

Superabsorbent Polymeric Materials. XIII. Effect of Oxyethylene Chain Length on Water Absorbency for the Sodium Acrylate and Poly(ethylene glycol) Methyl Ether Acrylate (PEGMEA_n) Copolymeric Gels

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ABSTRACT: In a previous study, we prepared a series of xerogels based on sodium acrylate (NaA) and 2-hydroxyethyl methacrylate (HEMA, OE = 1) or poly(ethylene glycol) methacrylate (PEGMA, OE = 6) with different oxyethylene (OE) units. The effect of the contents of HEMA and PEGMA in the copolymeric gel on the swelling behavior in deionized water and various saline solutions was studied. Their results showed that the water absorbencies for these two series gels were effectively improved by adding a small amount of HEMA or PEGMA. In this article, a series of novel xerogels based on NaA and hydrophilic monomer poly(ethylene glycol) methyl ether acrylate (PEGMEA_n), which was synthesized from acryloyl chloride and poly(ethylene glycol) monomethyl ether with three oxyethylene (OE = 9, 16, 45) chain lengths, were prepared by inverse suspension poly-

merization. The effects of OE chain length in the copolymeric gel on the water absorption behavior and initial absorption rate for the present xerogels were investigated. Results showed that adding a small amount of PEGMEA_n could effectively increase the water absorbency of the gels. In addition, the water absorbency decreased with an increase of the OE chain length in PEGMEA_n. The initial absorption rate for the present copolymeric gels increased with increasing OE chain length in PEGMEA_n and the content of PEGMEA_n in the copolymeric gels. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 927–934, 2006

Key words: superabsorbent; water absorbency; sodium acrylate; inverse suspension polymerization; poly(ethylene glycol) methyl ether acrylate

INTRODUCTION

Superabsorbent polymers are water insoluble and can absorb a large amount of aqueous fluids and retain the absorbed fluids even under some pressure. Therefore, superabsorbents have great advantages over traditional water-absorbing materials. Because of their excellent characteristics, superabsorbents 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} Since the first superabsorbent polymer was reported by the US Department of Agriculture in 1961.⁹ Hence, lots of researchers attempted to modify these absorbent polymers to enhance their absorbency, gel strength, and absorption rate.^{2,10–23}

Superabsorbents based on acrylic acid (AA) have been extensively studied because AA is cheap and easily polymerized to a high molecular weight polymer. In our previous studies, a series of superabsor-

bents were prepared to investigate the swelling behavior in deionized water and various saline solutions, such as poly(sodium acrylate) [poly(NaA)] containing nonionic comonomer 2-hydroxyethyl methacrylate (HEMA)²⁴; zwitterionic monomer 3,3-dimethyl methacryloyloxyethyl ammonium propane sulfonate (DMAPS),²⁵ 3,3-dimethyl acrylamidopropyl ammonium propane sulfonate (DMAAPS)²⁶; anionic monomer sodium 2-acrylamido-2-methyl propane sulfonate (NaAMPS)²⁷; cationic monomer trimethyl methacrylamido propyl ammonium iodide (TMMAAI)²⁸; and poly(NaA) with various initial total monomer concentrations.²⁹

A series of xerogels based on NaA and HEMA (OE = 1) or poly(ethylene glycol) methacrylate (PEGMA, OE = 6) were prepared in a previous study. Their results showed that the water absorbencies for these two series gels were effectively improved by adding a small amount of HEMA or PEGMA. The initial absorption rates in deionized water were faster for PEGMA-series gels than HEMA-series gels.³⁰ To further understand the effect of OE chain length in the copolymeric gel on the water absorption behavior, different OE chain lengths in poly(ethylene glycol) methyl ether acrylate (OE = 9, 16, and 45) were de-

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TABLE I
Feed Compositions of NaA/PEGMEAn Xerogels with Different Ethylene Oxide Chain Lengths

Sample codes	NaA (g)	PEGMEA _n (g)	NMBA (g)	Yield (%)	Water solubles (%)
HA ₀	20	0	0.07	94.5	7
P ₉ A ₁	19.95	0.24 (2.5 × 10 ⁻³)	0.07	96.4	6
P ₉ A ₂	19.85	0.73 (7.5 × 10 ⁻³)	0.07	96.9	8
P ₉ A ₃	19.7	1.45 (1.5 × 10 ⁻²)	0.07	99.2	8
P ₉ A ₄	19.55	2.18 (2.25 × 10 ⁻²)	0.07	98.2	9
P ₁₆ A ₁	19.95	0.43 (2.5 × 10 ⁻³)	0.07	93.23	5
P ₁₆ A ₂	19.85	1.28 (7.5 × 10 ⁻³)	0.07	86.64	9
P ₁₆ A ₃	19.7	2.57 (1.5 × 10 ⁻²)	0.07	89.03	7
P ₁₆ A ₄	19.55	3.86 (2.25 × 10 ⁻²)	0.07	87.7	8
P ₄₅ A ₁	19.95	1.1 (2.5 × 10 ⁻³)	0.07	92.8	7
P ₄₅ A ₂	19.85	3.28 (7.5 × 10 ⁻³)	0.07	87.7	9
P ₄₅ A ₃	19.7	6.56 (1.5 × 10 ⁻²)	0.07	83.6	10
P ₄₅ A ₄	19.55	9.86 (2.25 × 10 ⁻²)	0.07	84.5	10

Molar ratio are given in parenthesis.

signed and incorporated into poly(NaA) gels. The effects of different OE chain lengths in PEGMEA on water absorbency and initial absorption rate for the present xerogels were investigated.

EXPERIMENTAL

Materials

Acrylic acid (AA), which was purified by vacuum distillation at 63°C/25 mmHg, poly(ethylene glycol) methyl ether acrylate (PEGMEA₉, $M_n = 454$, OE = 9), acryloyl chloride, poly(ethylene glycol) monomethyl ether, and *N,N'*-methylene-bisacrylamide (NMBA) as a crosslinking agent were obtained from Aldrich (St. Louis, MO). Sodium hydroxide, PEGMEA₉, 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 (Tokyo, Japan). Methanol and cyclohexane were of reagent analytical grade.

Preparation of NaA monomer solution

NaA monomer was prepared as reported previously.²⁴

Preparation of poly(ethylene glycol) methyl ether acrylate (PEGMEA_n)³¹

A solution containing poly(ethylene glycol) monomethyl ether and triethylamine in 100 mL benzene was added into a 100 mL volume flask equipped with a stirrer, a condenser, and a thermometer. To this, the acryloyl chloride was slowly added under nitrogen below 0°C and stirred for 6 h. The mixture was then separated by filtration. The filtrate was then concentrated by rotary evaporation. The products were pu-

rified by vacuum distillation. The boiling point of PEGMEA₁₆ (OE = 16) is 183°C/6 mmHg and melting point of PEGMEA₄₅ (OE = 45) is 67°C.

Inverse suspension polymerization

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

The crosslinking agent, NMBA, and the appropriate amount of PEGMEA_n monomer were introduced into NaA 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 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 100°C for 1 day. The white powdered polymer was obtained and the yield was over 90%. The feed compositions and water solubles of the samples are listed in Table I.

Measurement of water absorbency

Suction filtration method

The samples (50 mg) were immersed in an excess amount of deionized water or 0.9 wt % NaCl (aq) solutions for at least 8 h to reach the swelling equilib-

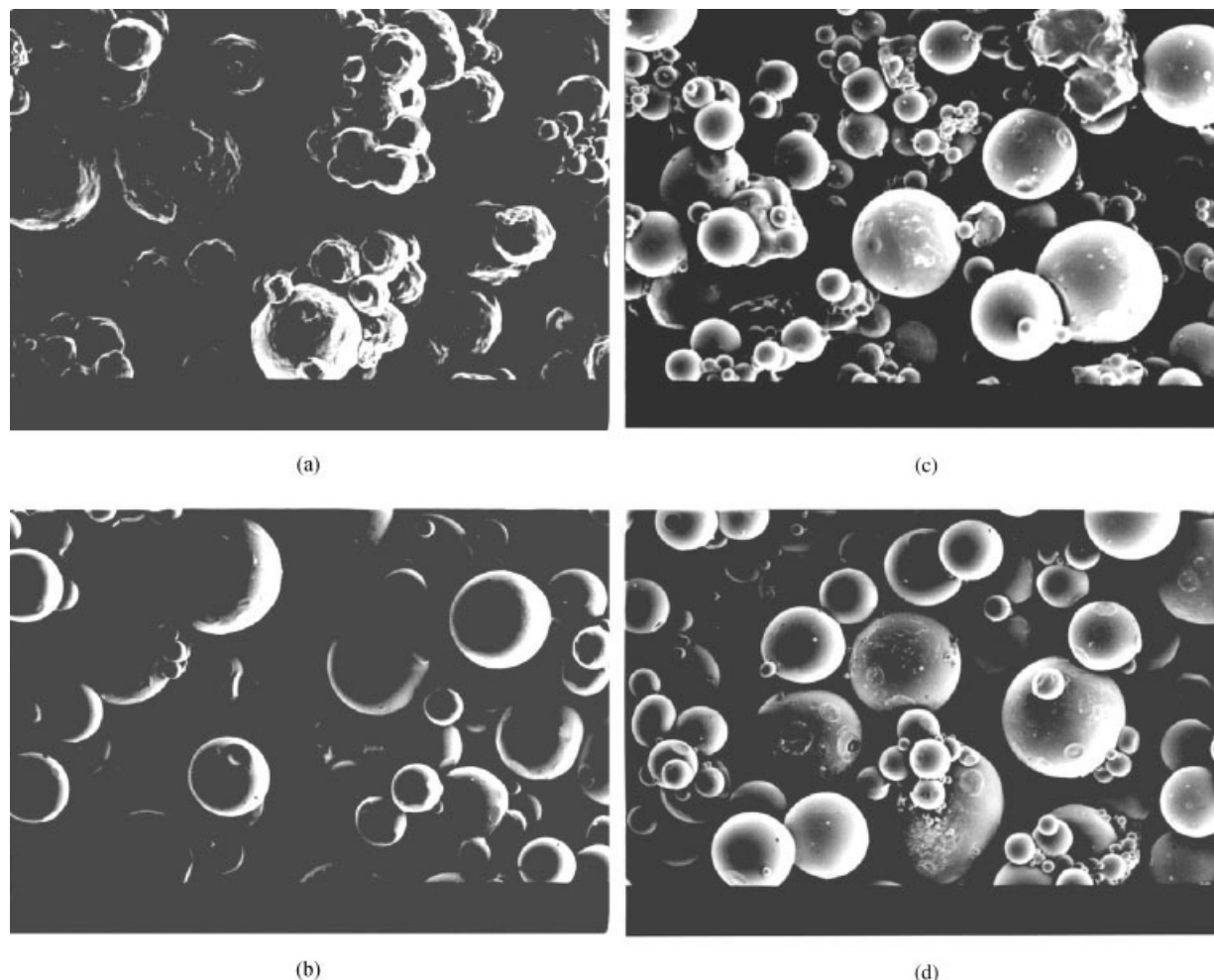


Figure 1 Scanning electron micrographs for dried PEGMEA₉-series gels ($\times 150$): (a) P₉A₁; (b) P₉A₂; (c) P₉A₃; (d) P₉A₄.

rium 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:

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

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 until the swelling equilibrium, and then hung up 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 amount of various saline solutions with different concentrations [NaCl (aq), CaCl₂ (aq), FeCl₃ (aq)] for at least 8 h. The swollen samples were filtered with suction and weighed to determine their water absorbencies in the above 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 water 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 was easily measured. The absorbency at every time interval was calculated by the following equation:

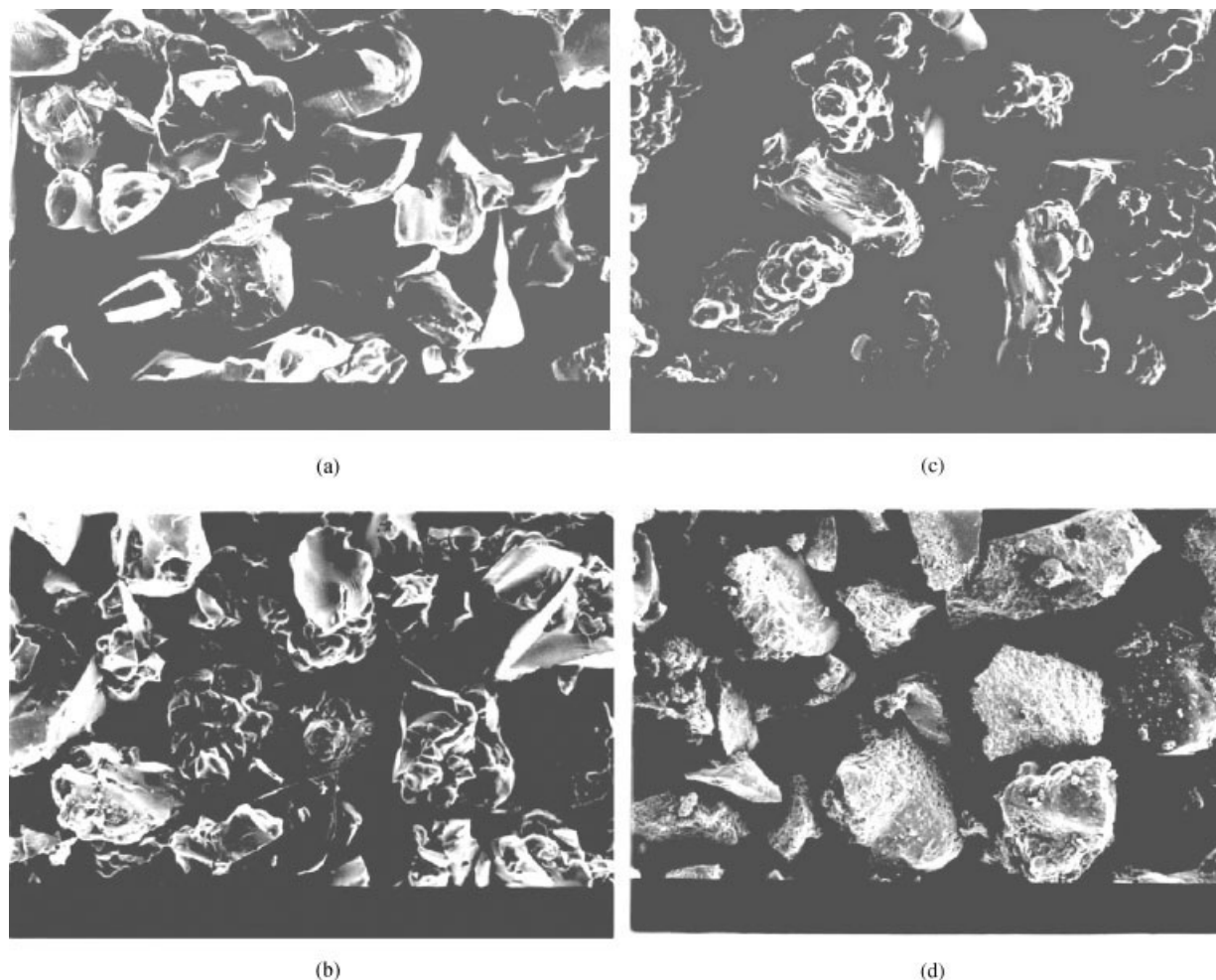


Figure 2 Scanning electron micrographs for dried PEGMEA₁₆-series gels ($\times 150$): (a) P₁₆A₁; (b) P₁₆A₂; (c) P₁₆A₃; (d) P₁₆A₄.

$$Q = \frac{V_s \times d_{\text{H}_2\text{O}}}{W_d} \quad (2)$$

where Q is the characteristic absorbency, V_s is the absorbed volume, $d_{\text{H}_2\text{O}}$ is the density of water, and W_d is the weight of dry sample.

Morphology

The dried specimens were examined for morphological details by using scanning electron microscopy (SEM) (JEOL JXA8600, Tokyo, Japan) with an acceleration voltage of 15 kV. The specimens were coated with a gold metal layer to provide proper surface conduction.

RESULTS AND DISCUSSION

Scanning electron microscopy

SEM microphotographs of the particle size for PEGMEA_{*n*}-series gels were shown in Figures 1–3. As

shown in Figure 1, the shapes of xerogel particles of PEGMEA₉-series gels were spherical, but in Figures 2 and 3, the xerogel particles exhibited some aggregates. The results in these Figures also indicated that the particle sizes for the present gels decrease with an increase of the EO chain length in PEGMEA_{*n*}-series gels.

Effect of PEGMEA content on water absorbency in deionized water for NaA/PEGMEA copolymeric gels

A typical profile of water absorbency in deionized water measured by suction filtration and tea-bag methods and as a function of the molar ratio of PEGMEA₉ in the copolymeric gels is shown in Figure 4. The similar results for PEGMEA₁₆ and PEGMEA₄₅ were observed in the experiment (not shown). The results in Figure 4 indicate that the maximum water absorbency for the PEGMEA₉ appeared at the molar ratio of 2.5×10^{-3} . That is, the water absorbency increased with increasing molar ratio of PEGMEA₉,

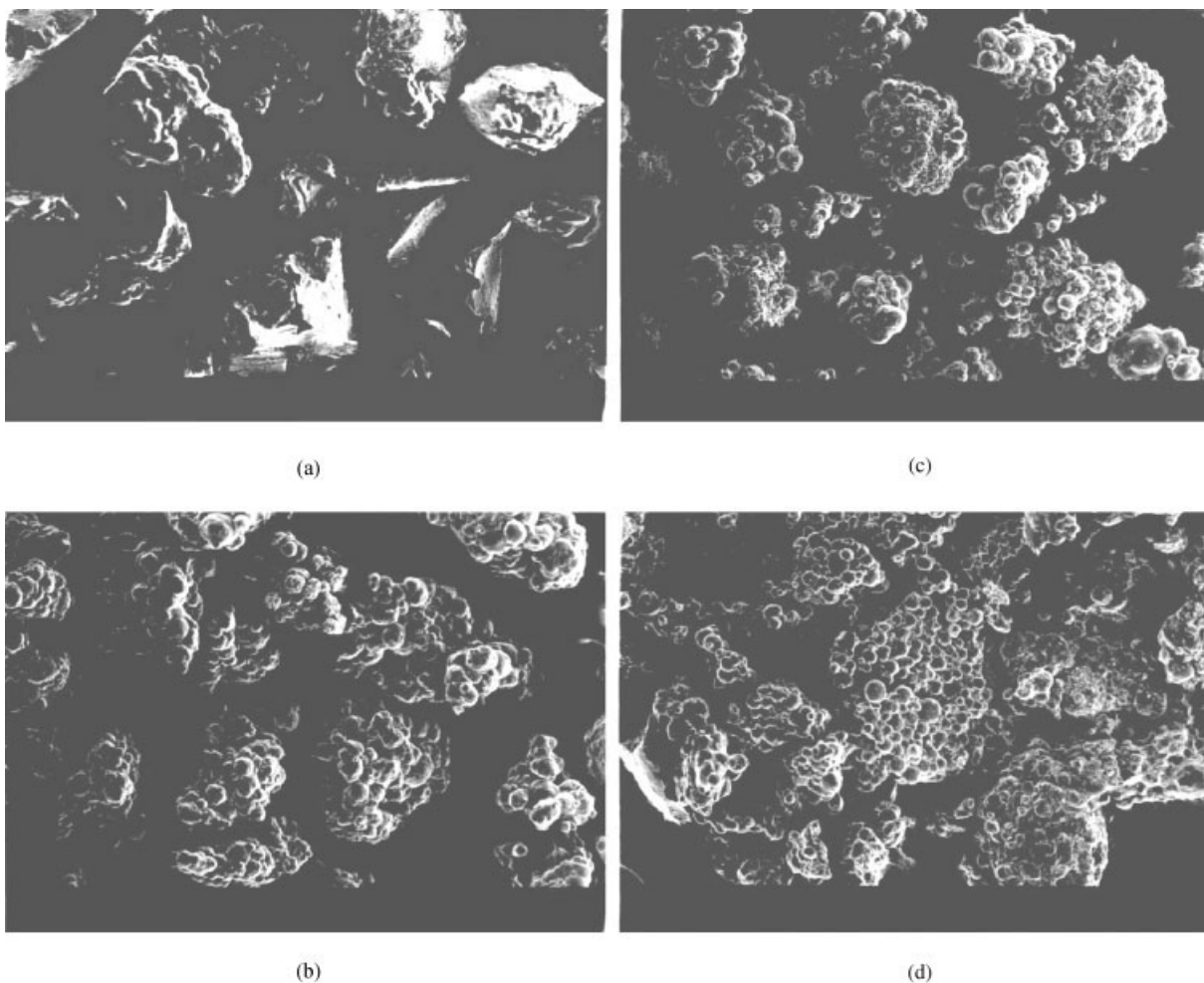


Figure 3 Scanning electron micrographs for dried PEGMEA₄₅-series gels (×150): (a) P₄₅A₁; (b) P₄₅A₂; (c) P₄₅A₃; (d) P₄₅A₄.

when the molar ratio was less than 2.5×10^{-3} , then the water absorbency decreased when the molar ratio of PEGMEA₉ was greater than 2.5×10^{-3} .

According to the Flory's swelling theory for ionic gels,³² the following equation was given

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

where q_m is the water absorbency of the network at equilibrium, $i/2v_\mu$ is the concentration of fixed charge 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_0/v_e is the crosslinking density of the gel. Hence, the water absorbency of the gel was dependent on ionic osmotic pressure, crosslinking density, and the affinity of the gel toward water. Because the crosslinker content of the copolymeric gels, the ionic concentration in the external solution, and ionic osmotic pressure were fixed, the water absorbency for the gels was mainly dependent on the affinity of the gel for water. Hence, when the molar

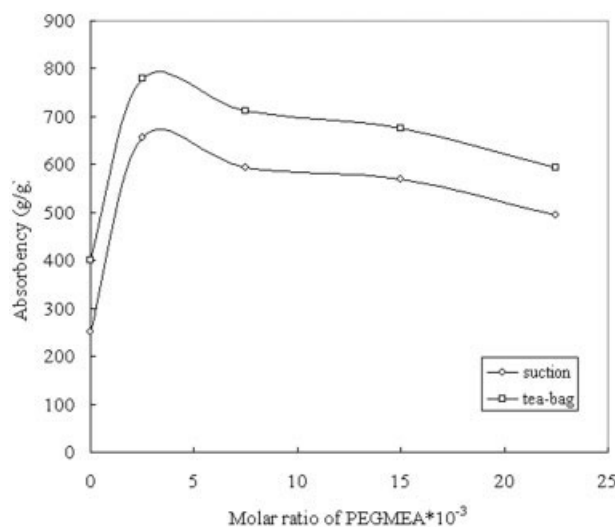


Figure 4 Effect of PEGMEA content for the poly(NaA/PEGMEA₉) gels on water absorbency in deionized water by tea-bag method and suction method.

ratio of PEGMEA₉ was greater than 2.5×10^{-3} , the affinity of the copolymeric gel decreased, and the more the PEGMEA₉ contents was, the lower the affinity was, and the lower the water absorbency was.

The similar behavior was observed from our previous studies,³⁰ which reported that the maximum water absorbency for NaA/PEGMA and NaA/HEMA copolymeric gels occurred at molar ratio of 7.5×10^{-3} and 15×10^{-3} for PEGMA ($n = 6$) and HEMA ($n = 1$), respectively. From the above results, we found that the maximum water absorbency for NaA/PEGMEA_{*n*} series gels shifted to low molar ratio of PEGMEA_{*n*} with increase in OE chain length. This result conforms to our expectation. In addition, from this Figure, the results also showed that the water absorbency measured by tea-bag method was larger than that measured by suction method. The reason for this behavior was described in our previous related studies.^{24,30}

Figure 5 shows the water absorbency of the PEGMEA_{*n*} series gels in deionized water measured by suction filtration. The results indicated that the maximum water absorbencies were in the order of 655, 613, and 516 g/g polymer for PEGMEA₉, PEGMEA₁₆, and PEGMEA₄₅, respectively. But, in comparison with our previous report,³⁰ the maximum water absorbencies for NaA/HEMA ($n = 1$) and NaA/PEGMA ($n = 6$) gels are 606 and 660 g/g polymer, respectively. From these results, we found that the longer chain length of the oxyethylene unit in PEGMEA_{*n*} will not avail to enhance the water absorbency of the gel. The explainable reason is that the longer oxyethylene chain unit in PEGMEA formed a more entanglement structure in the copolymeric gels.

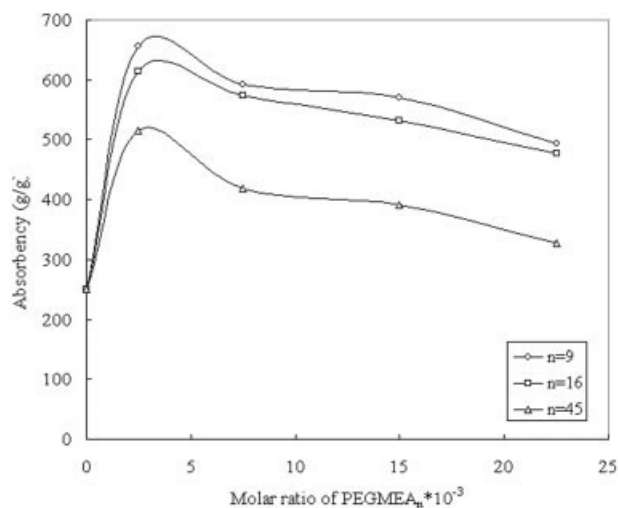


Figure 5 Effect of the PEGMEA_{*n*} content for the poly(NaA/PEGMEA_{*n*}) gels on water absorbency in deionized by suction method.

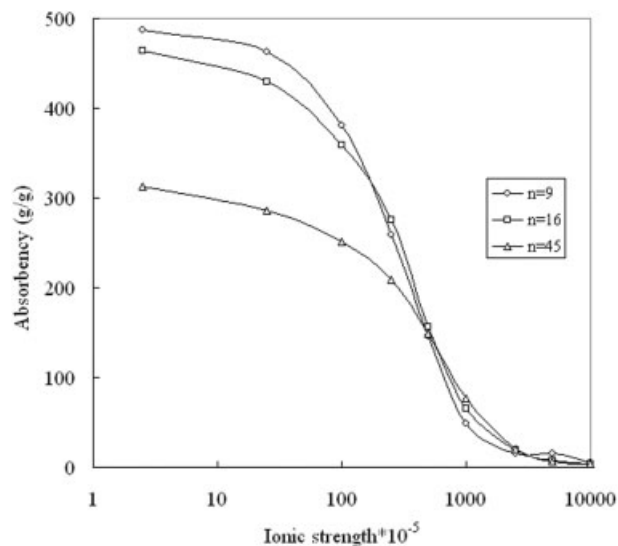


Figure 6 Water absorbency of sample P₉A₄ for the poly(NaA/PEGMEA_{*n*}) gels in the CaCl₂ (aq) with various ionic strengths.

Water absorbency in various salt solutions

A typical profile of water absorbency as a function of different ionic strengths for the poly(NaA-co-PEGMEA_{*n*}) copolymeric gels in CaCl₂ (aq) are shown in Figure 6. The water absorbencies for sample P₉A₄ in different valence salt solutions are shown in Figure 7. The water absorbencies for the copolymeric gels in various salt solutions shown in Figures 6 and 7 decreased with an increase of the ionic strength of salt solutions. This could be attributed to the cations, such as the sodium ion, the calcium ion, and the ferric ion, which would neutralize the carboxylate group

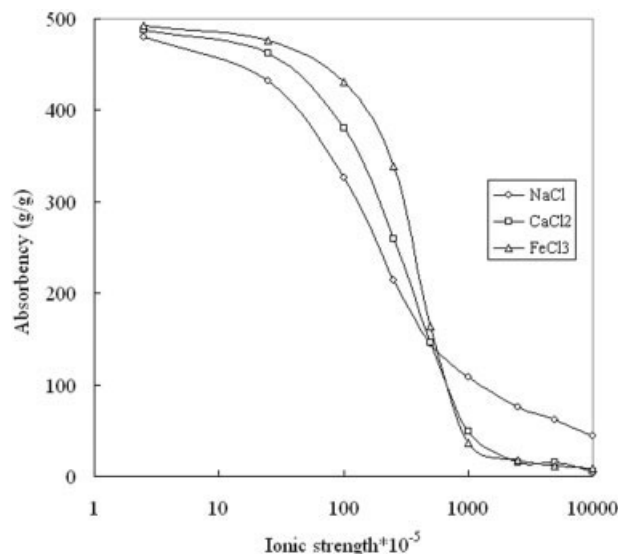


Figure 7 Water absorbency of sample P₉A₄ in the NaCl (aq), CaCl₂ (aq), and FeCl₃ (aq) with various ionic strengths.

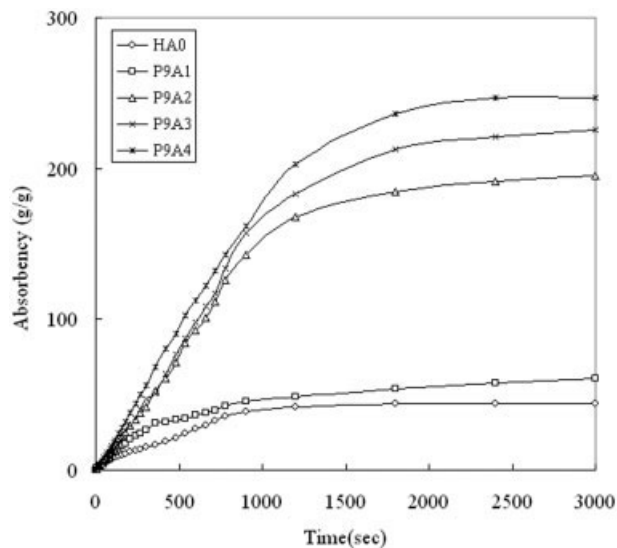


Figure 8 Absorption rate in deionized water for the PEGMEA₉-series gels by DW method.

(COO⁻). In addition, the curve of water absorbency for monovalent cationic salt solution was flatter than those for divalent and trivalent cationic salt solution (see Fig. 7). This is because the divalent calcium ion and trivalent ferric ion would form complexes with the carboxylate group. Hence, the water absorbencies converge to zero for the gels in the divalent and trivalent cationic salt solutions at 0.1M ionic strength. These results are also observed from Figure 6. This result also implies that the water absorbency of the gel in concentrated salt solutions would not be affected by the chain length of the oxyethylene unit in PEGMEA.

The results also show that the tendency of water absorbency for the gel is in the order $Fe^{3+} > Ca^{2+} > Na^{+}$ in the dilute solution. This is because when the gel resides in the dilute solution, the effect of ionic osmotic pressure is very small. Hence, the affinity of the ion for water is in the order $Fe^{3+} > Ca^{2+} > Na^{+}$ in the dilute solution, and this caused the water absorbency of the gel in the order of $Fe^{3+} > Ca^{2+} > Na^{+}$ in the dilute solution. This behavior was observed from our previous studies.^{24–28,30}

Effect of PEGMEA content on absorption rate for the present copolymeric gels

Buchholz³³ has suggested that the swelling kinetics for the absorbent is significantly influenced by swelling capacity, size distribution of powder particles, specific surface area, and apparent density of the polymer. Figures 8–10 showed the absorption rate in deionized water for PEGMEA_n-series gels. The results shown in these figures indicated that the initial absorption rate increased with increasing content of PEGMEA. According to Flory's swelling theory,³² the swelling ratio

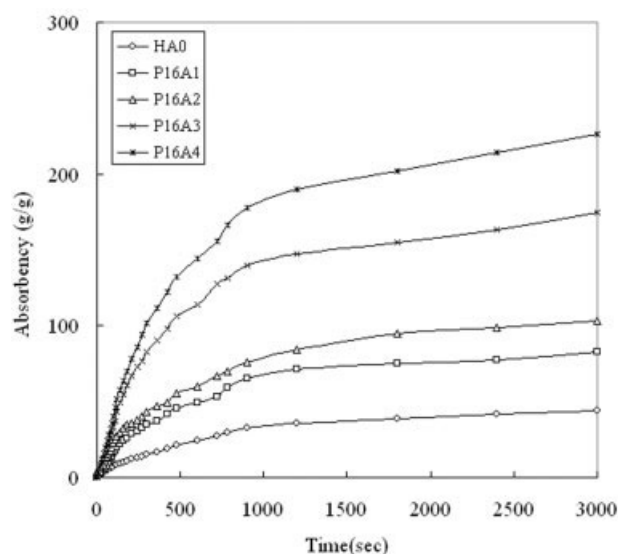


Figure 9 Absorption rate in deionized water for the PEGMEA₁₆-series gels by DW method.

has a relation to the affinity of the gel for water. The more PEGMEA monomer was introduced into the copolymeric gel, the absorption rate was more rapid. The characteristic absorption data for these series gels shown in Table II indicated that the longer the EO chain in PEGMEA, the higher the initial absorption rate for poly(NaA/PEGMA) at initial 30 s, i.e., $PnA_1 < PnA_2 < PnA_3 < PnA_4$. In comparison with PnA_4 and HA0 gels at initial 30 s, the initial absorption rate enhances 1.54, 4.62, and 6.48 times for P_9A_4 , $P_{16}A_4$, and $P_{45}A_4$ gels, respectively. This is because the longer EO chain, which provided hydrophilic groups can more easily bind the water and form a rapid microstream

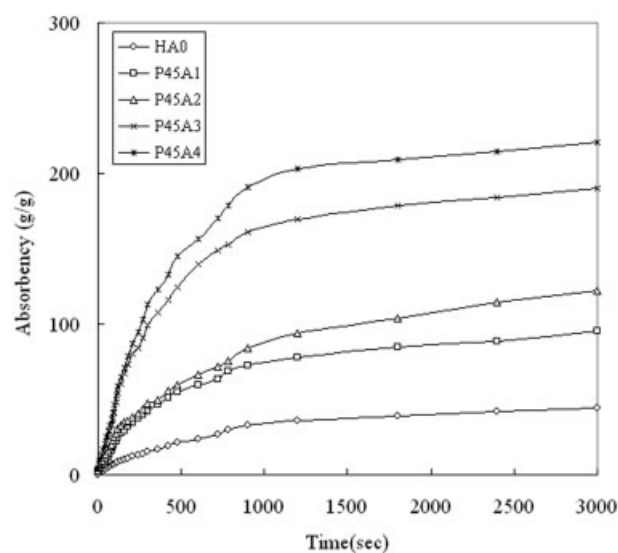


Figure 10 Absorption rate in deionized water for the PEGMEA₄₅-series gels by DW method.

TABLE II
Absorption Characteristics for NaA/PEGMA_n
Copolymeric Gels Systems in Deionized Water

Sample	Initial absorption rate (Q/min)		
	30 s	30 s–1 min	1–3 min
HA ₀	5.20	4.00	3.20
P ₉ A ₁	6.00	6.00	5.65
P ₉ A ₂	6.30	12.61	7.88
P ₉ A ₃	6.38	6.38	9.57
P ₉ A ₄	8.03	12.05	11.04
P ₁₆ A ₁	7.91	7.91	8.89
P ₁₆ A ₂	13.61	13.20	10.62
P ₁₆ A ₃	19.25	13.36	22.30
P ₁₆ A ₄	24.00	24.00	23.00
P ₄₅ A ₁	11.97	10.96	10.42
P ₄₅ A ₂	17.90	14.14	9.80
P ₄₅ A ₃	24.01	24.73	24.52
P ₄₅ A ₄	33.72	24.00	25.00

channel of water. We think that this action can offer the so-called “capillary effect” that would enhance the absorption rate of the gels. Another factor that affected the initial absorption rate is the size distribution of the gel powder. From SEM morphologies shown in Figures 1–3, the particle size of the gels became smaller as the EO chain length in the PEGMEA increases such as P₄₅A₄ series gel. The surface areas became larger when the particle size became smaller. Hence, the initial absorption rate of PEGMA-series gels increased with an increase of the EO chain lengths in PEGMA_n-series gels.

CONCLUSIONS

A series of novel xerogels based on NaA and hydrophilic monomer poly(ethylene glycol) methyl ether acrylate (PEGMEA_n) with three oxyethylene (OE = 9, 16, 45) chain lengths were successfully prepared by inverse suspension polymerization. The maximum water absorbency of the gels could effectively increase by adding a small amount of PEGMEA_n, but the water absorbency decreased with an increase of the OE chain length in PEGMEA_n. The initial absorption rate for the present copolymeric gels increased with increasing of OE chain length in PEGMEA_n and the content of PEGMEA_n in the copolymeric gels. The deswelling behavior of these gels occurred as the ionic strength of external salt solution increased, especially for the mul-

tivalent salt solutions. This deswelling was attributed to the complexation of multivalent cations with the carboxylate group on the polymeric chain.

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