Superabsorbent Polymeric Materials VII: Swelling Behavior of Crosslinked Poly[Sodium Acrylate-*co*-Trimethyl Methacrylamido-propyl Ammonium Iodide] in Aqueous Salt Solutions

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ABSTRACT: A series of xerogels based on sodium acrylate (SA), cationic comonomer trimethyl methacrylamidopropyl ammonium iodide (TMMAAI), and *N,N*-methylene-bis-acrylamide (NMBA) were prepared by inverse suspension polymerization. The water absorbency and the swelling behavior for these highly absorbent polymers in deionized water and various saline solutions were investigated. Results indicated that the water absorbency increased when a small amount of TMMAAI monomer was introduced into the SA gel. The water absorbency decreased with increase in TMMAAI content, but the contrary result was observed for initial absorption rate. Moreover, with more crosslinking agent, the water absorbency was lower. Finally, the adsorption of copper ion by these gels was also investigated. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1749–1759, 2000

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

INTRODUCTION

Superabsorbent polymers, which can absorb and hold a large amount of water, are not dissolved in water, unlike other water-absorbing materials. The traditional absorbing materials are natural products such as cotton, paper, and sponge. Making use of the capillary principle, water is absorbed into the gaps of such a substrate. The water absorbency of the traditional materials is usually quite poor, and the water retention under pressure is also very poor.

Superabsorbent polymers were first reported by the U.S. Department of Agriculture, and much attention was paid to their applications. Because of their excellent characteristics, these polymers are widely used in many fields, such as disposable diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water-blocking tapes, medicine for the drug delivery system, absorbent pads, etc.[1–8] In such applications, water absorbency or water retention is essential. Hence, some researchers attempt to improve their absorbent polymers to enhance absorbency, gel strength, and initial absorption rate.[9–23]

Flory[24] explained the swelling mechanism for hydrophilic polymers as being with a nonionic network or ionic network structure. Ogawa et al.[25] studied the kinetics of the swelling of poly-(sodium acrylate)[poly(SA)] by picture analysis with a microscope-VTR system, calorimetry, and gravimetry techniques.

Because the poly(SA) has advantages of higher gel strength, is easy to manufacture, and has

lower cost, it is widely used to prepare the superabsorbent materials. A series of superabsorbent polymers, for study of swelling behavior in deionized water and various saline solutions, were reported in our previous articles, such as poly(SA) containing nonionic comonomer 2-hydroxyethyl methacrylate (HEMA),[26] zwitterionic monomer 3,3-dimethyl methacryloyloxyethyl ammonium propane sulfonate (DMAPS),[27] 3,3-dimethyl acrylamidopropyl ammonium propane sulfonate (DMAAPS),[28] anionic monomer sodium 2-acrylamido-2-methyl propane sulfonate (NaAMPS),[29] poly(SA) with various initial total monomer concentrations.[30]

According to our previous studies, the SA gels containing nonionic comonomer HEMA had reduced water absorbency but improved initial absorption rate. However, contrary results, for those containing the zwitterionic comonomer DMAPS, DMAAPS, and anionic comonomer NaAMPS, were obtained. In addition, the water absorbency decreased when the initial total monomer concentration of poly(SA) increased, but the opposite result for initial absorption rate was obtained. Because the poly(SA) gels containing cationic comonomer were not found in the previous literature, a series of superabsorbent gels based on SA and TMMAAI were prepared in this work. The water absorbency and swelling behavior for these xerogels in deionized water and various saline solutions were investigated.

EXPERIMENTAL

Materials

The materials used were purchased from Tokyo Kasei Industries Ltd., including acrylic acid (AA), N,N'-methylene-bis-acrylamide (NMBA). Sodium hydroxide and NMBA were used directly. 4,4′-Azobis(4-cyanovaleric acid) (ACVA), as an initiator, and sorbitan monostearate (Span 60), as an inverse suspension stabilizer, were also purchased from Tokyo Kasei Industries Ltd. Methanol and cyclohexane were of analytical grade.
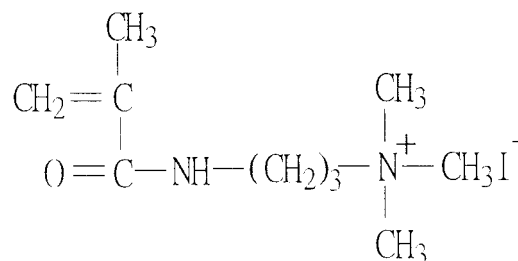
Preparation of SA Monomer Solution

SA monomer was prepared as reported previously.[26]

Synthesis of TMMAAI Monomer

The monomer trimethyl methacrylamido propyl ammonium iodide (TMMAAI) was prepared as

reported previously.[31] Yield: 92%, m.p.: 112°C. The structure is given as follows:

Inverse Suspension Polymerization

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

The crosslinking agent, NMBA, and the appropriate amounts of TMMAAI monomer, were introduced into SA monomer solution, and the mixture was stirred until the NMBA was dissolved completely. The monomer solution and 0.15-g initiator, ACVA (dispersion phase), were introduced into 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 4 h. After the reaction, the suspension solution was cooled and then precipitated by 800 mL cold methanol under stirring. The product was filtered and washed several times by the mixture of water and methanol (1 : 9 in volume). The product was then dried in a vacuum oven at 70°C for 1 day. A white powdered polymer was obtained, and the yield was over 95%. The compositions of samples are listed in TableI.

Measurement of Property

The samples were dried in a vacuum oven at 70°C before any tests. All of the samples were used with the particle size in the range of 60 and 100 mesh.

Saturated Absorbency

The sample (50 mg) was immersed in an excess of deionized water or 0.9 wt % NaCl(aq) for at least 8 h to reach the swelling equilibrium at room temperature.

Suction Filtration Method

When the sample reach swelling equilibrium, the residual water was removed by suction filtration

Table I Compositions of SA/TMMAAI Xerogels

Sample No.	SA (g)	TMMAAI (g)	NMBA (g)	Yield (%)	Water Soluble (%)
TA1	20	0	0.07 (2.14×10^{-3})	98.7	4
TA2	19.95	0.166 (2.5×10^{-3})	0.07 (2.14×10^{-3})	99.8	3
TA3	19.85	0.498 (7.5×10^{-3})	0.07 (2.14×10^{-3})	99.4	5
TA4	19.7	0.996 (1.5×10^{-2})	0.07 (2.14×10^{-3})	97.8	6
TA5	19.55	1.494 (2.25×10^{-2})	0.07 (2.14×10^{-3})	97.5	4
TA6	19.4	1.998 (3.01×10^{-2})	0.07 (2.14×10^{-3})	99.4	7
TA7	19.4	1.998 (3.01×10^{-2})	0.05 (1.53×10^{-3})	96.2	5
TA8	19.4	1.998 (3.01×10^{-2})	0.10 (3.06×10^{-3})	96.5	6
TA9	19.4	1.998 (3.01×10^{-2})	0.14 (4.29×10^{-3})	95.7	3
TA10	19.4	1.998 (3.01×10^{-2})	0.21 (6.43×10^{-3})	98.9	4

The total mol is 0.213 mol.

with an aspirator (250 mmHg) for 5 min. The gel was weighed and the equilibrium absorbency Q_{eq} was calculated by the following equation:

$$Q_{eq} = \frac{W_{wet} - W_{dry}}{W_{dry}} \quad (1)$$

where W_{dry} is the weight of the dried sample and W_{wet} is the weight of the swollen sample.

"Tea Bag" Method

The "tea bag" was made of 250 mesh nylon screen. The "tea bag" containing the sample (50 mg) was immersed entirely in deionized water or the saline solution and kept there until the swelling equilibrium was reached, and then hung up for 15 min to drain the excess solution and weighed. The equilibrium absorbency was calculated by eq. (1).

Absorbency in Various Saline Solutions

The dried samples (50 mg) were immersed in an excess of various saline solutions with different concentrations [LiCl(aq), NaCl(aq), KCl(aq), MgCl$_2$(aq), CaCl$_2$(aq), BaCl$_2$(aq), FeCl$_3$(aq), CH$_3$COONa(aq), NaNO$_3$(aq), NaClO$_4$(aq), Na$_2$SO$_3$(aq), Na$_2$SO$_4$(aq), Na$_2$S$_2$O$_3$(aq), KF(aq), KCl(aq), KBr(aq), KI(aq)] and remained there for at least 8 h. The samples were filtered with suction and weighed. The water absorbency in the above saline solutions could be obtained.

Kinetics of Swelling

A technique based on the demand wettability (DW) method was adopted.[16] 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 with the saline solution, the burette was closed at the top and air was introduced while the xerogel 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 following equation (2)

$$Q = \frac{V_s \times d_{H_2O}}{W_d} \quad (2)$$

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

Measurement of Adsorption in Salt Solutions

Each dried sample (50 mg) was immersed in 50 mL of various concentrations (C_0) of CuCl$_2$(aq) solution to adsorb and remain there until equilibrium. The sample was filtered and the residue volume (V_1) was measured. The residual concentration of the copper ion (C_1) in aqueous solution was analyzed at 815 nm by UV-spectrophotometer (Jasco V530). The adsorption amount was calculated by following formula:

$$AD = \frac{C_0 \times 0.05 - C_1 \times V_1}{W_d} \quad (3)$$

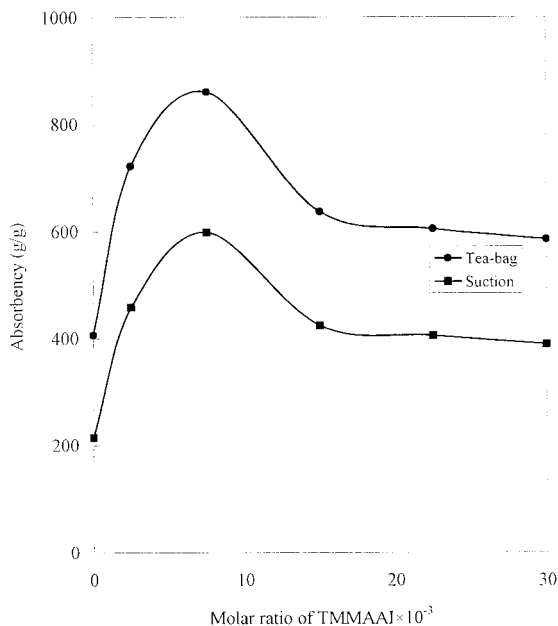where AD is the adsorbed amount of the copper ion and W_d is the weight of the dried sample.

Figure 1 Effect of TMMAAI content in poly(SA-TMMAAI) gels on water absorbency in deionized water measured by "tea-bag" method and suction method.

RESULTS AND DISCUSSION

The swelling behavior of the superabsorbents depends on the nature of the polymer and the characteristics of the external solution. The polymer's nature involves the nature of the charge, ionic content, and crosslinking density. The characteristics of the external solution include the charge number and ionic strength.

The swelling behavior of SA superabsorbents was studied in our previous articles.[26–32] A series of SA/TMMAAI superabsorbent polymers is discussed in this article. The effect of TMMAAI content on water absorbency and absorption rate was investigated.

Effect of TMMAAI Content on Saturated Absorbency

The effect of TMMAAI content for SA/TMMAAI copolymeric gels on water absorbency in deionized water measured by the tea bag method and the suction method as shown in Figure 1. The results indicate that the water absorbency of the present copolymeric xerogels is larger than that of poly(SA) (TA1), and the water absorbency decreases with increasing of the molar ratio of TMMAAI. According to P. J. Flory's swelling theory,[24]

$$Q^{5/3} = [(i/2V_uS^{1/2})^2 + (1/2 - \chi_1)/v_1]/(v_e/V_o) \quad (4)$$

where i/V_u is the concentration of fixed charge referred to unswollen network, S is ionic concentration in the external solution, $(1/2 - \chi_1)/v_1$ is the affinity of the gel for water, and v_e/V_o is the crosslinking density of the gel.

Hence, the water absorbency of the gel is dependent on ionic osmotic pressure, crosslinking density, and the affinity of the gel for water. The crosslinking density of SA/TMMAAI copolymeric gels and the ionic concentration in the external solution were fixed. The water absorbency for the gel is dependent on the concentration of the fixed charge in the gel and the affinity of the gel for water. When the cationic monomer TMMAAI was introduced into the copolymeric gel, the iodide ion (I^-) was dissociated and the quaternary ammonium group (R_4N^+) with a positive charge was formed. The affinity of the quaternary ammonium group (R_4N^+) is stronger than that of the carboxylate group (COO^-). Therefore, the water absorbency of the present gel is higher than that of poly(SA) (TA1) when the cationic monomer TMMAAI is introduced into the copolymeric gel.

However, the quaternary ammonium group (positive charge) would bind with the carboxylate group (negative charge), and therefore, the fixed charge concentration of the polymer network decreases. This behavior reduces the negative charge repulsion of the polymer network, and the water absorbency of the gel decreases.

Furthermore, the water absorbencies in deionized water, measured by the tea bag method and the suction method are 406–860 and 389–598 g water/g dry sample, respectively (see Table II). The water absorbency in 0.9 wt % NaCl(aq), mea-

Table II Absorbency Characteristics for SA/TMMAAI Copolymeric Gel Systems in Deionized Water and 0.9 wt % NaCl Aqueous Solution

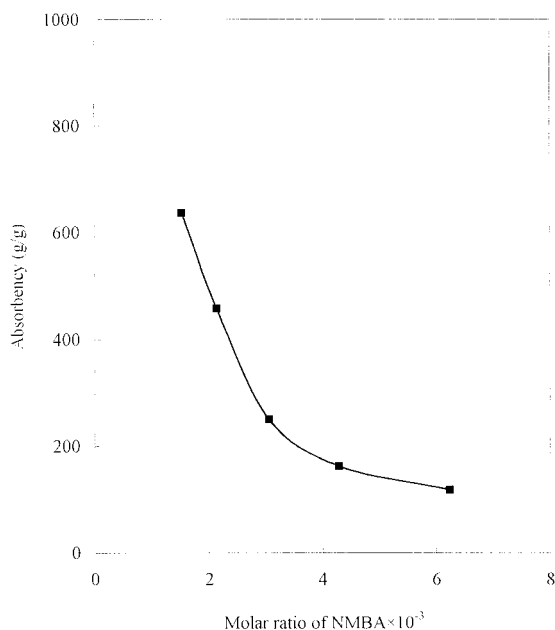| Sample No.	H$_2$O		0.9 wt % NaCl	
	Suction Filtration	Tea Bag	Suction Filtration	Tea Bag
TA1	213	406	11.3	48.4
TA2	458	421	22.4	64.8
TA3	598	860	23.2	70.6
TA4	423	636	20.9	62.3
TA5	405	604	19.9	60.4
TA6	389	585	18.7	58.8

Figure 2 Effect of the extent of crosslinking agent for poly(SA-TMMAAI) gels on water absorbency in deionized water.

sured by the tea bag method and suction method, are 48.4–70.6 and 18.7–23.2 g water/g dry sample, respectively. From these data, we can find that the water absorbency, measured by the tea bag method, is larger than that measured by the suction method. This is because the tea bag method cannot remove the free water from the gel particles. On the other hand, the results observed from Table II also indicate that the water absorbency in 0.9 wt % NaCl(aq) is lower than that in water. This is attributed to an increase of the concentration of the sodium ion in the external solution, and the difference of ionic osmotic pressure between the gel and the external solution decreases. Thus, the water absorbency of the gel is significantly decreased. Similar results were observed in our previous work.[27,29,30]

Effect of the Extent of Crosslinking Agent on Water Absorbency

The effect of the extent of crosslinking agent on water absorbency for SA/TMMAAI copolymeric gels is shown in Figure 2. The results in Figure 2 indicate that with more crosslinking agent, the lower the water absorbency. The copolymeric gel containing 3.01×10^{-2} the molar ratio of TMMAAI exhibits water absorbency of 636 g water/g dry sample when the molar ratio of NMBA is 1.53

$\times 10^{-3}$ (TA7), but the water absorbency decreases to 118 g water/g dry sample when the molar ratio of NMBA is 6.43×10^{-3} (TA10). This phenomenon obeys the P. J. Flory theory: the water absorbency is also related to the elastic force between the polymer chains. With more crosslinking agent, the higher the crosslinking density the stronger the elastic force of the polymer chain, the lower the water absorbency. This occurrence also corresponds to our previous study for poly(SA-*co*-NaAMPS).[31]

Effect of Salt Solution on Water Absorbency

To investigate the effect of saline solution on water absorbency for the present copolymeric gels in various salt solutions, samples TA2 and TA6 were chosen. The water absorbency for sample TA2 in various saline solutions with different cations, and the water absorbency for sample TA6 in different halides and different salt solutions with acid groups, were studied.

Water Absorbency in Various Salt Solutions

The water absorbency for the present poly(SA-*co*-TMMAAI) copolymeric gels in NaCl(aq), CaCl$_2$(aq), and FeCl$_3$(aq) are shown in Figures 3, 4, and 5,
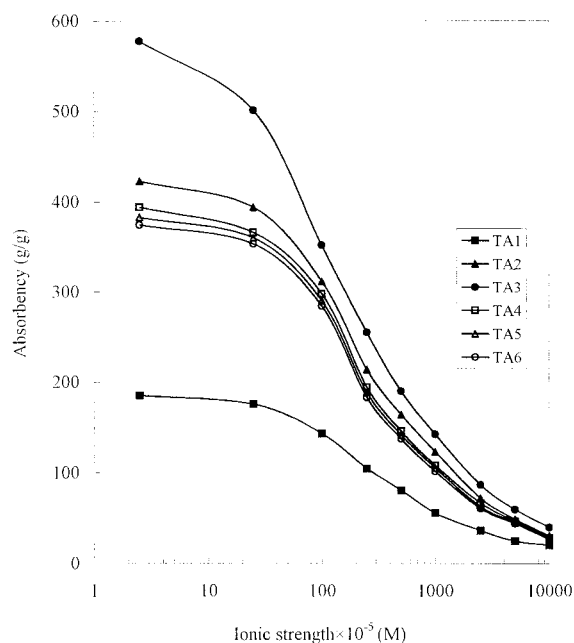

Figure 3 Water absorbency of poly(SA-TMMAAI) gels in the NaCl aqueous solutions with various ionic strengths.
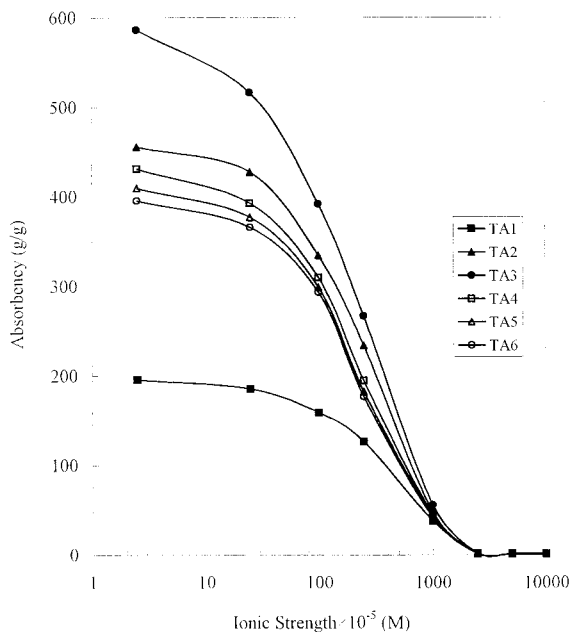
Figure 4 Water absorbency of poly(SA-TMMAAI) gels in the CaCl₂ aqueous solutions with various ionic strengths.

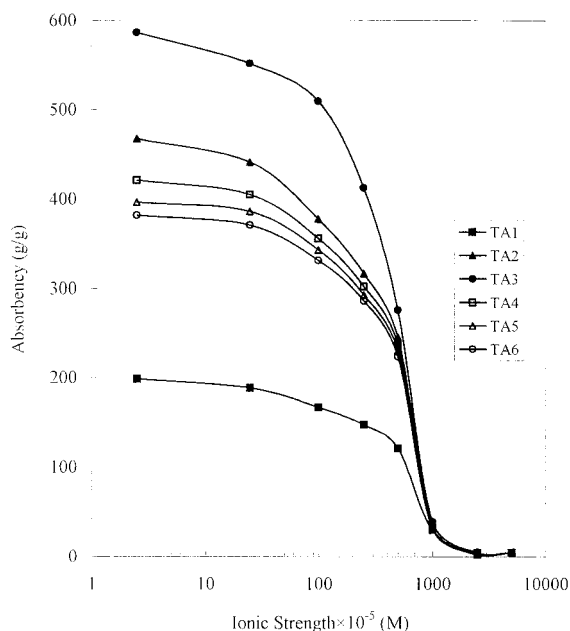respectively. The water absorbency for the sample TA2 in different valence salt solutions is shown in Figure 6.

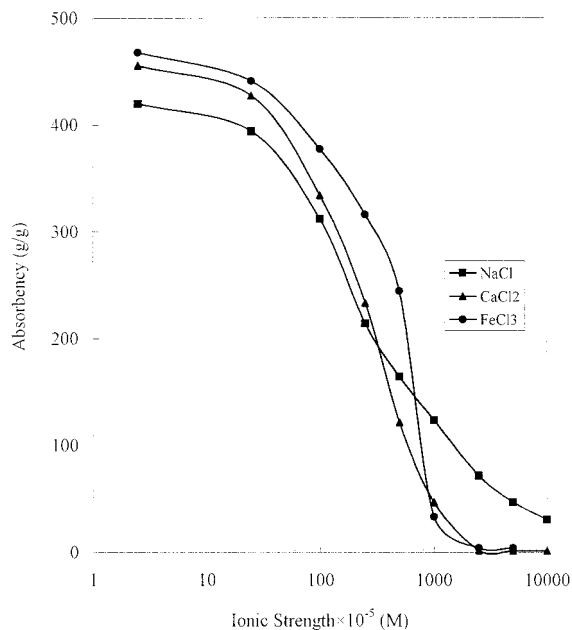**Figure 5** Water absorbency of poly(SA-TMMAAI) gels in the FeCl₃ aqueous solutions with various ionic strengths.

Figure 6 Water absorbency of sample TA2 for poly-(SA-TMMAAI) gels in the NaCl, CaCl₂, and FeCl₃ aqueous solutions with various ionic strengths.

The results shown in these figures indicate that the water absorbency for the copolymeric gels in various salt solutions decreases with increasing ionic strength of salt solution. This can be attributed to the cations in the water, such as the sodium ion (Na^+), the calcium ion (Ca^{2+}), and the ferric ion (Fe^{3+}) in this article. The cation would neutralize the carboxylate group (COO^-). Based on the Donnan membrane equilibrium theory, the difference in the ionic osmotic pressure between the gel and the external solution decreases as the ionic strength of the salt solution increases. Therefore, the water absorbency decreases when the ionic strength in the external solution increases according eq. (4) (see Figs. 3–6).

Moreover, the swelling curves for divalent (Fig. 3) and trivalent (Fig. 4) salt solutions are steeper than those for monovalent (Fig. 5) salt solutions. The water absorbency converged to zero when those gels were immersed into the concentrated divalent and trivalent salt solutions ($>10^{-2}\ M$), but that did not occur when those gels were immersed into the monovalent salt solutions. This is because the divalent calcium ion (Ca^{2+}) and trivalent ferric ion (Fe^{3+}) would form complexes with the carboxylate group. Hence, the swelling curves apparently decrease at the gel transition concentration, and the water absorbency converges to zero in concentrated salt solutions.
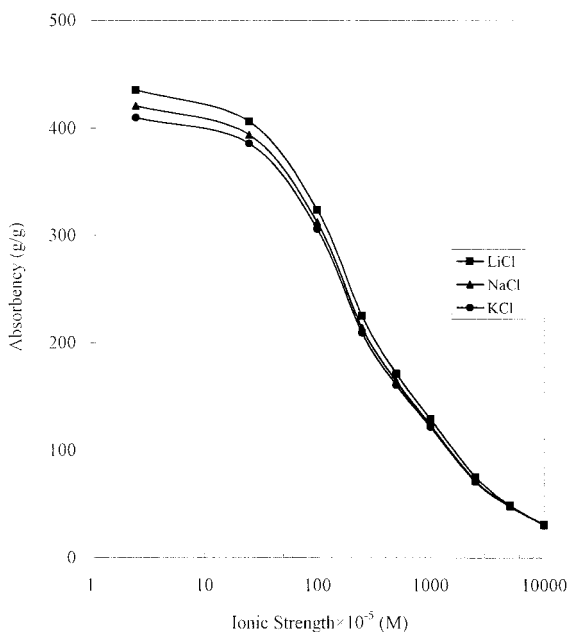
Figure 7 Water absorbency of sample TA2 for poly-(SA-TMMAAI) gels in the LiCl, NaCl, and KCl aqueous solutions with various ionic strengths.

Figure 8 Water absorbency of sample TA2 for poly-(SA-TMMAAI) gels in the MaCl$_2$, CaCl$_2$, and BaCl$_2$ aqueous solutions with various ionic strengths.

On the other hand, the tendency of water absorbency for the gel is in the order $Fe^{3+} > Ca^{2+} > Na^+$ in the dilute solution ($<10^{-4}$ M). In other words, the influence of monovalent, divalent, and trivalent anions with common cation (Na^+) on water absorbency shows a trend of trivalent > divalent > monovalent cations in the dilute solution. The result is related to the charge number of the ion. This occurrence makes the hydration ability become stronger, and the water absorbency increases. Similar results were observed from our previous reports[27-31] and conform to the formation constant of complexation.

Effect of Salt Solutions with Different Cations with a Common Anion (Cl$^-$) Salt Solution

The water absorbencies for sample TA2 in monovalent and divalent cations with a common anion (Cl$^-$) salt solutions are shown in Figures 7 and 8, respectively. The results show that the water absorbency for the copolymeric gel in monovalent and divalent cations salt solution is in the order of LiCl > NaCl > KCl (Fig. 7) and MgCl$_2$ > CaCl$_2$ > BaCl$_2$ (Fig. 8), respectively. These results imply that the smaller the cationic radius, the higher the water absorbency. This is because the smaller the cationic radius, the stronger the hydration
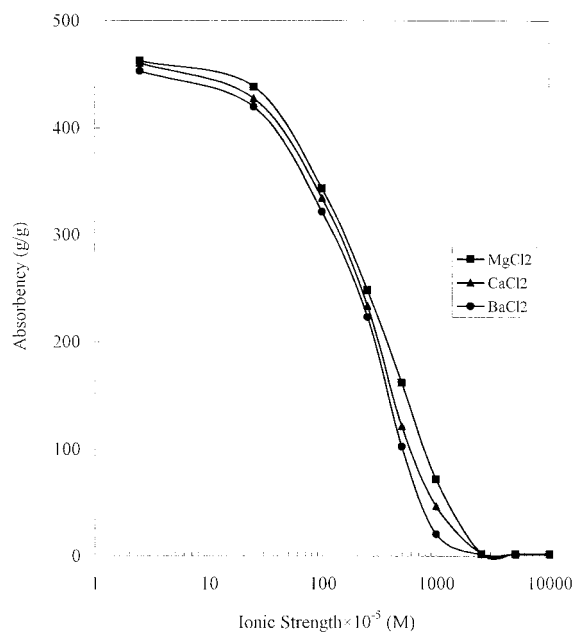
ability of the cation, that is, the binding ability to the carboxylate group is weakened, and leads to the water absorbency increase.
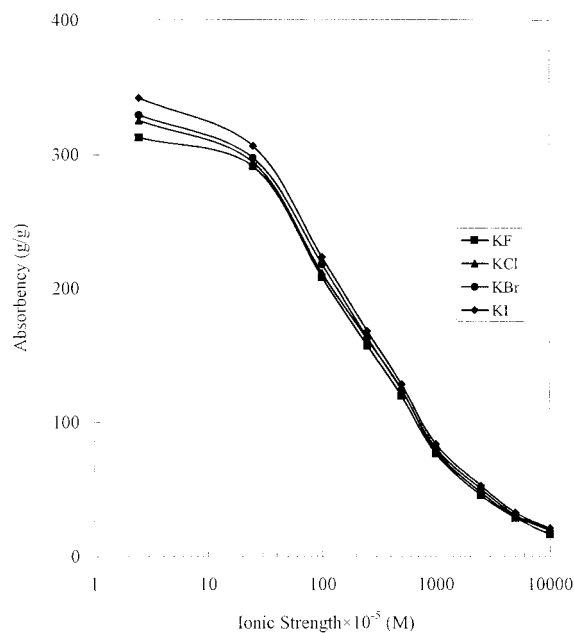

Figure 9 Water absorbency of sample TA6 for poly-(SA-TMMAAI) gels in the KF, KCl, KBr, and KI aqueous solutions with various ionic strengths.
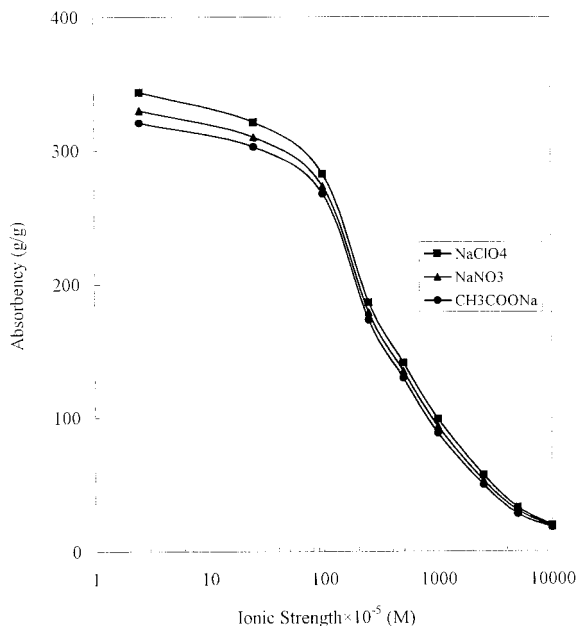
Figure 10 Water absorbency of sample TA6 for poly-(SA-TMMAAI) gels in the CH_3COONa, $NaNO_3$, and $NaClO_4$ aqueous solutions with various ionic strengths.

Effect of the Different Halide Ions with a Common Cation (K^+) Salt Solution

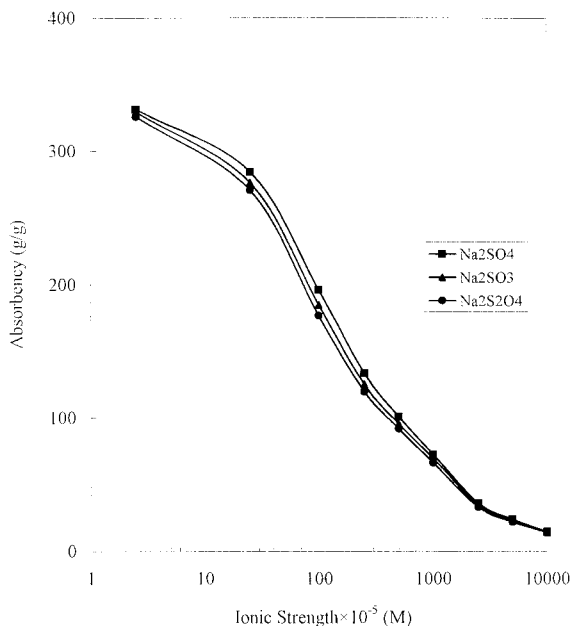The water absorbencies for the sample TA6 in salt solutions of halides with a common cation (K^+)

Figure 11 Water absorbency of sample TA6 for poly(SA-TMMAAI) gels in the Na_2SO_4, $NaSO_3$, and $Na_2S_2O_3$ aqueous solutions with various ionic strengths.

salt solutions are shown in Figure 9. The results reveal that the water absorbency for the copolymeric gel in different halide ion salt solutions is in the order of KI > KBr > KCl > KF. This is because the larger anion with common cation is easily polarized, and binds to the quaternary ammonium group (R_4N^+) on the polymeric chain. For this result, the shielding effect between the quaternary ammonium group (R_4N^+) and the carboxylate group (COO^-) reduces, and the water absorbency increases. This tendency is similar to the result for the aqueous salt solution behavior for sulfobetaine-based copolymers in our previous reports.[33,34]

Effect of the Different Valent Acidic Groups with a Common Cation (Na^+) Salt Solution

The water absorbencies for the sample TA6, in aqueous salt solutions that have the different monovalent acidic groups with a common cation (Na^+), are shown in Figure 10. The results show that the water absorbencies for the copolymeric gel in monovalent acidic salt solution are in the order of $NaClO_4$ > $NaNO_3$ > CH_3COONa. The acetate ion (CH_3COO^-) is a weak acidic group that associates easily to form acetic acid in aqueous solution. The ClO_4^- ion is attracted to the polymeric side chain, and this attraction causes the polymeric chains to agglomerate. Similar results also conform to the result for the aqueous salt solution behavior of polysulfobetaines in our previous studies.[33,34]
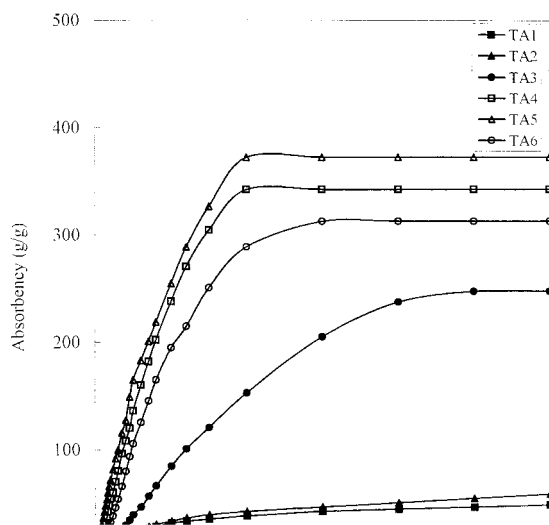

Figure 12 Absorption rate in deionized water for poly-(SA-TMMAAI) gels by DW method.
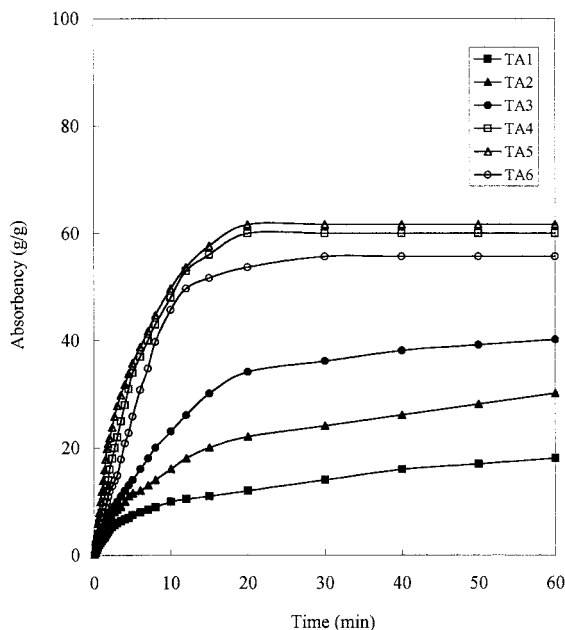
Figure 13 Absorption rate in 0.9 wt % NaCl aqueous solution for poly(SA-TMMAAI) gels by DW method.

In addition, the water absorbencies for the copolymeric gel in divalent acidic solution with a common anion (Na^+) are shown in Figure 11. The results show that the water absorbency for the copolymeric gel in divalent acidic cations salt solution is in the order of $Na_2SO_4 > Na_2SO_3 > Na_2S_2O_3$. This phenomenon was explained by Pearson's theory[26] and conforms to the result reported in the previous papers.[35,36]

Effect of TMMAAI Content on Absorption Rate for SA/TMMAAI Copolymeric Gels

The swelling kinetics of spherical polyacrylamide absorbents were described in the model by Tanaka and Fillmore,[37] and was generalized by Candau et al.,[38] who considered a single isolated gel sphere partly swollen and put in an excess of solvent. There is an osmotic pressure difference, and the gel swells to reach a new equilibrium volume. The swelling behavior of the absorbent was explained by water penetrating into the polymeric network. Buchholz[39] has suggested that the swelling kinetic for the absorbent is significantly influenced by swelling capacity, size distribution of powder particles, specific surface area, and apparent density of the polymer.

Figures 12 and 13 show the absorption rate for a series of poly(SA-*co*-TMMAAI) gels in deionized water and 0.9 wt % NaCl(aq). The results shown in these figures indicate that the initial absorption rate increases with increasing content of TMMAAI. This is due to the cationic TMMAAI monomer introduced into the copolymeric gel: the iodide ion was dissociated and the quaternary ammonium group (R_4N^+) was formed. The affinity of the quaternary ammonium group in the cationic TMMAAI monomer introduced into the copolymeric gel would enhance the absorption rate for the copolymeric gel.

Moreover, the initial absorption rates for these gels, for the initial 30-s period in 0.9 wt % NaCl(aq), is slower than that in deionized water (see Table III). This is primarily attributed to the re-

Table III   Absorption Characteristics for SA/TMMAAI Copolymeric Gel Systems in Deionized Water and 0.9 wt % NaCl Aqueous Solution

Conditions	TA1	TA2	TA3	TA4	TA5	TA6
			Deionized Water			
Initial absorption rate (g/min)						
(30 s)	6.0	6.0	6.0	16.0	27.8	11.9
(1–3 min)	4.0	5.0	7.0	30.0	32.0	21.0
t_{req} (min)	120	120	50	20	30	30
Q_{eq} (g H_2O/g)	56	66	247	342	372	312
			0.9 wt % NaCl			
Initial absorption rate (g/min)						
(30 s)	3.0	4.0	4.0	8.0	11.9	6.0
(1–3 min)	1.7	2.8	3.0	7.0	8.0	4.5
t_{req} (min)	120	40	60	20	20	60
Q_{eq} (g H_2O/g)	22	28	40	60	62	56

Table IV Absorption Characteristics for Poly(SA-TMMAAI) Gel Systems on the Characteristic Swelling Time (T), the Swelling Kinetic Constant (K), and the Characteristic Absorbency (Q) in Deionized Water and 0.9 wt % NaCl Aqueous Solution

Sample No.	T (min)		K (min^{-1})		Q (g H$_2$O/g Dried Sample)	
	H$_2$O	0.9 wt % NaCl	H$_2$O	0.9 wt % NaCl	H$_2$O	0.9 wt % NaCl
TA1	91.3	93.6	0.033	0.022	35.4	13.9
TA2	93.1	85.4	0.034	0.031	41.7	17.7
TA3	48.6	56.5	0.093	0.048	156.1	25.3
TA4	23.2	22.9	0.208	0.135	216.1	37.9
TA5	21.6	22.1	0.228	0.141	235	39.2
TA6	31.4	31.8	0.151	0.095	197.2	35.4

duction of the difference in ionic osmotic pressures between the gel and the external solution.

According to Yao and Zhou,[40] the swelling rate can be described by the following equation:

$$-\log(Q_{eq} - Q) = K/2.303\ T \qquad (5)$$

where Q_{eq} is the equilibrium absorbency, Q is the characteristic absorbency, K is the swelling kinetic constant, and T is the characteristic swelling time. From eq. (5), the T is defined at $Q = 0.632\ Q_{eq}$. Table IV presents the influences of the content of TMMAAI on T, K, and Q of the Poly(SA-*co*-TMMAAI) absorbent in deionized water and in the saline solution. Table IV reveals that T decreases and Q increases with decreasing the content of TMMAAI. The K for the copolymeric gel in deionized water is larger than those in the saline solution.

Adsorption of Copper Ion

Figure 14 shows the adsorbed amount of copper ion (Cu^{2+}) by TA1 and TA3 gels in various concentrations of CuCl$_2$(aq). The results show that the more the carboxylate group content in the gel, the stronger is the adsorptive ability (TA1 > TA3) [Fig. 14(a)]. The adsorption of copper ion is primarily attributed to the number of carboxylate groups in the gel, that is, with more carboxylate groups in the gel, the higher the adsorbed amount of the copper ion. Furthermore, the optimum adsorbed amount is with the original copper concentration of 750 ppm [Fig. 14(b)]. These results also conform to the result for poly(SA-*co*-sulfobetaines).[32]

CONCLUSION

The swelling behavior of the superabsorbents prepared from SA and TMMAAI indicated that the water absorbency and initial absorption rate were improved when a small amount of the TMMAAI monomer was introduced into the copolymeric gels. However, the greater the extent of the crosslinking agent, the lower the water absorbency.

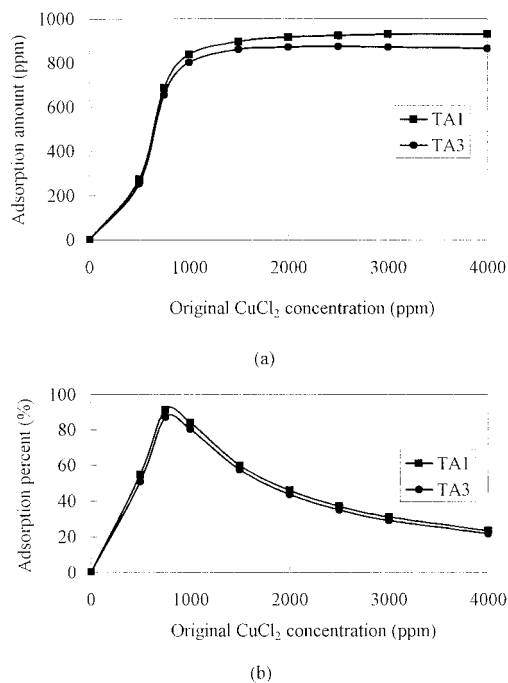The water absorbency for the copolymeric gels in various salt solutions decreases with increas-

(a)

(b)

Figure 14 Adsorption amount (a) and adsorption percent (b) of Cu^{2+} in various CuCl$_2$ concentrations by TA1 and TA3 gels.

ing the ionic strength of the salt solution. The water absorbency converges to zero when these gels are immersed into the concentrated divalent and trivalent salt solutions (10^{-2} M), but this is not so when these gels are immersed into the monovalent salt solutions.

Finally, with more carboxylate groups in the gel, the stronger the ability for the gel to adsorb copper ion (Cu^{2+}) is, and furthermore, the optimum adsorbed amount of copper ion (Cu^{2+}) is with the original copper concentration of 750 ppm.

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