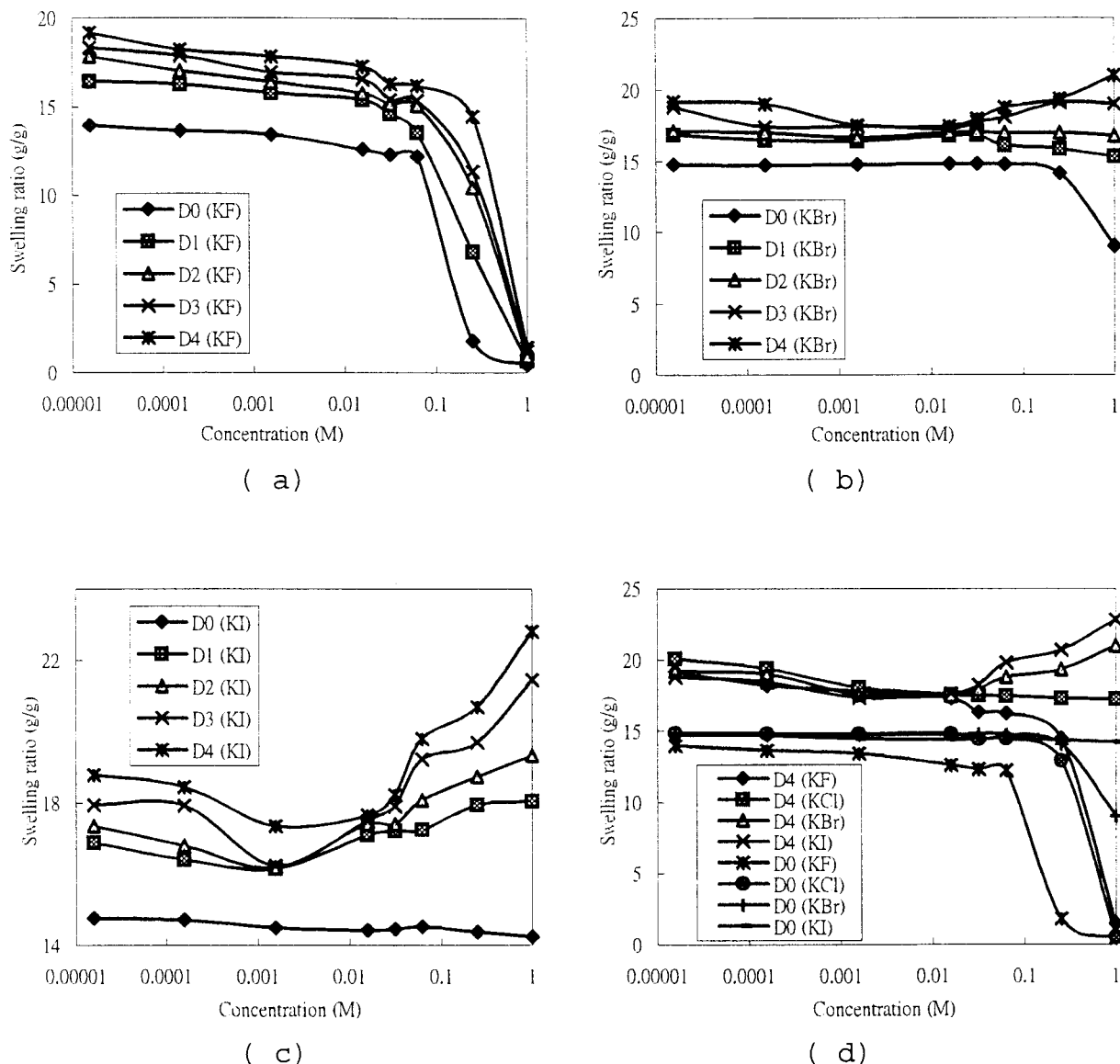
Figure 6 Swelling ratios as a function of aqueous salt solutions for NIPAAm/ DMAAPS copolymeric gels at 25°C. (a) KF$_{(aq)}$; (b) KBr$_{(aq)}$; (c) KI$_{(aq)}$; and (d) D4 and D0.

monium group (R_4N^+) of DMAAPS. This is because the ion with smaller charge density can be easily polarized during the ionization of salt nearby and bound on the quaternary ammonium group (R_4N^+) of DMAAPS. The larger anion, therefore, can easily infiltrate into ionically crosslinked network and expand the molecular chain.[22] Hence, if the anion size in the external salt solution is bigger, the antipolyelectrolyte's swelling behavior of hydrogels is more obvious.

From the above results, we found that the anion effect is greater than the cation effect in the presence of a common anion (Cl^-) with different

cations [Fig. 5(d) and Fig. 6(d)] and a common cation (K^+) with different anions [Fig. 7(d)] for the hydrogels. The results coincide with the Pearson principle[29] and our previous reports.[30]

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^-, NO_2^-, and CH_3COO^-) with a common cation (Na^+) on the swelling ratio for D0 and D4 gels was investigated. The results are shown in Figure 7. The swelling behaviors are similar to that for the
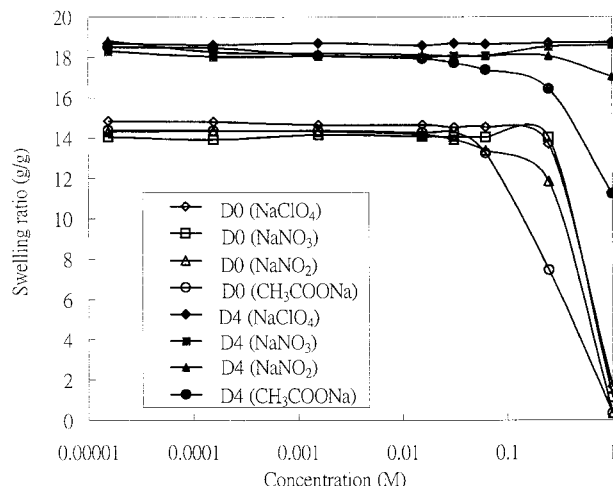
Figure 7 Swelling ratios as a function of $NaClO_{4(aq)}$, $NaNO_{3(aq)}$, $NaNO_{2(aq)}$, and $CH_3COONa_{(aq)}$ for D0 and D4 copolymeric gels at 25°C.

hydrogels in monovalent and divalent chloride salt solutions. When the salt concentration is greater than the MSC of the poly(DMAAPS), the hydrogels exhibit an antipolyelectrolyte's swelling behavior. The swelling ratio for D4 increases when the salt concentration is increased. This phenomenon is only found in $NaClO_4$ and $NaNO_3$ solutions, but not in $NaNO_2$ and CH_3COONa solutions. This is because ClO_4^- and NO_3^- ions are larger and the MSCs for poly(DMAAPS) are smaller.

The swelling ratios shown in Figure 7 for D4 and D0 in the salt concentration of $NaClO_4$, $NaNO_3$, $NaNO_2$, and CH_3COONa solutions, respectively, also indicate that the swelling behaviors of the hydrogels are similar to Figure 6(d) and are in the order $CH_3COO^- < NO_2^- < NO_3^- < ClO_4^-$ for CH_3COONa, $NaNO_2$, $NaNO_3$, and $NaClO_4$, respectively. This tendency is compared with the aqueous salt solution behavior of poly-(DMAAPS).[22]

Figure 8 shows the swelling ratios for samples D0 and D4 in salt solutions of Na_2SO_4, Na_2SO_3, and $Na_2S_2O_3$, respectively. The results indicate that the swelling ratio decreases with an increase of the salt concentration. This is because divalent acid groups with larger charge density and the neighboring quaternary ammonium group (R_4N^+) on the side chain of DMAAPS were both easily attracted in aqueous solution at the same time. This attraction would result in coagulation of the side chains. This occurrence would reduce the hydrogel network expansion resulting from de-

stroying the ionically crosslinked network. The results show that the influence of different divalent acidic ions with a common cation (Na^+) on the swelling ratio of sample D4 and sample D0 are not significant.

CONCLUSIONS

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

In the diffusion transport mechanism, the results indicate that the swelling exponents "n" for all NIPAAm/DMAAPS 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 activation energy has the following tendency, D0 > D1 > D2 > D3 > D4. In other words, the higher the DMAAPS content, the smaller the activation energy of diffusion, i.e., the water is more easily diffused into hydrogels containing more DMAAPS.

The effect of salt solution on the swelling ratio for these series gels shows a special behavior. The swelling ratios for these NIPAAm/DMAAPS copolymeric gels can be effectively increased when the salt concentration is greater than the MSC of
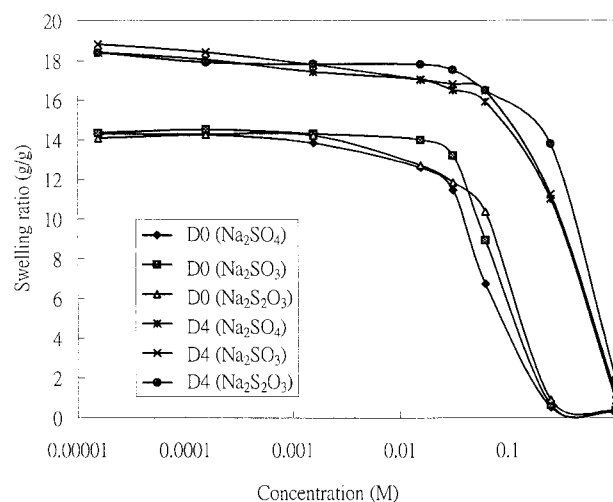

Figure 8 Swelling ratios as a function of $Na_2SO_{4(aq)}$, $Na_2SO_{3(aq)}$, and $Na_2S_2O_{3(aq)}$ for D0 and D4 copolymeric gels at 25°C.

poly(DMAAPS). However, the swelling ratios for these copolymeric gels do not significantly change when the external salt concentration is lower than the MSC of poly(DMAAPS). In addition, only D4 exhibits swelling behavior when the salt concentration is greater than the MSC of poly-(DMAAPS). It is found that the swelling ratio of hydrogel in salt solution can be improved when the zwitterionic monomer is appropriately introduced.

Finally, the anion effect is greater than the cation effect, in the presence of common cation (K^+) with different anions, and common anion (Cl^-) with different cations, for the hydrogels.

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