Superabsorbent Polymeric Materials IX: Effect of Cationic Structure on Swelling Behavior of Crosslinked Poly(sodium acrylate-*co*-cationic monomers) in Aqueous Salt Solutions

WEN-FU LEE, YU-LIN HUANG

Department of Chemical Engineering, Tatung University, Taipei, Taiwan, Republic of China

ABSTRACT: Two series of xerogels based on sodium acrylate (SA), trimethyl methacrylamidopropyl ammonium iodide (TMMAAI), trimethyl methacryloyloxyethyl ammonium iodide (TMMAI), and N,N'-methylene-*bis*-acrylamide (NMBA) as a crosslinker were prepared by inverse suspension polymerization. The water absorbency and swelling kinetic behavior for these xerogels in water or various saline solutions were investigated. The results showed that the swelling behaviors of these absorbents are related to their chemical structures, their compositions, and the type of external salt solutions. There would be effective improvement in the water absorbency of these two gel series by copolymerizing SA with a small amount of cationic monomer (TMMAAI or TMMAI). The initial absorption rates in deionized water were found to be faster for TM series gels than for TA series gels. The two series of superabsorbents had a tendency to absorb water in dilute nitrate aqueous solutions in the order: Fe^{3+}, Ni^{2+}, Ca^{2+}, Cu^{2+}, and Na^+ for $Fe(NO_3)_3$, $Ni(NO_3)_2$, $Ca(NO_3)_2$, $Cu(NO_3)_2$, and $NaNO_3$ aqueous solution, respectively. The absorbency and initial absorption rate for these gels were related to the gel compositions and salt concentrations. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1827–1837, 2001

Key words: superabsorbent; water absorbency; swelling behavior; xerogel; sodium acrylate; cationic monomer; inverse suspension polymerization

INTRODUCTION

Superabsorbent polymers can absorb and hold a large amount of water as compared to traditional water-absorbing materials, in which the absorbed water is barely removable, even under some pressure.

Superabsorbent polymers were first reported by the U.S. Department of Agriculture, and wide attention was paid to their applications. Because of their excellent characteristics, these polymers are widely used in many fields, including dispos-able diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water-blocking tapes, medicine for drug delivery systems, and absorbent pads. In such applications water absorbency or water retention is essential. Therefore, many researchers have attempted to improve these absorbent polymers by enhancing their absorbency, gel strength, and absorption rate.

Flory first presented the swelling principle for hydrophilic polymers with either a nonionic network or an ionic network structure. Ogawa et al. studied the kinetics of the swelling of poly(SA) [poly(sodium acrylate)] using picture analysis with a microscope–VTR system, calorimetry, and gravimetry techniques. We previously reported the swelling behaviors in water and in various

Table I Compositions of SA–TMMAAI and SA–TMMAI Xerogels

Sample No.	SA (g)	TMMAAI (g)	TMMAI (g)
A1	20	—	—
TA1	19.95	0.166 (0.25)	—
TA2	19.85	0.498 (0.75)	—
TA3	19.7	0.996 (1.50)	—
TA4	19.55	1.494 (2.25)	—
TA5	19.4	1.998 (3.01)	—
TM1	19.95	—	0.159 (0.25)
TM2	19.85	—	0.476 (0.75)
TM3	19.7	—	0.951 (1.5)
TM4	19.55	—	1.427 (2.25)
TM5	19.4	—	1.908 (3.01)

Values within parentheses represent molar percent of cationic monomer based on total monomer.

saline solutions of a series of superabsorbent polymers,[26–30] including SA copolymerized with the nonionic comonomer 2-hydroxyethyl methacrylate (HEMA),[26] with the zwitterionic monomer 3,3-dimethyl methacryloyloxyethyl ammonium propane sulfonate (DMAPS),[27] with 3,3-dimethyl acrylamidopropyl ammonium propane sulfonate (DMAAPS),[28] and with the anionic monomer sodium 2-acrylamido-2-methyl propane sulfonate (NaAMPS).[29]

The swelling kinetic behaviors for these two series of superabsorbents, SA–DMAPS and SA–DMAAPS, were investigated in our previous report.[30] Results showed that the higher the content of the sulfobetaine in the copolymer, the larger the water absorbency. The tendency of these gels to be absorbent in dilute salt solutions ranked as follows: Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}.

In our previous reports,[31–32] the SA–TMMAAI and SA–TMMAI absorbent polymers were prepared, and their swelling behaviors in aqueous salt solutions were investigated. Because these gels had a gel transition near the concentration of $2 \times 10^{-3}M$ in a salt solution, the main purpose of the current study was to investigate swelling kinetic behaviors of these gels near their gel transition concentration in various nitrate aqueous solutions.

EXPERIMENT

Materials

The materials used in this study were purchased from Tokyo Kasei Industries Ltd. (Tokyo, Japan),

including acrylic acid (AA), dimethylaminopropyl acrylamide, dimethylaminoethyl methacrylate, sodium hydroxide, methyl iodide, and N,N'-methylene-*bis*-acrylamide (NMBA). Sodium hydroxide and NMBA were used directly. 4,4′-Azobis(4-cyanovaleric acid) (ACVA), used as an initiator, and sorbitan monostearate (Span 60), used as an inverse suspension stabilizer, were also purchased from Tokyo Kasei Industries Ltd. Methanol and cyclohexane were of analytical grade.

Preparation of SA Monomer Solution

SA monomer was prepared as reported previously.

Synthesis of TMMAAI Monomer

The monomer TMMAAI was prepared as reported previously (yield: 92%; mp: 112°C). Its structure is as follows:
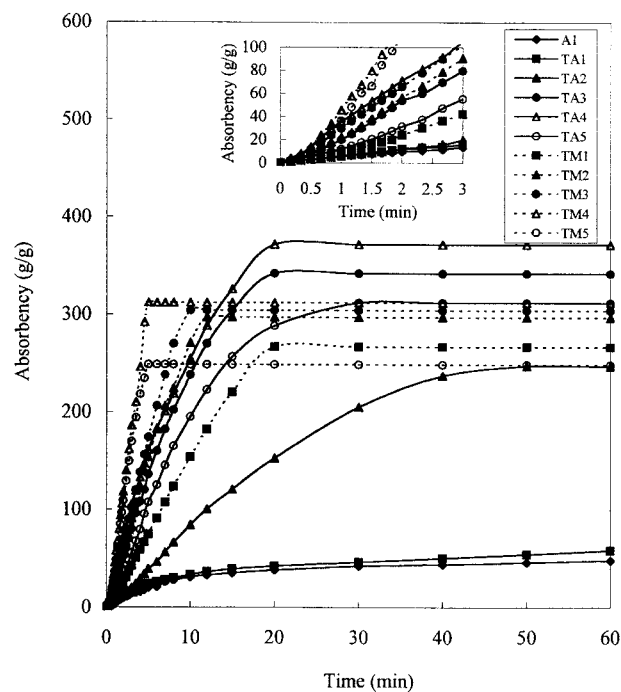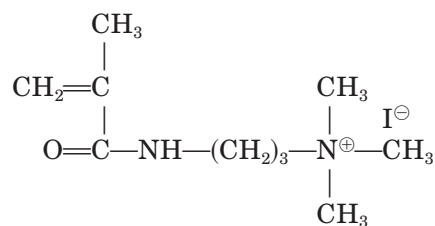

Figure 1 Swelling behaviors of various xerogels in deionized water by DW method.

Table II Absorption Characteristics of SA, SA–TMMAAI, and SA–TMMAI Copolymeric Gels in Deionized Water

Conditions	A1	TA1	TA2	TA3	TA4	TA5	TM1	TM2	TM3	TM4	TM5
Initial absorption rate (g/min)											
30 sec	6.0	6.0	6.0	16.0	27.8	11.9	8.1	20.2	24.0	28.0	20.2
1–3 min	4.0	5.0	7.0	30.0	35.0	22.0	16.2	34.3	36.0	70.0	66.6
t_{req} (min)	120	120	50	20	20	30	20	12	10	5	5
Q'_{eq} (g H$_2$O/g)	56	66	247	342	372	312	267	297	304	312	248
Q_{eq} (g H$_2$O/g)	213	458	598	413	405	389	566	491	441	315	255

t_{req}, time required to approach equilibrium; Q'_{eq}, equilibrium water absorbency by DW method; Q_{eq}, equilibrium water absorbency by suction method.

Synthesis of TMMAI Monomer

The monomer TMMAI was prepared as reported previously (yield: 92%, mp: 184°C). Its structure is as follows:
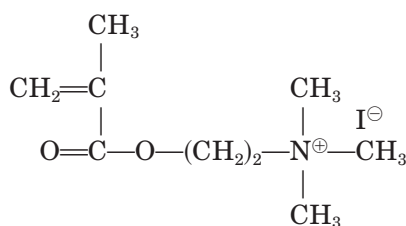
Inverse Suspension Polymerization

A 300-mL four-necked separable flask equipped with a reflux condenser, a stirring rod, and a thermometer was charged with 60 mL of cyclohexane and 0.15 g of sorbitan monostearate, which was stirred until the sorbitan monostearate was dissolved (continuous phase).

The crosslinking agent, NMBA [0.07 g (0.214 mol % based on the total monomer content)], and the appropriate amounts of cationic monomer (TMMAAI or TMMAI) were introduced into SA monomer solution, and the mixture was stirred
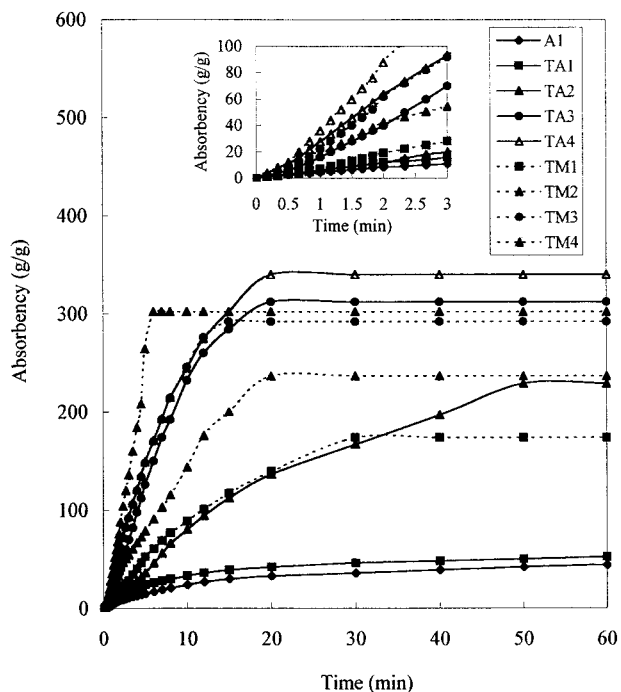

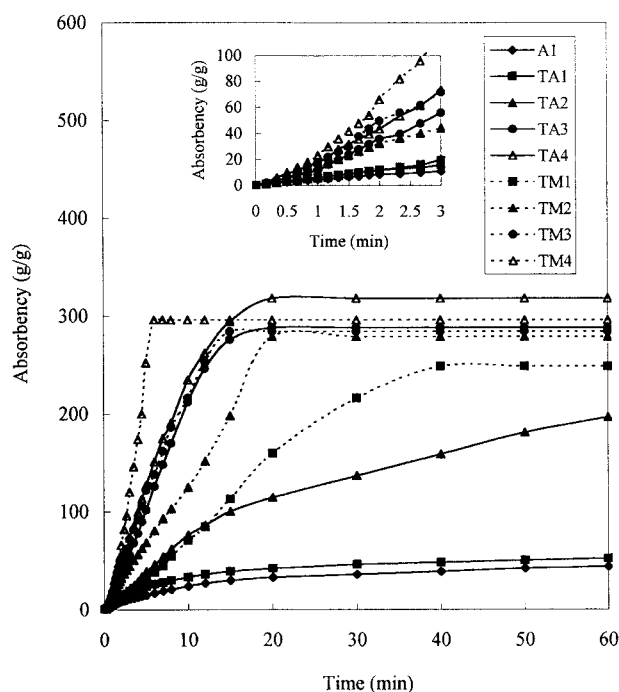**Figure 2** Swelling behaviors of various xerogels in 2 × 10^{-4}M NaNO$_3$ by DW method.

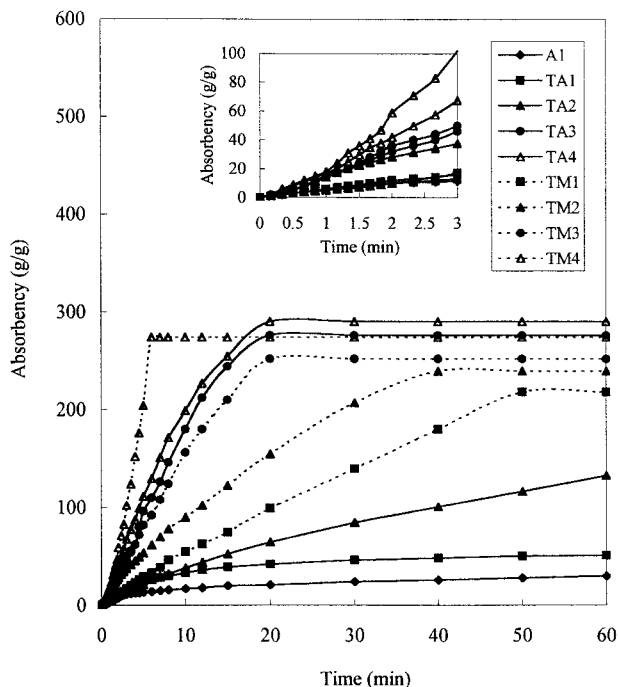**Figure 3** Swelling behaviors of various xerogels in 2 × 10^{-4}M Cu(NO$_3$)$_2$ by DW method.

Figure 4 Swelling behaviors of various xerogels in 2 $\times 10^{-4}M$ Ca(NO$_3$)$_2$ by DW method.

until the NMBA was dissolved completely. The monomer solution and 0.15 g of the initiator, ACVA (dispersion phase), were introduced into
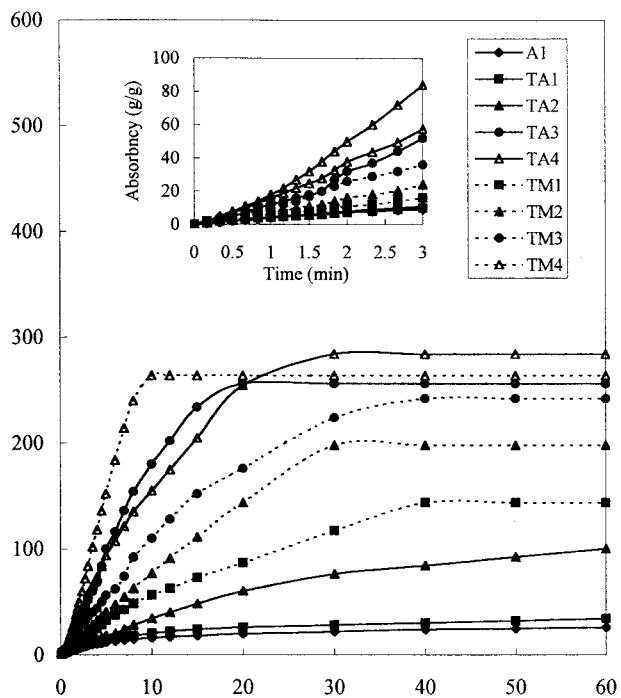

Figure 5 Swelling behaviors of various xerogels in 2 $\times 10^{-4}M$ Ni(NO$_3$)$_2$ by DW method.

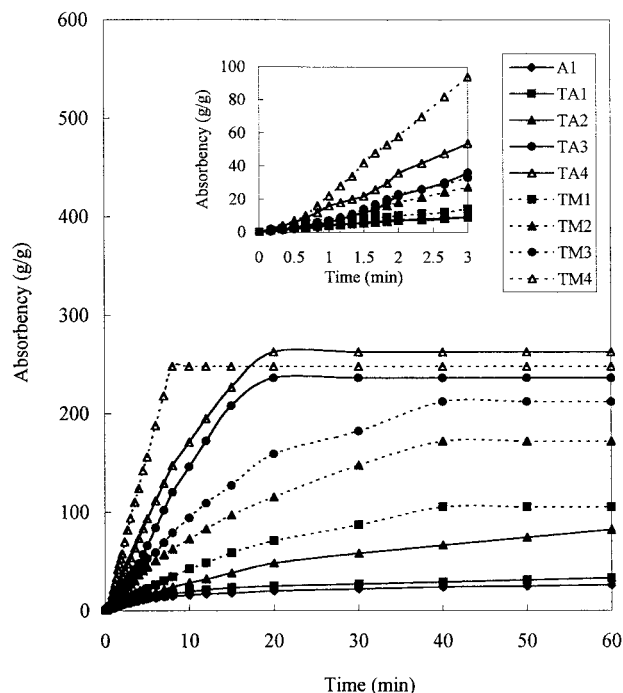**Figure 6** Swelling behaviors of various xerogels in 2 $\times 10^{-4}M$ Fe(NO$_3$)$_3$ by DW method.

the reactor. Air was flushed from the reactor by introducing nitrogen until the entire process was completed. The stirrer speed was maintained at 250 rpm. The polymerization was set at 70°C for 4h. After the reaction was completed, the suspension solution was cooled and then precipitated by 800mL of cold methanol under stirring. The product was filtered and washed several times by the mixture of water and methanol (1:9 v/v). The product was then dried in a vacuum oven at 70°C for 1 day. A polymer of white powder was obtained, and the yield was more than 95%. The compositions of the samples are listed in Table I.

Measurement of Property

All samples with particle size in the range of 60 and 100 mesh were dried in a vacuum oven at 70°C before any tests. The saturated or equilibrium absorbency, Q_{eq}, measured by suction filtration method is described elsewhere.[26–30]

Kinetics of Swelling

A technique based on the demand wettability (DW) method was adopted.[16,27] A graduated burette with an air inlet at the bottom was linked by a flexible tube to a plate covered with a metallic grid (250 mesh). After filling the burette with the

Table III   Absorption Characteristics of SA–TMMAAI Copolymeric Gel Systems before Gel Transition Concentration

Conditions	A1	TA1	TA2	TA3	TA4
			$2 \times 10^{-4} M$ Fe(NO$_3$)$_3$		
Initial absorption rate (g/min)					
(30 sec)	6.0	6.0	6.0	12.0	21.9
(1–3 min)	3.2	5.0	7.0	27.0	33.0
t_{req} (min)	180	120	50	20	20
Q_{eq} (g H$_2$O/g)	61	64	229	312	340
			$2 \times 10^{-4} M$ Ni(NO$_3$)$_2$		
Initial absorption rate (g/min)					
(30 sec)	6.0	6.0	6.0	12.0	17.9
(1–3 min)	3.0	5.0	7.0	22.0	28.0
t_{req} (min)	180	120	60	20	20
Q_{eq} (g H$_2$O/g)	57	58	197	288	318
			$2 \times 10^{-4} M$ Ca(NO$_3$)$_2$		
Initial absorption rate (g/min)					
(30 sec)	6.0	6.0	6.0	12.0	15.9
(1–3 min)	3.0	5.0	7.0	15.5	25.5
t_{req} (min)	180	120	80	20	22
Q_{eq} (g H$_2$O/g)	55	57	157	276	298
			$2 \times 10^{-4} M$ Cu(NO$_3$)$_2$		
Initial absorption rate (g/min)					
(30 sec)	6.0	5.8	5.8	10.0	13.9
(1–3 min)	3.0	2.8	3.3	20.0	21.0
t_{req} (min)	240	180	120	20	30
Q_{eq} (g H$_2$O/g)	50	53	139	256	289
			$2 \times 10^{-4} M$ Na(NO$_3$)$_3$		
Initial absorption rate (g/min)					
(30 sec)	4.0	5.2	5.0	6.0	11.9
(1–3 min)	2.0	2.3	2.6	15.0	19.0
t_{req} (min)	240	180	120	20	20
Q_{eq} (g H$_2$O/g)	46	48	118	236	276

See Table II for definitions.

saline solution, it was closed at the top, and air was introduced while the xerogellant absorbed water. The sample (50 mg) of absorbent was placed on the grid, and the swelling kinetics were easily measured. The absorbency at every time interval was calculated by the following equation:

$$Q' = Vs \times d_{H_2O}/Wd \qquad (1)$$

where Q' is the characteristic absorbency, Vs is the sorbed volume, d_{H2O}, is the density of water, and W_d is the weight of the dry sample.

RESULTS AND DISCUSSION

The swelling behavior of superabsorbents depends on the nature of the polymer and the char-

acteristics of the external solution. The characteristics of the polymer's nature are its charge, ionic content, and crosslinking density. The characteristics of the external solution include the charge number and ionic strength.

Effect of Cationic Monomer on Saturated Water Absorbency

Figure 1 shows the swelling behavior of various xerogels in deionized water, as determined by the DW method. The results in Figure 1 indicate that water absorbencies and initial absorption rates are effectively enhanced when the cationic monomer TMMAAI or TMMAI is introduced. According to Flory's theory,[24] the swelling force of a gel is dependent on the ionic osmotic pressure, the rubbery elastic force, and the affinity of the gel to-

Table IV   Absorption Characteristics of SA–TMMAI Copolymeric Gel Systems before Gel Transition Concentration

Conditions	A1	TM1	TM2	TM3	TM4
			$2 \times 10^{-4}M$ Fe(NO$_3$)$_3$		
Initial absorption rate (g/min)					
(30 sec)	6.0	8.1	14.1	16.0	20.0
(1–3 min)	3.2	10.6	18.2	35.0	50.0
t_{req} (min)	180	40	20	15	6
Q_{eq} (g H$_2$O/g)	61	254	286	292	302
			$2 \times 10^{-4}M$ Ni(NO$_3$)$_2$		
Initial absorption rate (g/min)					
(30 sec)	6.0	8.1	8.1	12.0	16.0
(1–3 min)	3.0	6.7	12.1	36.0	39.0
t_{req} (min)	180	40	30	20	8
Q_{eq} (g H$_2$O/g)	57	248	279	284	296
			$2 \times 10^{-4}M$ Ca(NO$_3$)$_2$		
Initial absorption rate (g/min)					
(30 sec)	6.0	8.1	8.1	10.0	12.0
(1–3 min)	3.0	6.1	12.1	32.0	32.0
t_{req} (min)	180	40	40	20	8
Q_{eq} (g H$_2$O/g)	55	188	246	257	293
			$2 \times 10^{-4}M$ Cu(NO$_3$)$_2$		
Initial absorption rate (g/min)					
(30 sec)	6.0	6.1	6.1	8.0	12.0
(1–3 min)	3.0	6.1	12.1	24.0	28.0
t_{req} (min)	240	40	40	30	10
Q_{eq} (g H$_2$O/g)	50	118	204	218	286
			$2 \times 10^{-4}M$ Na(NO$_3$)$_3$		
Initial absorption rate (g/min)					
(30 sec)	4.0	5.3	6.1	8.0	12.0
(1–3 min)	2.0	5.8	10.1	20.0	36.0
t_{req} (min)	240	40	40	30	10
Q_{eq} (g H$_2$O/g)	46	105	172	196	272

See Table II for definitions.

ward water. From this theory, it can be determined that water absorbency is related to the affinity of the gel toward water. The cationic monomer unit dissociates into an iodide ion (I$^-$) and a quaternary ammonium group (R$_4$N$^+$) when the copolymeric gel contacts water. The affinity of the quaternary ammonium group toward water is stronger than the carboxylate group (COO$^-$). Therefore, water absorbencies should be enhanced when the TMMAAI or TMMAI monomer is incorporated into the SA absorbent composition.

The results of further investigation of the characteristic absorption data of these two series of the gels, shown in Table II, indicate that the initial absorption rates for TM gels are faster than are those for TA gels. This may be primarily the result of the presence of hydrophilic groups in

TMMAAI and TMMAI, that is, the quaternary ammonium group (R$_4$N^{++}), the amido group (—CONH—), and the ester group (—COO—). The tendency of these three groups to be hydrophilic is in this order from strongest to weakest: quaternary ammonium group, amido group, ester group. Because the hydrophilicity of the ester group in TM gels is weaker than that of the amido group in TA gels, according to our previous article,[33] from the viewpoint of the structure of these two compounds, the hydrophilicity of the ethylene unit in TM gels is higher than that of the propylene unit in TA gels. This makes the absorption rate for the TM series gels faster than that for the TA series gels. Similar results were also observed in a previous article on poly(SA-co-sulfobetaine).[30]

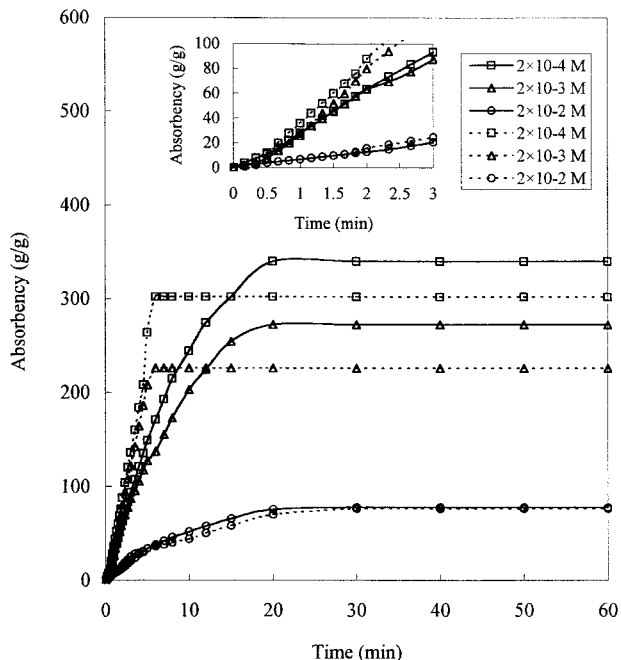Figure 1 and Table II also show that the initial absorption rate decreases when the amount of

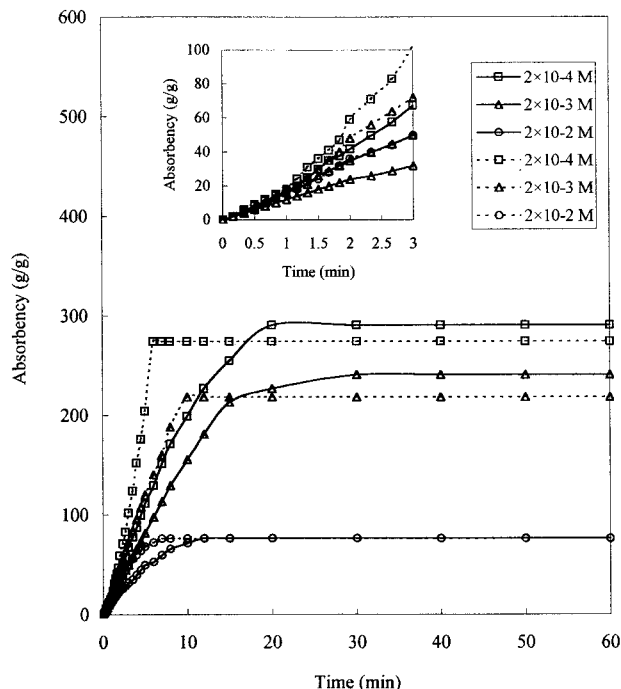**Figure 7** Swelling behaviors for (——) TA4 and (ṫ) TM4 in $2 \times 10^{-4}M$ NaNO$_3$ by DW method.

cationic monomer introduced is more than 2.25 mol % (TA5 and TM5). This is because the fixed charge concentration of the network would be re-

Figure 8 Swelling behaviors for (——) TA4 and (ṫ) TM4 in $2 \times 10^{-4}M$ Cu(NO$_3$)$_2$ by DW method.

Figure 9 Swelling behaviors for (——) TA4 and (ṫ) TM4 in $2 \times 10^{-4}M$ Ca(NO$_3$)$_2$ by DW method.

duced as a result of the introduction of the cationic monomer. This phenomenon leads to the reduction of repulsion of the network. Hence, the
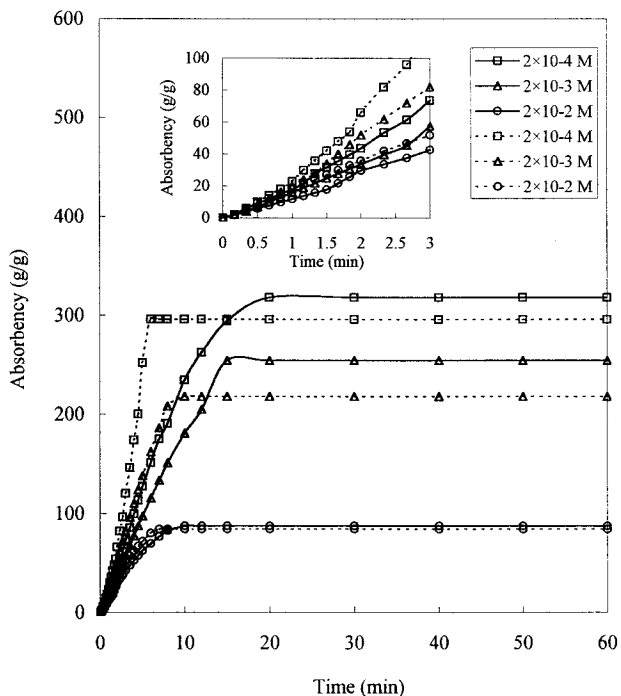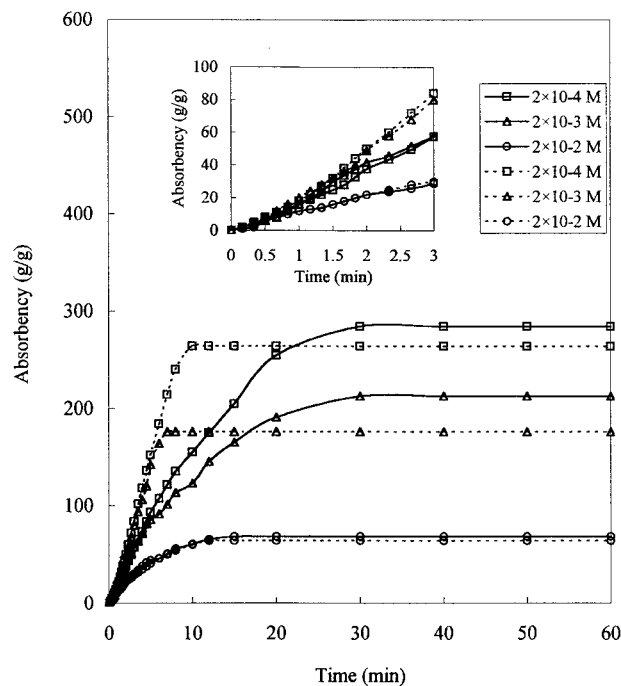

Figure 10 Swelling behaviors for (——) TA4 and (ṫ) TM4 in $2 \times 10^{-4}M$ Ni(NO$_3$)$_2$ by DW method.

initial absorption rate and the water absorbency decrease.

However, the results observed from Table II also show that water absorbency measured by the suction method (Q_{eq}) is larger than by the DW method (Q'_{eq}). Water absorbency measured by the suction method decreases with an increasing content of cationic monomer, but the contrary result is observed from the DW method. This is because the water absorbency measured by the suction method is saturated absorbency: it is related mainly to the concentration of the fixed charge of the network. The introduction of cationic monomer would cause the concentration of negative charge of the network decrease, that is, the water absorbency would decrease. The water absorbency measured by the DW method is the water absorbency within 4 h. It is related primarily to the content of cationic monomer. The absorption rate is effectively improved when cationic monomer is introduced. Hence, the gel could absorb a lot of water, and the water absorbency would increase when the content of cationic monomer increases.

Effect of Various Salt Solutions on Swelling Behavior for the Two Series of Superabsorbents (Before Gel Transition Concentration)

To investigate the initial absorption rate of these two series of superabsorbents around the gel transition concentration (GTC), A1, TA1–TA4, and TM1–TM4 were chosen to measure the initial absorption rate of the present gels in various nitrate solutions.

Figures 2–6 show the water absorbency of the xerogels of poly(SA-co-TMMAAI) and poly(SA-co-TM-MAAI) in a concentration of $2 \times 10^{-4}M$ (before the GTC) Fe(NO$_3$)$_3$(aq), Ni(NO$_3$)$_2$(aq), Ca(NO$_3$)$_2$(aq), Cu(NO$_3$)$_2$(aq), and NaNO$_3$(aq). The results shown in these figures indicate that the water absorbencies for the TM series are higher than those for the TA series when the content of the cationic monomer is below 0.75 mol % (TA1, TA2, TM1, and TM2). However, the opposite result for the initial absorption rate is obtained when the content of the cationic monomer is more than 0.75 mol % (TA3, TA4, TM3, and TM4). This is because the initial absorption rate is too slow when the content of the TMMAAI is below 0.75 mol % (TA1 and TA2).

The results in Tables III and IV indicate that for the TA series the initial absorption rate during the first 30-s period is similar to that for the
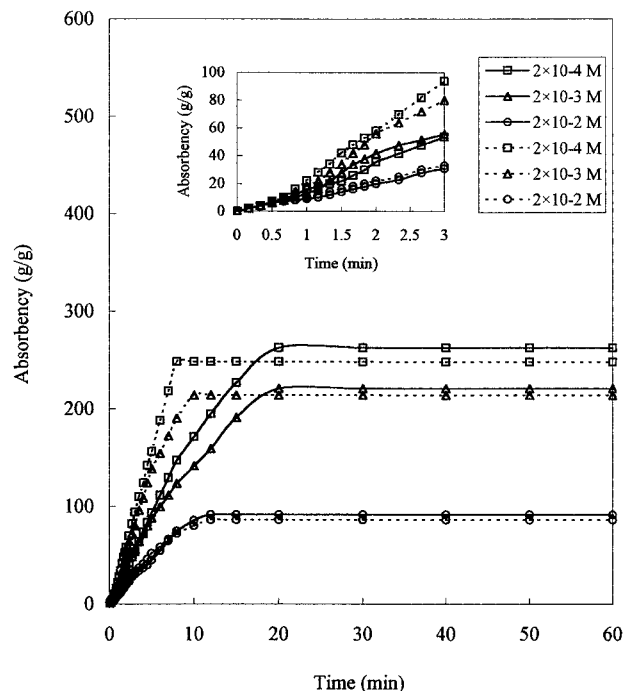

Figure 11 Swelling behaviors for (——) TA4 and (ṫ) TM4 in $2 \times 10^{-4}M$ Fe(NO$_3$)$_3$ by DW method.

TM series, but the TM series is obviously higher than that of the TA series for the 1–3 min period. Otherwise, the equilibrium times for the TA series are also shorter than for the TM series.

Contrasting Figures 2–6 to Tables III and IV, the results indicate that the tendency of the water absorbency for the said gels is in the order Fe^{3+}, Ni^{2+}, Ca^{2+}, Cu^{2+}, Na$^+$ in Fe(NO$_3$)$_3$(aq), Ni(NO$_3$)$_2$(aq), Ca(NO$_3$)$_2$(aq), Cu(NO$_3$)$_2$(aq), and NaNO$_3$(aq). This result may be attributed to the hydration ability of the cation. The higher the valence of the cation, the higher is the hydration number and the stronger the affinity of the cation toward water. In other words, the tendency of the cation to be hydrophilic is as follows: trivalent, divalent, monovalent. In addition, the tendency for the divalent cation is in the order of Ni^{2+}, Ca^{2+}, Cu^{2+} because the hydration ability of the cation is Ni^{2+}, Ca^{2+}, Cu^{2+}.

Effect of Salt Concentration on Swelling Behavior for the Two Series of Superabsorbents

The swelling kinetics for TA4 and TM4 gels in the three concentrations ($2 \times 10^{-4}M$, $2 \times 10^{-3}M$, $2 \times 10^{-2}M$) of Fe(NO$_3$)$_3$(aq), Ni(NO$_3$)$_2$(aq), Ca(NO$_3$)$_2$(aq), Cu(NO$_3$)$_2$(aq), and NaNO$_3$(aq) are shown in Figures 7–11, respectively. The results from these

Table V   Absorption Characteristics of SA–TMMAAI and SA–TMMAI Copolymeric Gel Systems in Gel Transition Concentration

Conditions	A1	TA1	TA4	TM1	TM4
			$2 \times 10^{-3}M$ Fe(NO$_3$)$_3$		
Initial absorption rate (g/min)					
(30 sec)	4.0	4.0	15.9	8.0	16.0
(1–3 min)	2.6	2.8	29.8	8.1	48.0
t_{req} (min)	180	180	20	30	6
Q_{eq} (g H$_2$O/g)	21	42	272	128	226
			$2 \times 10^{-3}M$ Ni(NO$_3$)$_2$		
Initial absorption rate (g/min)					
(30 sec)	5.2	5.2	13.9	6.1	16.0
(1–3 min)	2.8	3.3	20.9	6.1	31.0
t_{req} (min)	180	180	15	40	7
Q_{eq} (g H$_2$O/g)	26	38	255	116	218
			$2 \times 10^{-3}M$ Ca(NO$_3$)$_2$		
Initial absorption rate (g/min)					
(30 sec)	4.8	4.8	13.9	6.1	14.0
(1–3 min)	2.6	3.0	16.9	4.1	28.0
t_{req} (min)	180	180	30	40	10
Q_{eq} (g H$_2$O/g)	25	36	241	104	187
			$2 \times 10^{-3}M$ Cu(NO$_3$)$_2$		
Initial absorption rate (g/min)					
(30 sec)	4.8	4.8	11.9	6.1	12.0
(1–3 min)	2.6	3.0	20.9	4.1	30.0
t_{req} (min)	180	180	30	40	7
Q_{eq} (g H$_2$O/g)	23	34	213	96	176
			$2 \times 10^{-3}M$ NaNO$_3$		
Initial absorption rate (g/min)					
(30 sec)	4.0	4.0	11.9	6.1	12.0
(1–3 min)	2.8	3.0	21.4	4.0	31.0
t_{req} (min)	180	120	20	40	10
Q_{eq} (g H$_2$O/g)	30	40	221	121	214

See Table II for definitions.

figures show that water absorbency (Q′) and initial absorption rate gradually decreased with an increase in salt concentration. This is because of the decrease in the difference of osmotic pressure between the network of the gel and the external solution, that is, the water molecule is hard to infiltrate into the gel. Therefore, the Q′ values and the initial absorption rates decrease with increasing salt concentration.

The absorption characteristics for the SA–TMMAAI and SA–TMMAI copolymeric gels in these five salt solutions at the gel transition concentration $(2 \times 10^{-3}M)$ and beyond the gel transition concentration $(2 \times 10^{-2}M)$ are summarized in Tables V and VI, respectively.

Comparing the initial absorption rates for the stage of the first 30 s and the stage of 1–3 min, shown Tables V and VI, nearly identical initial

absorption rates for gels with a lower content of the cationic monomer can be observed. The initial absorption rates increase with increasing cationic monomer content.

The Q′$_{eq}$ values shown in Table V are in the following order for TA4 and TM4: Fe(NO$_3$)$_3$(aq), Ni(NO$_3$)$_2$(aq), Ca(NO$_3$)$_2$(aq), NaNO$_3$(aq), and Cu(NO$_3$)$_2$(aq). However, the initial absorption rates in the stage of the first 30 s for these gels are Fe(NO$_3$)$_3$(aq), Ni(NO$_3$)$_2$(aq), Ca(NO$_3$)$_2$(aq), Cu(NO$_3$)$_2$(aq), and NaNO$_3$(aq).

The Q′$_{eq}$ values at $2 \times 10^{-2}M$ concentration are in this order NaNO$_3$(aq), Ni(NO$_3$)(aq), Fe(NO$_3$)$_3$(aq), Ca(NO$_3$)$_2$(aq), Cu(NO$_3$)$_2$(aq). The initial absorption rate at the present concentration is in this order: NaNO$_3$(aq), Ni(NO$_3$)(aq), Ca(NO$_3$)$_2$(aq), Fe(NO$_3$)$_3$(aq), Cu(NO$_3$)$_2$(aq). Comparing Tables III and VI, the initial absorption

Table VI   Absorption Characteristics of SA–TMMAAI and SA–TMMAI Copolymeric Gel Systems after Gel Transition Concentration

Conditions	A1	TA1	TA4	TM1	TM4
			$2 \times 10^{-2}M$ Fe(NO$_3$)$_3$		
Initial absorption rate (g/min)					
(30 sec)	2.0	2.0	8.0	6.0	8.0
(1–3 min)	2.0	3.0	7.0	2.4	9.0
t_{req} (min)	240	240	30	50	30
Q_{eq} (g H$_2$O/g)	16	36	78	44	76
			$2 \times 10^{-2}M$ Ni(NO$_3$)$_2$		
Initial absorption rate (g/min)					
(30 sec)	3.0	4.0	11.9	6.1	12.0
(1–3 min)	2.2	3.0	15.4	6.1	17.0
t_{req} (min)	180	180	10	20	7
Q_{eq} (g H$_2$O/g)	21	34	87	71	84
			$2 \times 10^{-2}M$ Ca(NO$_3$)$_2$		
Initial absorption rate (g/min)					
(30 sec)	3.0	4.0	11.9	6.1	12.0
(1–3 min)	2.0	3.0	9.9	4.1	17.0
t_{req} (min)	180	180	12	30	7
Q_{eq} (g H$_2$O/g)	20	32	77	59	76
			$2 \times 10^{-2}M$ Cu(NO$_3$)$_2$		
Initial absorption rate (g/min)					
(30 sec)	3.0	4.0	11.9	6.1	12.0
(1–3 min)	2.0	3.0	8.4	4.0	9.0
t_{req} (min)	180	180	15	30	12
Q_{eq} (g H$_2$O/g)	18	30	69	71	64
			$2 \times 10^{-2}M$ NaNO$_3$		
Initial absorption rate (g/min)					
(30 sec)	3.0	4.0	11.9	4.0	12.0
(1–3 min)	3.0	3.0	10.9	3.0	11.5
t_{req} (min)	180	180	12	15	12
Q_{eq} (g H$_2$O/g)	24	36	91	42	86

See Table II for definitions.

rate for NaNO$_3$(aq) is similar before GTC and after GTC. This is because the sodium ion (Na$^+$) would reduce the difference of ionic osmotic pressure between the gels inside and outside: the initial absorption rate does not significantly change.

However, the divalent and trivalent cation would form complexes with the carboxylate group (COO$^-$) at the high concentration. In other words, it affects the absorption ability of the carboxylate group (COO$^-$). Therefore there are obvious decreases in water absorbency and the initial absorption rate.

CONCLUSIONS

The swelling kinetic behaviors of these superabsorbents are related to their chemical structures and the nature of the external salt solutions. The absorption rate would be effectively improved when the cationic monomers TMMAAI or TMMAI are introduced, but the absorption rate would decrease when the added amount of the cationic monomer is more than 2.25 mol % (TA5 and TM5). Water absorbency for the TM series is higher than that for the TA series when the content of the cationic monomer is less than 0.75 mol %. However, the contrary result for the initial absorption rate is obtained when the content of the cationic monomer is greater than 0.75 mol %.

The initial absorption rates for the gels in NaNO$_3$(aq) before and after GTC do not change significantly, but there is an obvious decrease in the initial absorption rates under the divalent and trivalent cation solutions because of the for-

mation of complexes with the carboxylate group (COO^-) at the high concentration.

REFERENCES

1. Buchholz, F. L. In Superabsorbent Polymers Science and Technology; Buchholz, F. L.; Peppas, N. A., Eds.; ACS Symposium Series 573, American Chemical Society, Washington, DC, 1994.
2. Sakiyama, T. C.; Chu, H.; Fujii, T.; Yano, T. J Appl Polym Sci 1993, 50, 2021.
3. Yoshida, M.; Asano, M.; Kumakura, M. Eur Polym J 1989, 25, 1197.
4. Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. J Appl Polym Sci 1992, 44, 249.
5. Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. J Appl Polym Sci 1993, 47, 113.
6. Hogari, K.; Ashiya, F.; In Advances in Superabsorbent Polymers; American Chemical Society: Washington, DC, 1994.
7. Ericksen, P. H.; Nguyen, H. V.; Oczkowski, B.; Olejnik, T. A. Eur. Pat. 40087 (1981).
8. Kobayashi, T. Kobunshi 1987, 36(8), 612.
9. Taylor, N. W.; Fanta, G. F.; Doane W. M.; Russell, C. R. J Appl Polym Sci 1978, 22, 1343.
10. Burr, R. C.; Fanta, G. F.; Doane, W. M. J Appl Polym Sci 1979, 27, 2713.
11. Fanta, G. F.; Burr, R. C.; Doane, W. M.; Russell, C. R. J Appl Polym Sci 1979, 24, 1384.
12. Kejun, Y.; Berlian, W. J Appl Polym Sci 1990, 41, 3079.
13. Fanta, G. F.; Burr, R. C.; Doane, W. M. J Appl Polym Sci 1979, 24, 2015.
14. Yoshinobu, M.; Morita, M, Sakata, I. J Appl Polym Sci 1992, 45, 805.
15. Lokhande, H. T.; Varadarjan, P. V.; Iyer, V. J Appl Polym Sci 1992, 45, 2031.
16. Castel, D.; Ricard, A.; Audebert, R. J Appl Polym Sci 1990, 39, 11.
17. Zoda, I. Functional Material 1986, 6, 76.
18. Isomi, K. Jpn Kokai, Tokyo Koho JP 1989, 56707.
19. Nagasuna, K.; Suminaga, N.; Kimura, K.; Shimonura, T. Jpn Kokai, Tokyo Koho JP 1989, 126234.
20. Imada, H.; Fujiwaka, M. Jpn Kokai, Tokyo Koho JP 1989, 141938.
21. Fujio, A.; Komae, T.; Yutaka, Y. Jpn Kokai, Tokyo Koho JP 1989, 210, 463.
22. Yada, S.; Shibano, T.; Ito, K. Jpn Kokai, Tokyo Koho JP 1990, 215, 801.
23. Sano, M.; Mikamo, H.; Suehiro, T.; Wakabayashi, N. Jpn Kokai, Tokyo Koho JP 1991, 258839.
24. Flory, P. J. Principle of Polymer Chemistry; Cornell University Press: Ithaca, NY,s 1953.
25. Ogawa, I.; Yamano, H.; Miyogawa K. J Appl Polym Sci 1993, 47, 217.
26. Lee, W. F.; Wu, R. J. J Appl Polym Sci 1996, 62, 1099.
27. Lee, W. F.; Wu, R. J. J Appl Polym Sci 1997, 64, 1701.
28. Lee, W. F.; Yeh, P. L. J Appl Polym Sci 1997, 66, 499.
29. Lee, W. F.; Hsu, C. H. J Appl Polym Sci 1998, 69, 229.
30. Lee, W. F.; Tu, Y. M. J Appl Polym Sci 1999, 72, 1221.
31. Lee, W. F.; Huang, Y. L. J Appl Polym Sci, to appear.
32. Lee, W. F.; Lin, G. H. J Appl Polym Sci (accepted).
33. Lee, W. F.; Tsai, C. C. Polymer 1994, 35, 2210.