Superabsorbent Polymeric Materials. XI. Effect of Nonionic Monomers on the Swelling Behavior of Crosslinked Poly(sodium acrylate-*co*-nonionic monomers) in Aqueous Salt Solutions

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ABSTRACT: A series of xerogels based on sodium acrylate, nonionic monomers such as 2-hydroxyethyl methacrylate (HEMA) and poly(ethylene glycol) methacrylate (PEGMA), and *N*,*N*′-methylene bisacrylamide were prepared by inverse suspension polymerization. The results indicate that the water absorbencies for these two gel series were effectively improved by the addition of a small amount of nonionic monomer (HEMA or PEGMA). The initial absorption rates in deionized water were faster for the PEGMA gels than for the HEMA gels. Scanning electron microscopy showed that the spherical particle size was smaller for the PEGMA gels than for the HEMA gels. In addition, the water absorbency of the gels in various salt solutions decreased with increasing ionic strength, especially for the multivalent salt solutions. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3666–3674, 2004

Key words: superabsorbent; poly(ethylene glycol) methacrylate; hydrogels; swelling

INTRODUCTION

Superabsorbent polymers are water-insoluble, hydrogel-forming polymers capable of absorbing a large amount of aqueous fluids and retaining the absorbed fluids, even under pressure. Therefore, superabsorbents have great advantages over traditional water-absorbing materials. Because of their excellent characteristics, superabsorbents are widely used in artificial snow,[1,2] agriculture,[3–5] horticulture,[6] drilling fluid additives,[7] polymer concrete suited for use in repairing cracks,[8] fighting fires,[9] sealing composites in long-distance cable,[10,11] and drug delivery.[12,13] The first superabsorbent polymer was reported by the U.S. Department of Agriculture in 1961;[14] much subsequent research has attempted to modify these absorbent polymers to enhance their absorbency, gel strength, and absorption rate.[15–28]

Superabsorbents based on acrylic acid (AA) have been extensively studied because AA is cheap and easily polymerized into a high-molecular-weight polymer. In previous investigations, we studied the swelling behavior of a series of superabsorbents in deionized water and various saline solutions, such as the poly(sodium acrylate) [poly(NaA)]-containing nonionic comonomer 2-hydroxyethyl methacrylate (HEMA),[29] the zwitterionic monomer 3,3-dimethyl methacryloyloxyethyl ammonium propane sulfonate,[30] 3,3-dimethyl acrylamidopropyl ammonium propane sulfonate,[31] the anionic monomer sodium 2-acrylamido-2-methyl propane sulfonate,[32] the cationic monomer trimethyl methacrylamido propyl ammonium iodide,[33] and poly(NaA) with various initial total monomer concentrations.[34]

Ionic monomers and poly(ethylene glycol) (PEO) are popularly used compounds for hydrophilicity modifications. Monomers containing PEO have unique physicochemical properties, including a high degree of hydrophilicity, very good solubility in water and organic solvents, and unique biological properties.[35,36] The hydrated long PEO chain can bind water and form a rapid microstream of water.

In this study, we introduced HEMA and poly(ethylene glycol) methacrylate (PEGMA) into a sodium acrylate (NaA) superabsorbent polymeric gel to compare the effects of the contents of HEMA and PEGMA in the copolymer on swelling behavior in deionized water and various saline solutions.

EXPERIMENTAL

Materials

HEMA, which was purified by vacuum distillation at 68°C/7 mmHg, was purchased from Wako Pure

TABLE I
Feed Compositions of NaA–HEMA and NaA–PEGMA Xerogels

Sample code	NaA (g)	HEMA–PEGMA (g; molar ratio)	Yield (%)	Water solubility (%)
HA0	20	0	94.5	7
HA1	19.95	0.0693 (2.5×10^{-3})	94.3	3
HA2	19.85	0.208 (7.5×10^{-3})	94.5	5
HA3	19.7	0.416 (1.5×10^{-2})	98.5	6
HA4	19.55	0.624 (2.25×10^{-2})	94.2	5
P_6A1	19.95	0.192 (2.5×10^{-3})	96.8	3
P_6A2	19.85	0.575 (7.5×10^{-3})	95.6	7
P_6A3	19.7	1.15 (1.5×10^{-2})	93.5	4
P_6A4	19.55	0.192 (2.25×10^{-2})	91.6	4

Chemical Co., Ltd. (Osaka, Japan). AA, which was purified by vacuum distillation at 63°C/25 mmHg; PEGMA (number-average molecular weight = 360); and N,N'-methylene bisacrylamide (NMBA), used as a crosslinking agent, were obtained from Aldrich Co. (Milwaukee, WI). 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. (Tokyo, Japan). Methanol and cyclohexane were reagent analytical grade.

Preparation of NaA monomer solution

The NaA monomer was prepared as reported previously.[29]

Inverse suspension polymerization

A 300-mL, four-necked separable flask equipped with a reflux condenser, a stirring rod, and a thermometer was charged with 65 mL of cyclohexane and 0.2 g of sorbitan monostearate (Span 60). The mixture was stirred until the sorbitan monostearate was dissolved (continuous phase).

The crosslinking agent (0.07 g), NMBA, and appropriate amounts of the HEMA or PEGMA monomer were introduced into the NaA monomer solution, and the mixture was stirred until the NMBA was dissolved completely. The monomer solution and 0.15 g of the initiator, ACVA (dispersion phase), were introduced into the reactor. Air was flushed from the reactor by the introduction of 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 of cold methanol under stirring. The product was filtered and washed several times by the mixture of water and methanol (1:9 vol/vol). The product was then dried in a vacuum oven at 100°C for 1 day. White powdered polymer

was obtained, and the yield was over 90%. The feed compositions of the samples are listed in Table I.

Morphology

The dried specimens were examined for morphological details with scanning electron microscopy (Jeol JXA8600) at an acceleration voltage of 15 kV. The specimens were coated with a gold metal layer to provide proper surface conduction.

Measurement of water absorbency

Suction filtration method

The sample (50 mg) was immersed in an excess of deionized water or 0.9 wt % $NaCl_{aqueous}$ solution for at least 8 h to reach its swelling equilibrium at room temperature. The residual water was removed by suction filtration with an aspirator (250 mmHg) for 5 min. The gel was weighed, and the equilibrium absorbency (Q_{eq}) was calculated by the following equation:

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

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. A tea bag containing the sample (50 mg) was immersed entirely in deionized water or the saline solution until the swelling equilibrium was reached, and the tea bag was then hung for 15 min to drain the excess solution and weighed. Q_{eq} was calculated by eq. (1).

Absorbency in various saline solutions

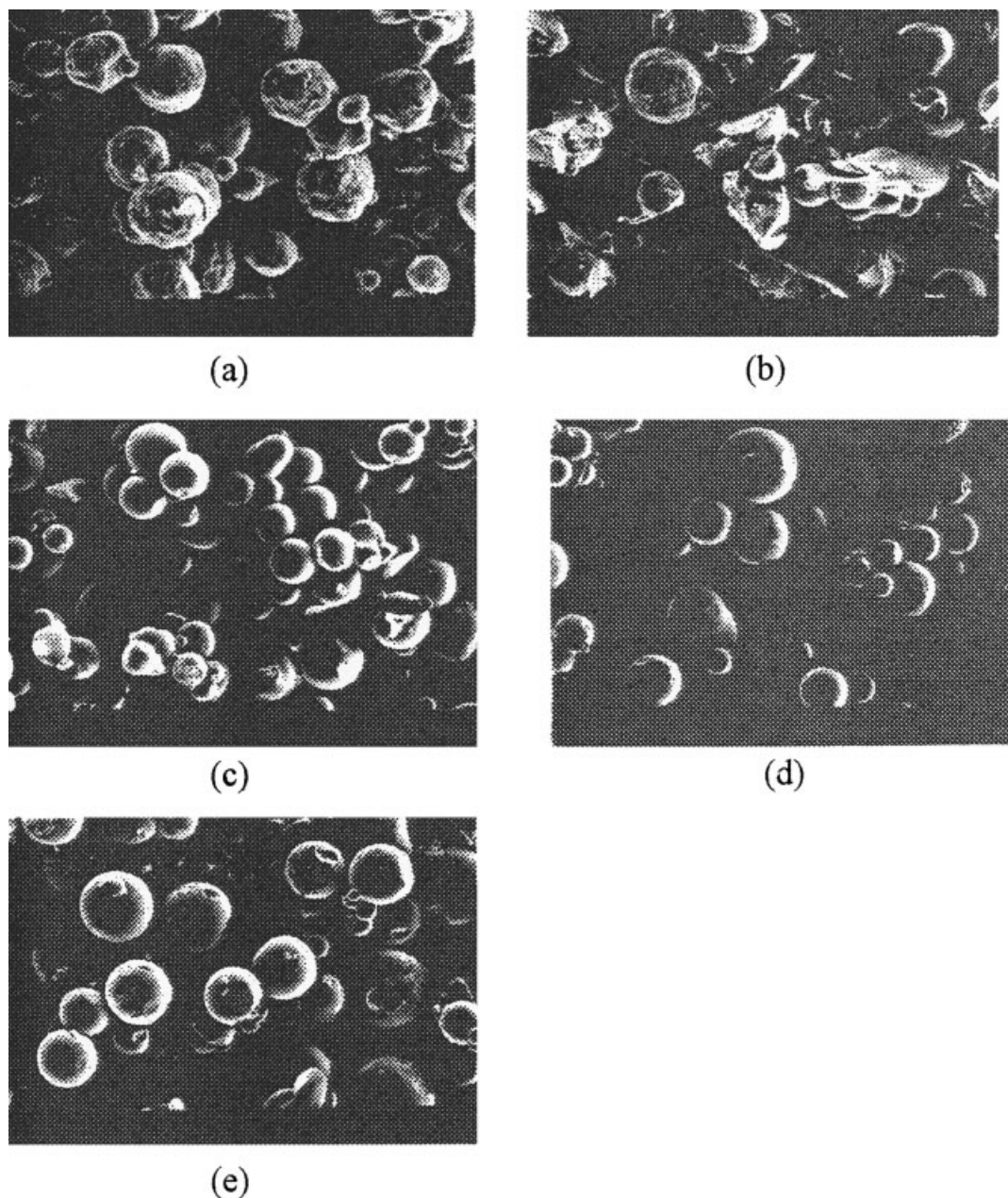The dried samples (50 mg) were immersed in an excess of various saline solutions ($NaCl_{aqueous,}$

Figure 1 Scanning electron micrographs for dried HEMA gels (150×): (a) HA0, (b) HA1, (c) HA2, (d) HA3, and (e) HA5.

$CaCl_{2,aqueous}$, and $FeCl_{3,aqueous}$) with different concentrations for at least 8 h. The swollen samples were filtered with suction and weighed to determine their water absorbencies in the previous saline solutions.

Kinetics of swelling

A technique based on the demand wettability (DW) method was adopted. 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 it was filled with deionized water, the burette was closed at the top, and air was introduced while

the xerogel absorbed water. The sample of absorbent (50 mg) was placed on the grid, and the swelling kinetics was easily measured. The absorbency at every time interval was calculated by the following equation:

$$Q = \frac{V_s \times dH_2O}{W_{dry}} \tag{2}$$

where Q is the characteristic absorbency, V_s is absorbed volume, d_{H20} is the density of water and W_{dry} is the weight of dry sample.

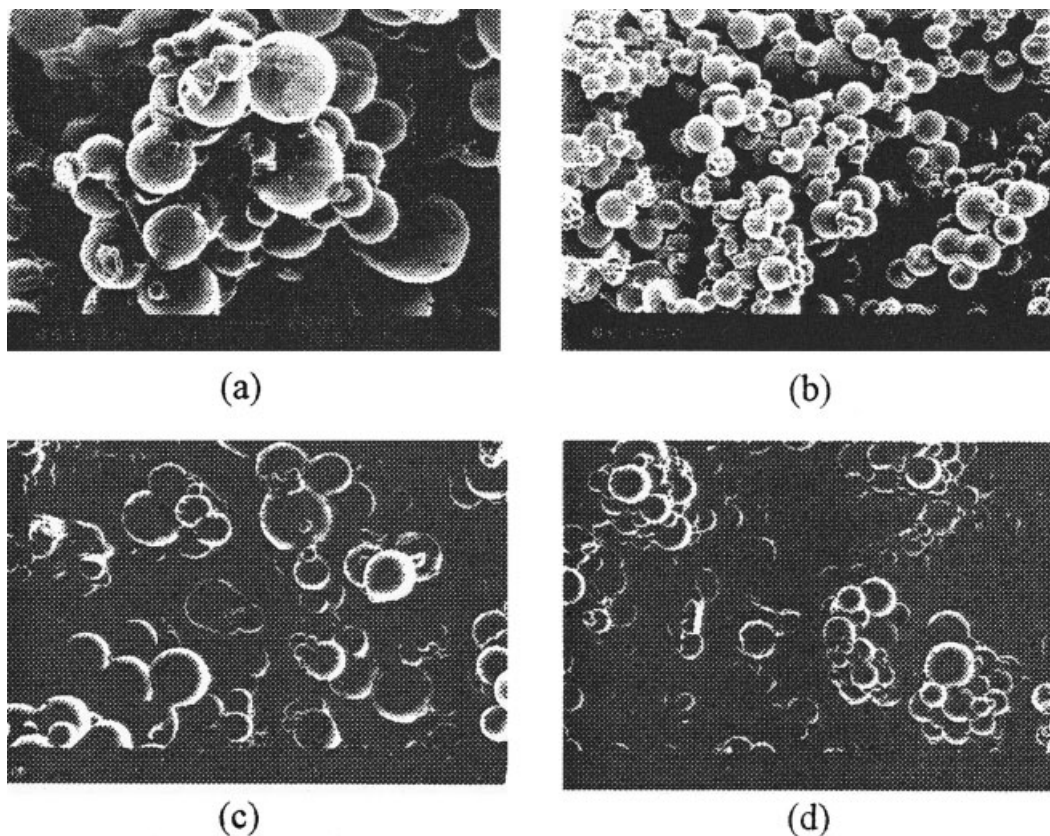**Figure 2** Scanning electron micrographs for dried PEGMA gels (150×): (a) P_6A1, (b) P_6A2, (c) P_6A3, and (d) P_6A4.

RESULTS AND DISCUSSION

Scanning electron microscopy

As shown in Figures 1 and 2, the particles of the HEMA and PEGMA gels were spherical. The results in Figures 1 and 2 show that the particle size was smaller for the PEGMA gels than for the HEMA gels.

Effect of HEMA content on the water absorbency in deionized water for the NaA–HEMA copolymeric gels

The water absorbency in deionized water measured by suction filtration and the tea bag methods and as a function of the molar ratio of HEMA in the copolymeric gels is shown in Figure 3. According to Flory's theory,[37] the following equation was used:

$$q_m^{5/3} = \frac{(i/2v_\mu S^{*1/2})^2 + (1/2 - \chi_1)/v_1}{V_0/v_e} \quad (3)$$

where q_m is the water absorbency of the network at equilibrium, $i/2v_\mu$ is the concentration of fixed charge in the unswollen network, S^* is the ionic concentration in the external solution, $(1/2 - \chi_1)/v_1$ is the affinity of the gel for water, and V_0/v_e is the crosslinking density of the gel.

Hence, the water absorbency of the gel was dependent on the ionic osmotic pressure, the crosslinking
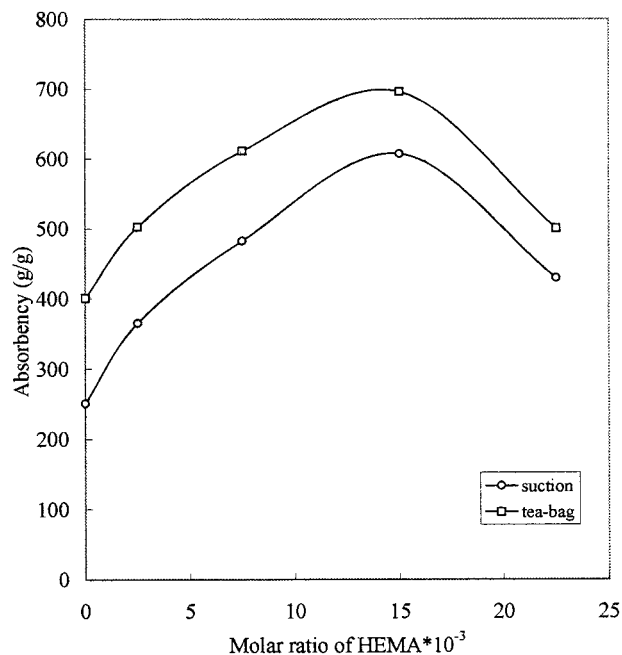

Figure 3 Effect of HEMA content in poly(NaA/HEMA) gels on the water absorbency in deionized water by the tea-bag and suction methods.

density, and the affinity of the gel toward water. Because the crosslinker content of the NaA–HEMA copolymeric gels, S^*, and ionic osmotic pressure were fixed, the water absorbency for the gels was dependent on the affinity of the gel for water. The results in Figure 3 show that the water absorbency increased with increasing molar ratio of HEMA when the molar ratio was less than 1.5×10^{-2}. This result shows that the addition of a small amount of the hydrophilic monomer HEMA to the copolymeric gels increased the affinity of the gels for water, and the water absorbency increased with increasing molar ratio of HEMA. However, when the molar ratio of HEMA was greater than 1.5×10^{-2}, the higher the HEMA content was, the lower the water absorbency was. This was due to the excess amount of HEMA; the hydrophilicity of HEMA is lower than that of NaA, and this caused the decrease in water absorbency. In addition, the hydroxy group is a weak hydrophilic group and can produce intramolecular or intermolecular hydrogen bonding in two neighbor chains. This may have also caused the gels to shrink.

As shown in Figure 3, we also found that the water absorbency measured by the tea bag method was larger than that measured by the suction method. Because the water absorbency was primarily attributed to the water absorbed by the gels and the free water residing between the gel particles, the smaller absorbency by suction was primarily due to the scarcity of free water between the gel particles. Similar phenomena were observed in some of our previous studies,[30,31,38,39] but a contrary result was found in our previous study on NaA–HEMA copolymeric gel series.[29] This was due to the higher molar ratio of HEMA, over 1.5×10^{-2}.

Figure 5 Effect of HEMA and PEGMA content in the gels on the absorbency in deionized water by the suction method.

Effect of PEGMA content on the saturated water absorbency in deionized water for the NaA–PEGMA copolymeric gels

Figure 4 shows the water absorbency in deionized water as measured by the suction filtration and tea bag methods as a function of the molar ratio of PEGMA in the copolymeric gels. The tendencies of water absorbency shown in Figure 4 were similar to those shown in Figure 3. The water absorbency as shown in Figure 4 increased with increasing molar ratio of PEGMA, and the molar ratio of PEGMA shifted to 7.5×10^{-3}. The water absorbency decreased then with increasing
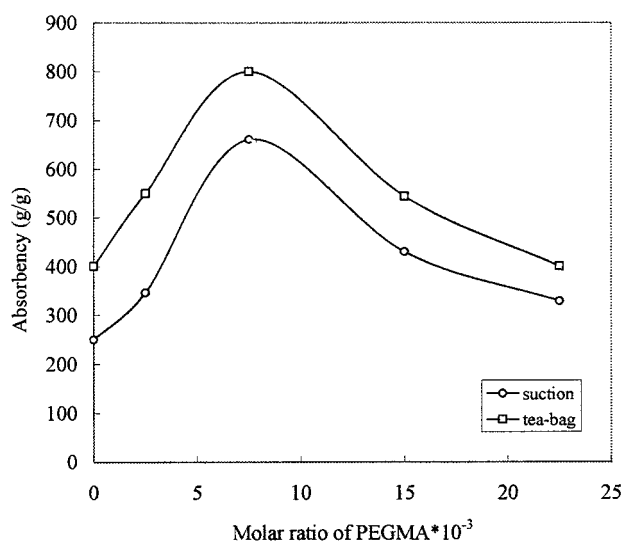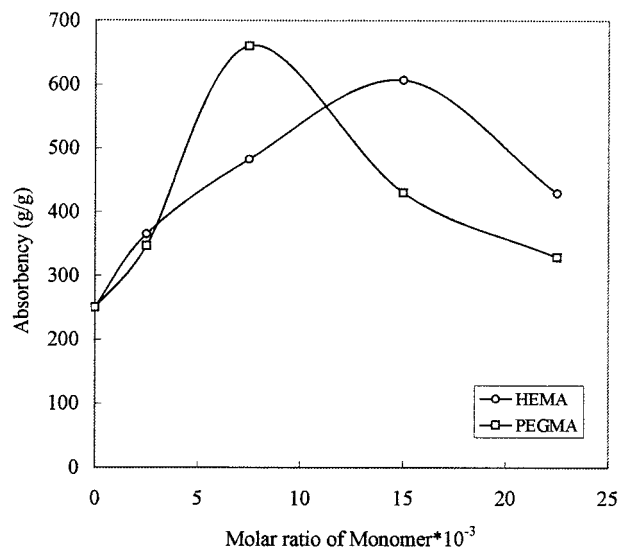
Figure 4 Effect of PEGMA content in poly(NaA/PEGMA) gels on the water absorbency in deionized water by the tea-bag and suction methods.
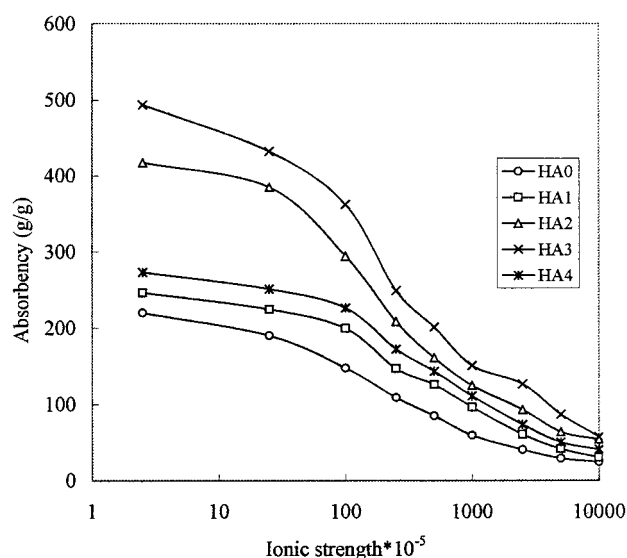
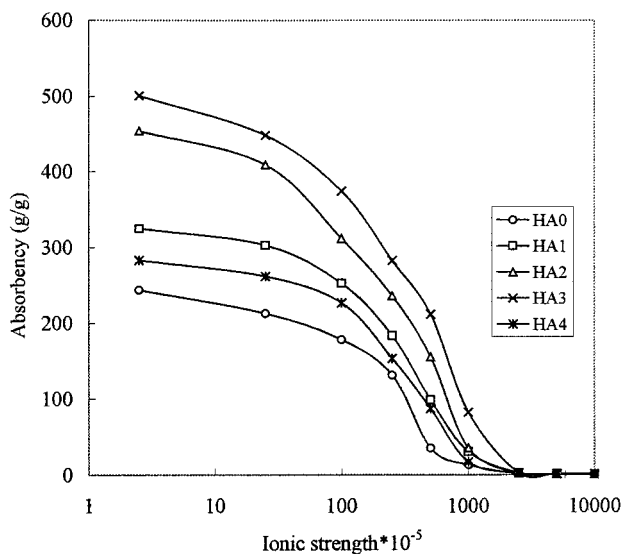**Figure 6** Water absorbency of the poly(NaA/HEMA) gels in NaCl$_{aqueous}$ with various ionic strengths.

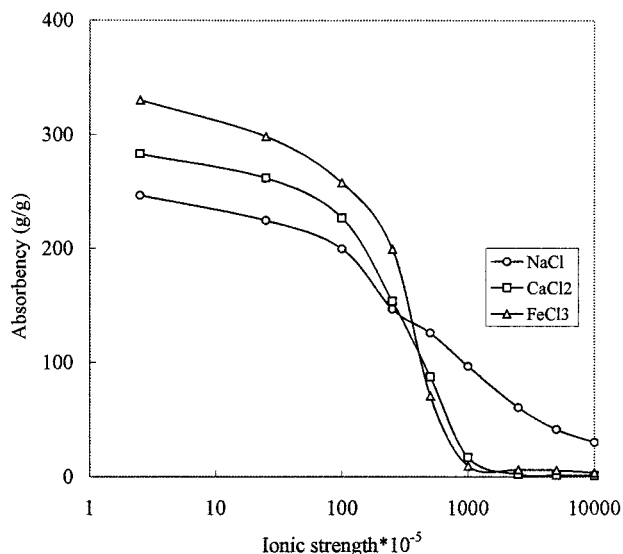**Figure 7** Water absorbency of the poly(NaA/HEMA) gels in $CaCl_{2,aqueous}$ with various ionic strengths.

Figure 9 Water absorbency of the HA4 gel in $NaCl_{aqueous}$, $CaCl_{2,aqueous}$, and $FeCl_{3,aqueous}$ with various ionic strengths.

molar ratio of PEGMA when the molar ratio of PEGMA was higher than 7.5×10^{-3}. The relationship between the water absorbency and the molar ratio of HEMA and PEGMA in deionized water is shown in Figure 5. The maximum value of water absorbency occurred at molar ratios of 7.5×10^{-3} and 1.5×10^{-2} for PEGMA and HEMA, respectively. For this result, we assumed that the presence of certain hydrophilic groups could have caused the water absorbency of the gels to increase. The results in Figure 5 indicate that the maximum absorbency for the NaA–PEGMA copolymeric gels occurred at a lower molar ratio of monomer than that for NaA–HEMA copolymeric gels.

This is because PEGMA possessed a stronger affinity toward water for the gel than HEMA.

Water absorbency in various saline solutions

The water absorbencies for a series of poly(sodium acrylate-*co*-2-hydroxyethyl methacrylate) copolymeric gels as a function of different ionic strengths for $NaCl_{aqueous}$, $CaCl_{2,aqueous}$, and $FeCl_{3,aqueous}$ are shown in Figures 6, 7, and 8, respectively. The water absorbencies for sample HA4 in different valence salt solutions are shown are Figure 9. Further, the water absorbencies for a series of poly[sodium acrylate-*co*-poly(ethyl-
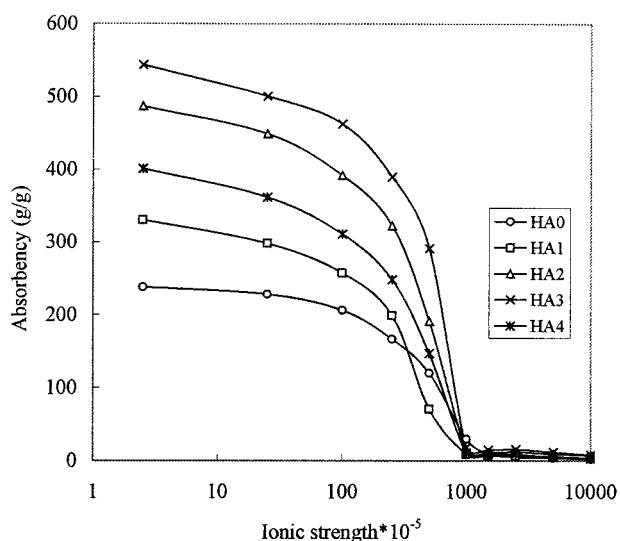

Figure 8 Water absorbency of the poly(NaA/HEMA) gels in $FeCl_{3,aqueous}$ with various ionic strengths.

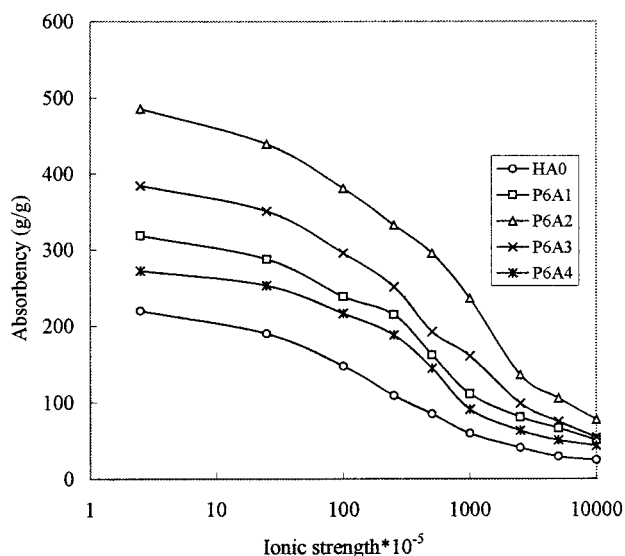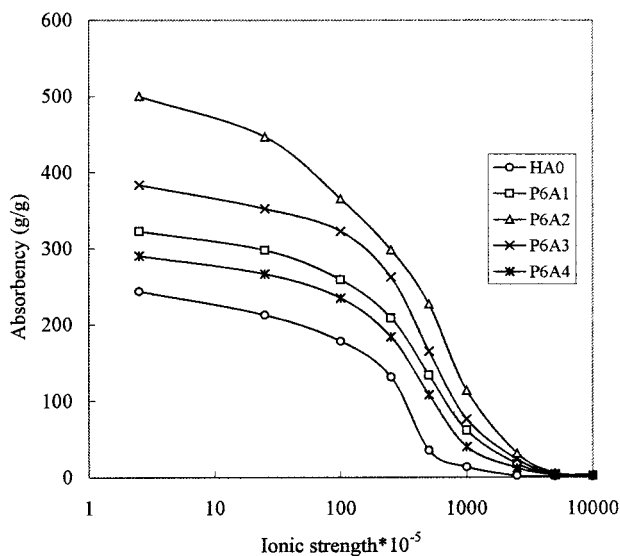**Figure 10** Water absorbency of the poly(NaA/PEGMA) gels in $NaCl_{aqueous}$ with various ionic strengths.

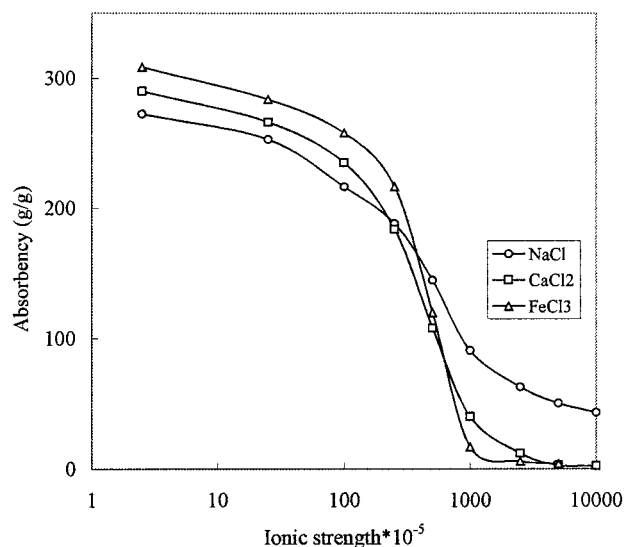**Figure 11** Water absorbency of the poly(NaA/PEGMA) gels in CaCl$_{2,aqueous}$ with various ionic strengths.

Figure 13 Water absorbency of the P$_6$A4 for gel in NaCl$_{aqueous}$, CaCl$_{2,aqueous}$, and FeCl$_{3,aqueous}$ with various ionic strengths.

ene glycol) methacrylate] copolymeric gels as a function of different ionic strengths for NaCl$_{aqueous}$, CaCl$_{2,aqueous}$, and FeCl$_{3,aqueous}$ are shown in Figures 10, 11, and 12, respectively, and the water absorbencies for sample P$_6$A4 in different valence salt solutions are shown in Figure 13.

According to Flory's swelling theory, the water absorbency for the copolymeric gels would be affected by the ionic strength of the salt solutions. The results shown in these figures indicate that the water absorbency for the copolymeric gel in various salt solutions decreased with increasing ionic strength of the salt

solutions. This can be attributed to the presence of cations in the water, such as the sodium ion (Na$^+$), the calcium ion (Ca^{2+}), and the ferric ion (Fe^{3+}) in this study. The cations present in the gel neutralized the carboxylate groups (COO$^-$). The ionic osmotic pressure difference between the gel and the external solution was reduced with an increase in the ionic strength of the salt solutions. Therefore, the water absorbency decreased when the ionic strength in the external solution increased; the curves of water absorbency for the monovalent cationic salt solution were flatter than those for the divalent and trivalent cationic salt solu-
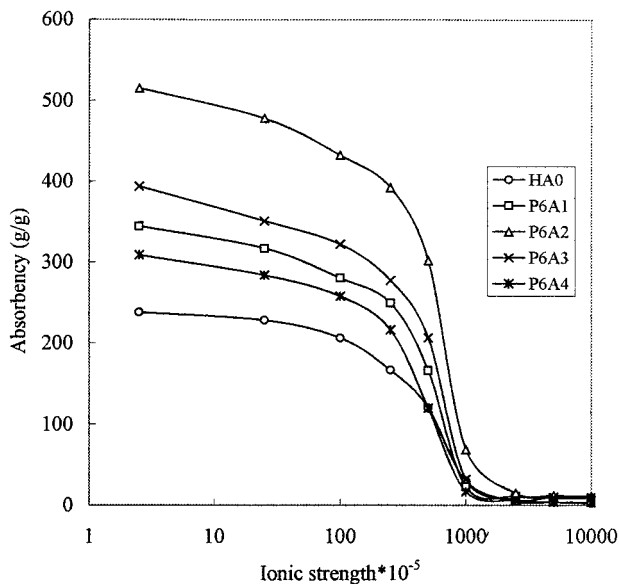

Figure 12 Water absorbency of the poly(NaA/PEGMA) gels in FeCl$_{3,aqueous}$ with various ionic strengths.
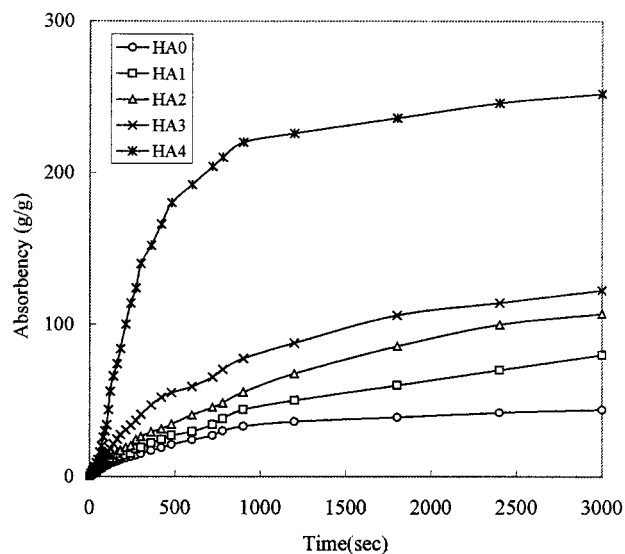

Figure 14 Absorption rate in deionized water for the poly(NaA/HEMA) gels by the DW method.
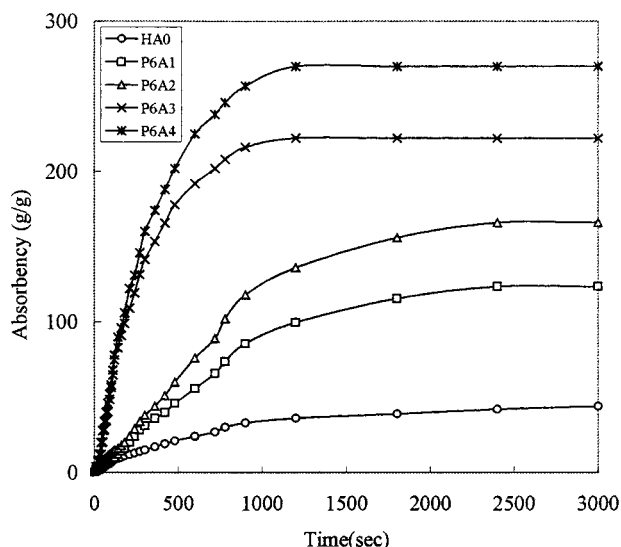
Figure 15 Absorption rate in deionized water for the poly(NaA/PEGMA) gels by the DW method.

tions. This was because the divalent calcium ion and trivalent ferric ion formed complexes with the carboxylate group.

Further, the tendency of water absorbency for the gel was in the order $Fe^{3+} > Ca^{2+} > Na^+$ in dilute solution; that is, there was a relationship between the charge number of the ion and the water absorbency. In the dilute solution, the effect of ionic osmotic pressure was very small, and the affinity of the ion for water was in the order $Fe^{3+} > Ca^{2+} > Na^+$. The hydration ability became stronger and the water absorbency increased with increasing charge number.

Effect of HKMA and PEGMA content on the initial absorption rate for NaA–PEGMA copolymeric gels

Buchholz[40] suggested that the swelling kinetics for the absorbent is significantly influenced by the swelling capacity, size distribution of powder particles, specific surface area, and apparent density of the polymer.

Figures 14 and 15 show the initial absorption rate in deionized water by the DW method for a series of poly(sodium acrylate/2-hydroxyethyl methacrylate) [poly(NaA/HEMA)] and poly[sodium acrylate/poly-(ethylene glycol) methacrylate] [poly(NaA/PEGMA)]

copolymeric gels, respectively. The results shown in these figures indicate that the initial absorption rate increased with increasing content of HEMA and PEGMA. This was because the hydrated ethylene oxide side chain of the nonionic HEMA and PEGMA monomers, introduced into the copolymeric gel, bound water easily and formed a rapid microstream of water. This enhanced the initial absorption rate for the copolymeric gel with increasing amounts of HEMA and PEGMA.

The results of the characteristic absorption data of these two series of gels are shown in Table II. According to Flory's theory for the gels, the swelling ratio has a relation to the crosslinking density and the affinity of the gels for water. The differences in the crosslinking densities for these copolymeric gels were very small, so the influence of the swelling ratio of the gels was the affinity of the gel for water. The results in Table II indicate that the initial absorption rate of the PEGMA gels was faster than that of the HEMA gels. This was due to the affinity of the gel toward water, which depended on the chain length of the oxyethylene repeating unit.

The particle size also affected the initial absorption rate for the gels. In the previous discussion, we showed that the particle size of PEGMA gels was smaller than that of the HEMA gels (cf. Figs. 1 and 2). If the particles were side by side, the surface area of the small particles was larger than that of the big particles, and the free volume of small particles was smaller than that of the big particles. For this reason, the initial absorption rate of the PEGMA gels was faster than that of the HEMA gels.

CONCLUSIONS

The spherical particle size of the PEGMA gels was smaller than that that of the HEMA gels. The swelling behavior of the superabsorbents prepared from NaA and HEMA or PEGMA indicated that the water absorbency was improved by the addition of a small amount of the HEMA or PEGMA monomer into the copolymeric gels, and the water absorbencies for the copolymeric gels containing PEGMA were higher than for those gels containing HEMA. Meanwhile, the initial absorption rate was improved when the hy-

TABLE II
Absorption Characteristics for NaA–HEMA and NaA–PEGMA Copolymeric Gel Systems in Deionized Water

Condition	Initial absorption rate (Q/min)								
	HA0	HA1	HA2	HA3	HA4	P_6A1	P_6A2	P_6A3	P_6A4
30 s	5.2	4.80	6.06	8.16	12	5.98	12	16.16	24
30 s–1 min	4	6	6.06	12.24	20	3.98	6	40.40	44
1–3 min	3.2	3.80	5.56	8.67	34	5.48	5.5	35.35	36

drated HEMA or PEGMA monomer was introduced into the copolymeric gels, and the initial absorption rates for the copolymeric gels containing PEGMA were higher than for those gels containing HEMA. The deswelling behavior of these gels occurred as ionic strength of external salt solution increased, especially for the multivalent salt solutions. This deswelling phenomenon was attributed to the complexation of multivalent cations with carboxylate groups on the polymeric chain.

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