

Superabsorbent Polymeric Materials. II. Swelling Behavior of Crosslinked Poly[sodium acrylate-co-3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate] in Aqueous Salt Solution

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Received 15 May 1996; accepted 12 October 1996

ABSTRACT: A series of xerogels based on sodium acrylate (SA), 3-dimethyl (methacryloyloxyethyl) ammonium propane sulfonate (DMAPS), and *N,N'*-methylene-bis-acrylamide (NMBA) are prepared by inverse suspension polymerization. The water absorbencies or swelling behaviors for these xerogels in water or various saline solutions are investigated. Results obtained from this study show that the water absorbency respectively exhibit a value of 1435 g H₂O/g sample and 96 g H₂O/g sample in deionized water and 0.9 wt % NaCl solution at a gel containing 1.88×10^{-3} molar ratio of DMAPS while the extent of 1.53×10^{-3} molar ratio (0.25 wt % based on total monomer) of NMBA was used in the polymerization. The absorbency in the chloride salt solutions decreases with an increase in the ionic strength of salt. For the same ionic strength of various salt solutions, the swelling amount has the following tendency: $\text{Na}^+ > \text{Fe}^{3+} > \text{Al}^{3+} > \text{Ca}^{2+}$ for the higher ionic strength of 5×10^{-3} – $2 \times 10^{-2} M$ and $\text{Na}^+ > \text{Fe}^{3+} > \text{Ca}^{2+} > \text{Al}^{3+}$ for the lower ionic strength of $< 2 \times 10^{-4} M$. The bound water found by DSC investigation is approximately equal to 2 g H₂O/g sample. The pH effect and thermal effect on the water absorbency for these xerogels are also investigated. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1701–1712, 1997

INTRODUCTION

Superabsorbents can absorb a large amount of water compared with general water-absorbing materials, in which the absorbed water is hardly removable even under some pressure. Because of their excellent characteristics, these superabsorbents are widely used in many products such as disposable diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water-blocking tapes, medicine for the drug delivery sys-

tem, absorbent pads, etc., where water absorbency or water retention is important.^{1–8} The modification of these absorbent polymers was carried out to enhance their absorbency, gel strength, and absorption rate by some researchers.^{9–23}

J. R. Gross reported that xerogellents are an extension of water-soluble polymer technology. There are five types of hydrophilic polymers: ampholytic, anionic, cationic, nonionic, and zwitterionic polymers. The polyampholytes and zwitterionic polymers have the potential to swell more in salt solutions than in pure water.²⁴ The mechanism of absorption of water of hydrophilic polymers was explained in nonionic network or ionic network structure by Flory.²⁵ Ogawa, Yamano, and Miyogawa studied the kinetics of the swelling

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of poly(sodium acrylate) by picture analysis with a microscope-VTR system, calorimetry, and gravimetry techniques.²⁶

In our previous report,²⁷ the swelling behavior of a series of crosslinked poly(sodium acrylate-*co*-hydroxyethyl methacrylate), [poly(SA-HEMA)] absorbents was presented. The results showed that the deswelling behavior occurred for the gel in the presence of divalent and trivalent chloride salt solutions and that the swelling amount has a tendency as follows: $\text{LiCl} = \text{NaCl} = \text{KCl}$; $\text{CaCl}_2 < \text{SrCl}_2 < \text{BaCl}_2$; and $\text{Fe}^{3+} < \text{Ca}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$. These orders are related to the complexing ability of metallic cation and carboxylate groups in the polymeric chains.

The superabsorbent polymers containing zwitterionic monomer or sulfobetaine's monomer are not found in the literature, although some ampholytic monomers and cationic monomers containing absorbent polymers were studied.²⁸⁻³⁴ A series of sulfobetaine monomers and corresponding cationic monomers, as well as the aqueous salt behavior of their polymers, were prepared and investigated in our laboratory.³⁵⁻³⁹ Hence, a series of crosslinked poly[sodium acrylate (SA)-*co*-3-dimethyl (methacryloyloxyethyl) ammonium propane sulfonate (DMAPS)]s are prepared by inverse suspension polymerization and the swelling behaviors of these xerogellants with various ratios of DMAPS/SA in aqueous salt solutions are investigated in this article.

EXPERIMENTAL

Materials

The materials used in this study were purchased from Tokyo Kasei Industries Ltd., including acrylic acid (AA), dimethylaminoethylmethacrylate, sodium hydroxide, propane sultone, and *N,N'*-methylene-bis-acrylamide (NMBA). Sodium hydroxide, propane sultone, and NMBA were used directly, and others were distilled under reduced pressure before use.

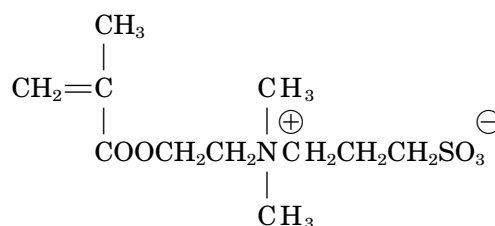
4,4'-Azobis(4-cyanovaleric acid) (ACVA) as an initiator and sorbitan monostearate (Span 60) as an inverse suspension stabilizer were also purchased from Tokyo Kasei Industries Ltd. Acetone was directly distilled and dried over anhydrous calcium chloride. Methanol and cyclohexane were the analytical grade. Deionized water was used in the polymerization system.

Preparation of Sodium Acrylate (SA) Monomer Solution

SA monomer was prepared as previously reported.²⁷

Synthesis of DMAPS Monomer

DMAPS was prepared as described previously.³⁵⁻³⁷ Yield: 92%, m.p.: 95°C. The structure is given as follows



Inverse Suspension Polymerization

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

The appropriate amounts of the DMAPS monomer and the crosslinking agent, NMBA, were introduced into SA monomer solution and the mixture was stirred until the NMBA was dissolved completely (monomer solution). The monomer solution and 0.02 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 set 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 120°C for 1 day. The white powdered polymer was obtained and the yield was 92–96%. The compositions of materials used are listed in Table I.

Measurement of Water Absorbency

The samples were dried in a vacuum oven at 60°C for 1 day before any tests. All of the samples were

Table I Compositions of Polymers. The Amount of Water and Monomer Was 60 g and 0.213 mol Respectively. Parentheses Denote the Molar Ratio of Each Monomer to Total Monomer (SA + DMAPS)

Sample/Monomer	SA (g)	DMAPS (g)	NMBA (g)
Ds1	20.000	0 (0)	0.10 (3.05×10^{-3})
Ds2	19.975	0.112 (1.88×10^{-3})	0.10 (3.05×10^{-3})
Ds3	19.950	0.223 (3.75×10^{-3})	0.10 (3.05×10^{-3})
Ds4	19.850	0.446 (7.51×10^{-3})	0.10 (3.05×10^{-3})
Ds5	19.700	0.891 (1.50×10^{-2})	0.10 (3.05×10^{-3})
Ds6	19.550	1.337 (2.25×10^{-2})	0.10 (3.05×10^{-3})
Ds7	20.000	0 (0)	0.07 (2.14×10^{-3})
Ds8	19.975	0.112 (1.88×10^{-3})	0.07 (2.14×10^{-3})
Ds9	19.950	0.223 (3.75×10^{-3})	0.07 (2.14×10^{-3})
Ds10	19.850	0.446 (7.51×10^{-3})	0.07 (2.14×10^{-3})
Ds11	19.700	0.891 (1.50×10^{-2})	0.07 (2.14×10^{-3})
Ds12	19.550	1.337 (2.25×10^{-2})	0.07 (2.14×10^{-3})
Ds13	20.000	0 (0)	0.05 (1.53×10^{-3})
Ds14	19.975	0.112 (1.88×10^{-3})	0.05 (1.53×10^{-3})
Ds15	19.950	0.223 (3.75×10^{-3})	0.05 (1.53×10^{-3})
Ds16	19.850	0.446 (7.51×10^{-3})	0.05 (1.53×10^{-3})
Ds17	19.700	0.891 (1.50×10^{-2})	0.05 (1.53×10^{-3})

used with a particle size in the range of 60–100 mesh.

Suction Filtration Method

The sample (50 mg) was immersed in an excess of deionized water or 0.9 wt % $\text{NaCl}_{(\text{aq})}$ aqueous solution until equilibrium was reached (at least 8 h) and the residual solution was then removed by a suction aspirator for 5 min (250 mm Hg, filter paper type: TOYO 5C). The absorbency, Q , was determined by weighing the swollen gel and calculated according to the following relationship.

$$Q = \frac{\text{mass of swollen gel} - \text{mass of dried sample}}{\text{mass of dried sample}} \quad (1)$$

Tea Bag Method

The tea bag was made of a 250 mesh nylon screen. The tea bag containing the sample (50 mg) was immersed entirely in deionized water or saline solution and stayed until equilibrium was reached. The tea bag was hung up for 15 min in order to drain the excess solution and weighed

(the weight of a tea bag would be deducted). The absorbency was calculated according to eq. (1).

Swelling Behaviors in Various Concentration Salt Solutions

Fifty milligrams of dried samples were immersed in the excess of various saline solutions with different concentrations [$\text{NaCl}_{(\text{aq})}$; $\text{MgCl}_{2(\text{aq})}$, $\text{CaCl}_{2(\text{aq})}$, $\text{BaCl}_{2(\text{aq})}$; $\text{AlCl}_{3(\text{aq})}$, $\text{FeCl}_{3(\text{aq})}$], and remained for at least 8 h. The sample was filtered with suction and weighed.

Effect of Various pH Solutions on Water Absorbency

The method was the same as the water absorbency in various saline solutions. The pH values of the external solution were adjusted by adding HCl solution or NaOH solution in water.

Thermal Effect on the Water Retention

15 g of saturated swollen gels were placed in an oven at 70°C under forcing convection. The gel was weighed at each time interval and the weight loss was calculated.

Bound Water Determined by DSC

The absorbency of polymer was controlled under 10 times, and the gel (~ 8 mg) was used for assessing the bound water with a DSC (Du Pont Thermal Analyzer 2000). The performed temperature ranged from -30°C to 30°C at the heating rate of $5^{\circ}\text{C}/\text{min}$ in a nitrogen atmosphere at the flow rate of $35\text{ mL}/\text{min}$. The endothermic heat per gram swollen gel was attained and the following relationship was carried out to calculate the bound water.

$$B = q - (E \times (q + 1)/333.5) \quad (2)$$

where B is the bound water in the dried polymer (g/g), q is the absorbency controlled by the polymer (g/g), E is the endothermic heat of the swollen gel (J/g), and 333.5 is the heat of fusion of water (J/g).

RESULTS AND DISCUSSION

Characterization of the Copolymeric Gels

The elemental analysis was performed to determine the content of carbon and hydrogen in the copolymeric gel composition because the content of the DMAPS in the copolymeric gel is very small and the content of sulfur in the gel below the detection limit of the measurement is not adopted. Table II lists the theoretical values and the observed values of carbon and hydrogen elements and the calibration values of hydrogen element. These data reveal that the copolymer composition conforms to the initial charge composition. The percentages of water solubles of various copolymeric gels are also listed in the Table II.

Effect of DMAPS Content on Saturated Absorbency

The swelling behavior of the absorbents depends on the nature of the polymer and the characteristics of the external solution. The polymer's nature involves several parameters such as the nature of the charge, ionic content, and crosslinking density. The characteristics of the external salt solution include the charge number and the ionic strength.

Buchanan, Hird, and Letcher⁴⁰ have plotted the water retention of polyacrylate networks as a function of the degree of neutralization, and a swelling maximum was also observed. It was suggested that the chain expanded to such an extent

that the distance between neighboring charges increased due to repulsion effects between the charges.

The effect of the DMAPS content in the copolymeric gel on the water absorbency measured by the tea bag and suction methods is shown in Figures 1 and 2, respectively. The results show that the water absorbency is increased abruptly with the molar ratio of DMAPS and then decreased gradually for the different contents of the crosslinking agent, NMBA. The maximum value appears at the molar ratio of 1.88×10^{-3} , and the water absorbency of the copolymeric gel is larger than poly(SA) in the experimental ranges. This occurrence implies that the water absorbency is efficiently improved, thereby copolymerizing SA series with a small amount of zwitterionic monomer (DMAPS). By copolymerizing SA with DMAPS, the fixed charge concentration in the polymeric network was increased, while the external water penetrated into the polymeric network. This occurs because the inner ionic ring of the sulfobetaine structure was ruptured when the sodium ion was dissociated from the sodium carboxylate group.^{36,37} The two hydrophilic groups, the quaternary ammonium group and the sulfonate group, on the DMAPS were formed at once and the hydrophilic ability was rapidly increased. According to the P. J. Flory theory,²⁵ the swelling ratio of the polymeric gels was proportional to the fixed charge concentration and the hydrophilic ability. By increasing the proportion of DMAPS to SA, two effects (fixed charge concentration and hydrophilic ability) were offset by reducing the repulsion of the network, because the repulsion (negative fixed charges play the main role of the whole network) was decreased evidently by the positive charge formed by opening the DMAPS's inner ring structure at the higher extent of DMAPS.^{36,38} In other words, the water absorbency was decreased.

Considering the effect of the extent of crosslinking agent on the water absorbency, the gel absorbency is also the same tendency as well-known results; that is, the higher the extent of the crosslinking agent, the lower the water absorbency (as shown in Figs. 1 and 2). The polymeric gel shown in Figure 1 exhibits an absorbency of $1435\text{ g H}_2\text{O}/\text{g}$ sample at the copolymeric gel containing 1.88×10^{-3} molar ratio of DMAPS, while the extent of NMBA is 1.53×10^{-3} molar ratio (0.05 g), but the water absorbency decreases to $701\text{ g H}_2\text{O}/\text{g}$ sample as the extent of NBMA increases to the molar ratio of 3.05×10^{-3} (0.1 g). Similarly,

Table II Elemental Analysis of Carbon and Hydrogen and Percentages of Water Solubles for SA/DMAPS Copolymeric Gels

Sample No.	Theoretical Value (%)		Found Value (%)			Water Solubles (%)
	C	H	C	H	H_{cal} (w %) ^a	
DS1	38.39	3.23	36.91	3.80	3.37 (3.98)	12
DS2	38.44	3.25	36.43	4.13	3.55 (5.55)	6
DS3	38.49	3.27	36.73	3.81	3.30 (4.78)	10
DS4	38.59	3.32	36.14	4.07	3.37 (6.76)	8
DS5	38.77	3.41	38.43	3.98	3.88 (0.98)	6
DS6	38.96	3.50	37.80	4.17	3.84 (3.04)	8
DS7	38.37	3.22	N ^b	N	N	10
DS8	38.42	3.25	36.92	4.13	3.70 (4.07)	6
DS9	38.46	3.27	35.99	4.03	3.32 (6.86)	10
DS10	38.56	3.32	N ^b	N	N	8
DS11	38.75	3.41	36.39	4.16	3.48 (6.48)	4
DS12	38.94	3.50	37.22	4.12	3.63 (4.63)	10
DS13	38.35	3.22	N ^b	N	N	10
DS14	38.40	3.24	36.65	4.03	3.53 (4.77)	6
DS15	38.45	3.27	36.36	4.20	3.60 (5.73)	2
DS16	38.55	3.31	37.41	4.19	3.86 (3.05)	6
DS17	38.74	3.41	37.73	4.56	4.28 (2.61)	8
Total average	38.52	3.32	36.94	4.10	3.62 (4.52)	7.65

^a $w(\%) = \frac{C_{theo} - C_{found}}{C_{found}}$, $H_{cal} = H_{found} - H_{water}$, $W = w(\%) \times M$, and $H_{water} = (2/18) \times W / (M + W)$ w : percentages of water in copolymer W : water weight in polymer M : total copolymer weight.
^b N: not detected.

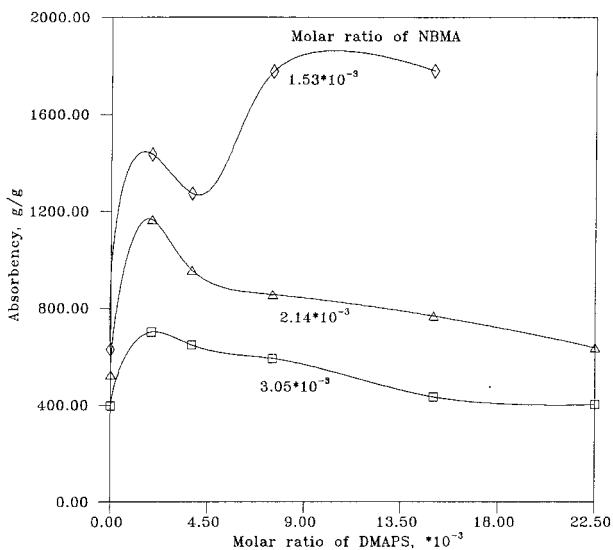


Figure 1 Effect of DMAPS content in DMAPS/SA copolymer gels on the water absorbency measured by tea bag method under different crosslinking agent contents.

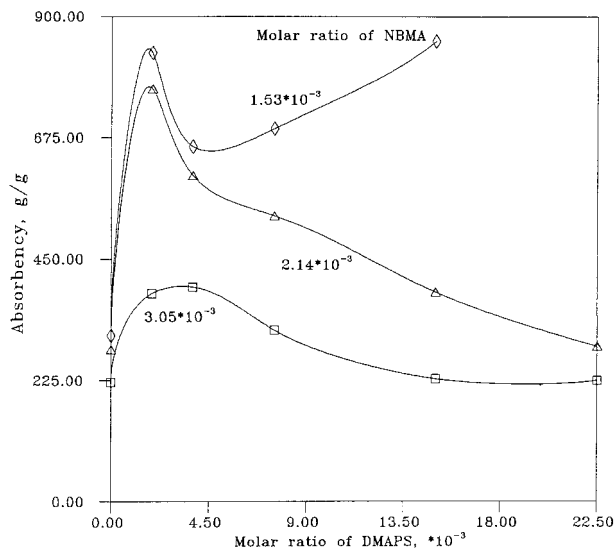


Figure 2 Effect of DMAPS content in DMAPS/SA copolymer gels on the water absorbency measured by suction method under different crosslinking agent contents.

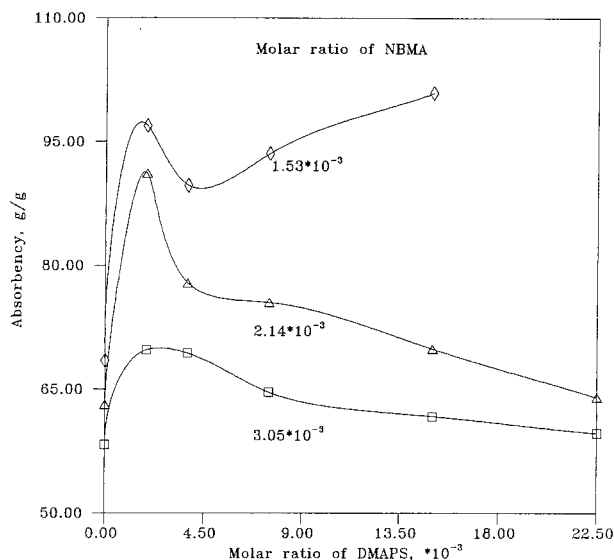


Figure 3 Effect of DMAPS content in DMAPS/SA copolymer gels on the water absorbency measured by tea bag method under different crosslinking agent contents. (in 0.9 wt % NaCl).

the same tendency of water absorbency is also obtained by the suction filtration method (see Fig. 2).

Comparing tea bag and suction filtration methods, their absorbencies show an extreme difference (see Figs. 1 and 2). This is because the absorbed water tends to store in the interstice of particles when the tea bag method is adopted, but it is lost when suction filtration (corresponding to gel bearing force) is used. Hence, the retention capacity obtained by the tea bag method was larger than that obtained by the suction filtration method. Conventionally, the tea bag method is used in the industry.

Figure 3 shows the water absorbency in 0.9 wt % NaCl_(aq) as a function of DMAPS content for the copolymeric gels. Their results are similar to those in deionized water. The water absorbencies in 0.9 wt % NaCl solution increase from 58, 63, and 68 g H₂O/g sample for poly(SA) gels to 69, 91, and 96 g H₂O/g sample at 1.88×10^{-3} molar ratio of DMAPS for the copolymeric gels containing 3.05×10^{-3} , 2.04×10^{-3} , and 1.53×10^{-3} molar ratio of NBMA, respectively. These results conform to our expectancy for which the zwitterionic (sulfobetaine) monomer could improve the water absorbency in salt solution. This result is mainly attributed to the decrease in the osmotic pressure difference between the polymeric gel and the external solution with high ionic strength. In other words, the difference of osmotic pressure in

the same salt concentration for poly(SA) gel is smaller than that for SA-DMAPS copolymeric gel, because the dissociated sodium ion could bind to the sulfonate group on the DMAPS chain and reduce the concentration gradient of the free sodium ion.^{36,38}

Effect of Salt Solution on the Water Absorbency

The swelling behavior of sodium acrylate absorbents could be significantly affected by various factors of the external solution such as its valencies and salt concentrations. SA-HEMA copolymeric gels have been reported in a previous paper,²⁷ which showed that the expansion of the gel network decreased because the repulsive counterion (carboxylate group) on the polymeric chain was shielded by the bound ionic charge (cation) and the osmotic pressure difference between the gel network and the external solution decreased with an increase in the ionic strength of the salt solution.

The effect of the salt solution with various concentrations of water absorbency obtained from suction method for a series of SA-DMAPS copolymeric gels is investigated in this section. Figures 4–6 show the typical absorbency of a series of SA-DMAPS copolymeric absorbents as a function of the ionic strength for NaCl, CaCl₂, and FeCl₃ solutions, respectively. These figures show that the

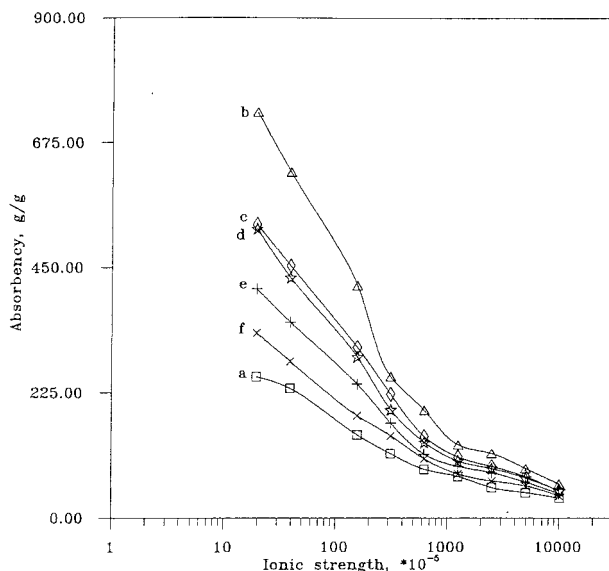


Figure 4 Absorbency obtained by suction method for crosslinked poly(SA-co-DMAPS) in various NaCl concentrations. (a) Ds 7; (b) Ds 8; (c) Ds 9; (d) Ds 10; (e) Ds 11; (f) Ds 12.

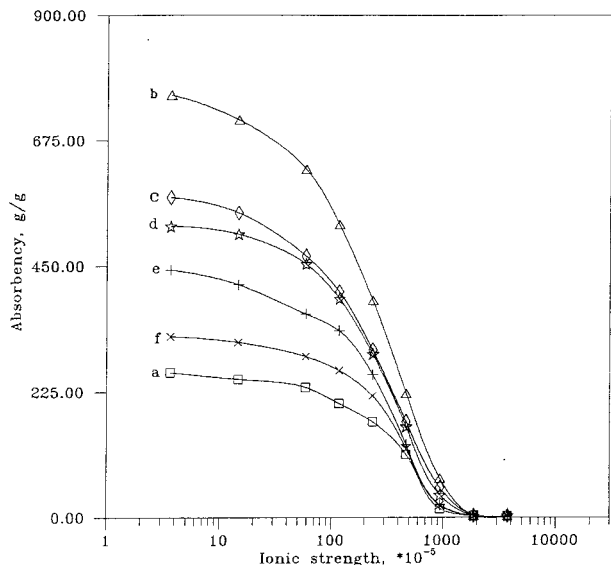


Figure 5 Absorbency obtained by suction method for crosslinked poly(SA-co-DMAPS) in various CaCl₂ concentrations. (a) Ds 7; (b) Ds 8; (c) Ds 9; (d) Ds 10; (e) Ds 11; (f) Ds 12.

water absorbency in various salt solutions decreases with increasing of the ionic strength of salt solutions, and the water absorbency in various solutions for a series of SA-DMAPS copolymeric gels is enhanced by the addition of the zwitterionic (sulfobetaine) monomer into the copolymeric compositions. These figures also show that

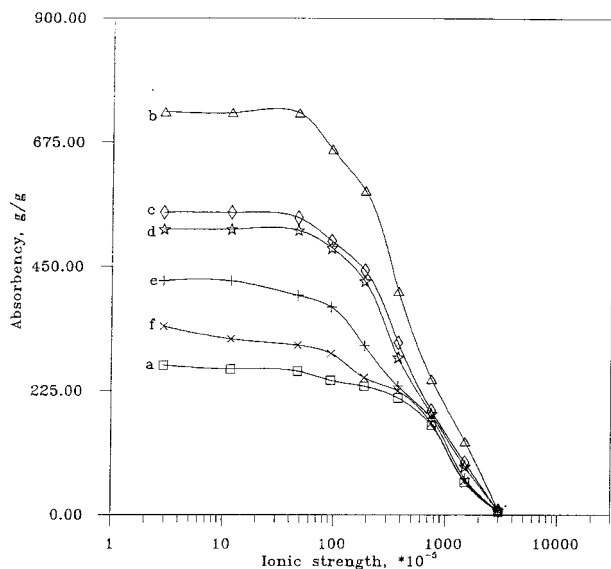


Figure 6 Absorbency obtained by suction method for crosslinked poly(SA-co-DMAPS) in various FeCl₃ concentrations. (a) Ds 7; (b) Ds 8; (c) Ds 9; (d) Ds 10; (e) Ds 11; (f) Ds 12.

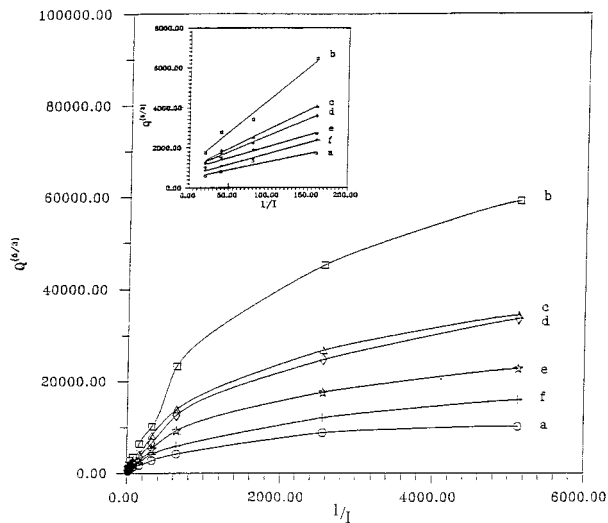


Figure 7 Absorbency plots against the ionic strength in NaCl solution. (a) Ds 7; (b) Ds 8; (c) Ds 9; (d) Ds 10; (e) Ds 11; (f) Ds 12.

the curves of water absorbency for monovalent cation salt solution (Fig. 4) are far flatter than those in divalent (Fig. 5) and in trivalent (Fig. 6) cation salt solutions. The experimental data (partly not shown) also demonstrate that water absorbency apparently decreases with an increase of the ionic strength in various salt solutions, such as MgCl₂, BaCl₂, and AlCl₃. These results are due to the fact that the osmotic pressure difference between the polymeric gel and the external solution is reduced with increasing of external solution concentration.

The effect of the ionic strength on water absorbency has been determined using the relation suggested by Hermans:⁴¹

$$Q_{eq}^{5/3} = A + Bi^2/I \tag{3}$$

where $Q_{(eq)}$ is the water absorbency at equilibrium, i is the concentration of the charges bound to the gel, I is the ionic strength of the external solution, and A and B are the empirical parameters. Good linear relationship shown in Figures 7 and 8 are achieved for a high ionic strength at the range of $1/I$ at 20–160 and at 100–440 M^{-1} for NaCl and CaCl₂ solutions, respectively. However, a discrepancy is observed from the range of low I values. These events are due to the fact that the swelling force is counteracted by the elastic force of chain. These phenomena were also observed in a series of gels of SA-HEMA²⁷ and a hydrolyzed polyacrylonitrile starch graft copolymer.¹⁶

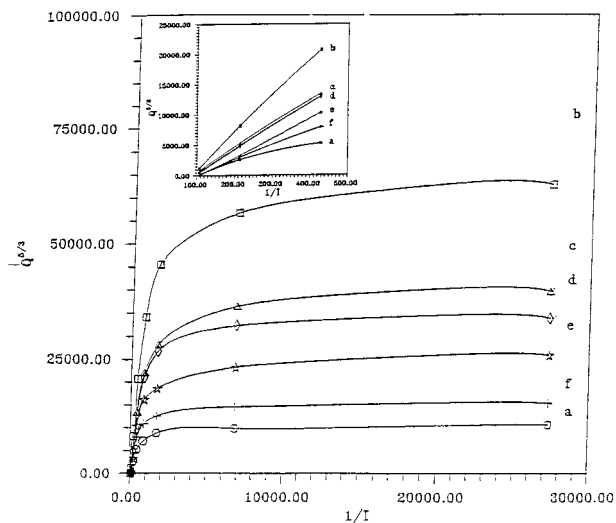


Figure 8 Absorbency plots against the ionic strength in CaCl_2 solution. (a) Ds 7; (b) Ds 8; (c) Ds 9; (d) Ds 10; (e) Ds 11; (f) Ds 12.

The influence of different cations with a common anion (Cl^-) on the water absorbency of SA-DMAPS xerogels is also investigated. Results obtained from the SA-DMAPS copolymeric gel systems show that the water absorbency decreases in the order $\text{Mg}_{(\text{aq})}^{2+} > \text{Ca}_{(\text{aq})}^{2+} > \text{Ba}_{(\text{aq})}^{2+}$ in the same ionic strength. This result is due to their cationic radius or their hydration force. The hydration radius grows as a result of the small cation surrounded with a large amount of water. In other words, the cationic charge density is low and the bonding ability to the carboxylate group is weak. The cation with a large radius therefore tends to enter the network and binds easily to the carboxylate groups.

Castel, Ricard, and Audebert¹⁶ reported that calcium ion can drastically decrease the swelling value for a hydrolyzed starch graft polyacrylonitrile, due to the complexing ability of the carboxylate group to induce the formation of intramolecular and intermolecular complexes. SA-HEMA gel systems, in our previous report, also showed similar results.²⁷ In order to understand the effect of DMAPS on the complexing ability for the SA-DMAPS systems, the said gels were immersed in various salt solutions, i.e., NaCl , CaCl_2 , FeCl_3 , and AlCl_3 , with various ionic strengths. Figures 9 and 10 summarize the results for SA gel (DS7 and DS8) and SA-DMAPS (DS7 and DS12) copolymeric gels, respectively. Those results demonstrate their tendency to be in various orders in different ranges of varying ionic strengths shown in Table III. The results shown in Table III dem-

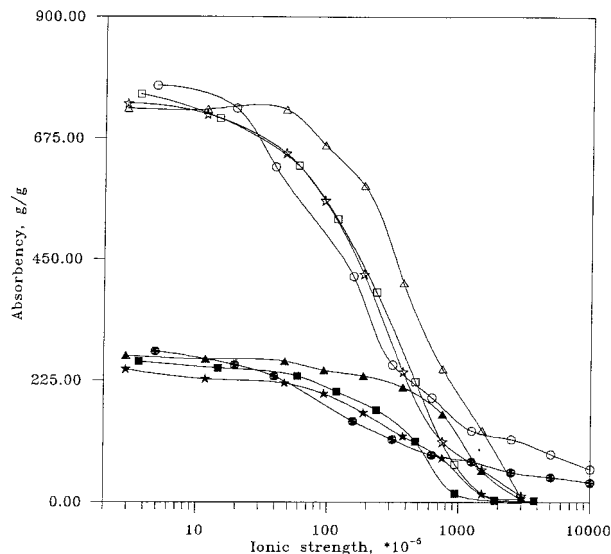


Figure 9 Absorbency obtained by suction method for crosslinked poly(SA-co-DMAPS) (Ds 7 and Ds 8) in various ionic strengths. (\bullet) Na^+ , Ds 7 (\blacksquare) Ca^{2+} , Ds 7 (\blacktriangle) Fe^{3+} , Ds 7 (\star) Al^{3+} , Ds 7; (\circ) Na^+ , Ds 8 (\square) Ca^{2+} , Ds 8 (\triangle) Fe^{3+} , Ds 8 (\star) Al^{3+} , Ds 8.

onstrate that the water absorbencies for the samples DS7 and DS12 have the same tendencies at various ranges of ionic strengths, i.e., $\text{Na}^+ > \text{Fe}^{3+} > \text{Ca}^{2+} > \text{Al}^{3+}$; $\text{Fe}^{3+} > \text{Ca}^{2+} > \text{Al}^{3+} > \text{Na}^+$; and $\text{Na}^+ > \text{Fe}^{3+} > \text{Al}^{3+} > \text{Ca}^{2+}$ in the ionic strength of $< 2 \times 10^{-4} \text{M}$, $2 \times 10^{-4} - 5 \times 10^{-3} \text{M}$, and 5

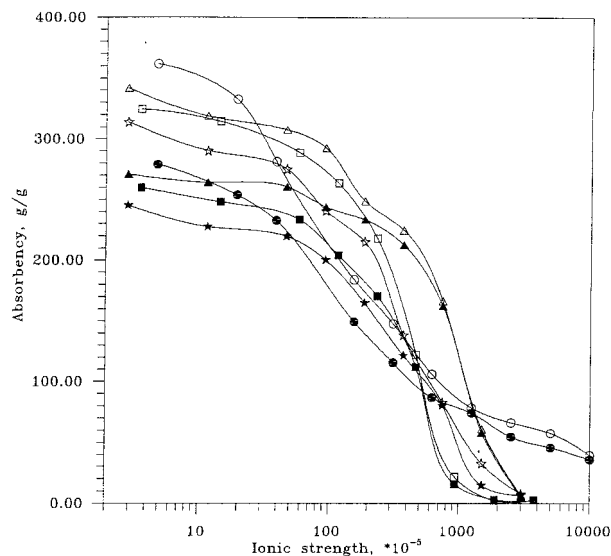


Figure 10 Absorbency obtained by suction method for crosslinked poly(SA-co-DMAPS) (Ds 7 and Ds 12) in various ionic strengths. (\bullet) Na^+ , Ds 7 (\blacksquare) Ca^{2+} , Ds 7 (\blacktriangle) Fe^{3+} , Ds 7 (\star) Al^{3+} , Ds 7; (\circ) Na^+ , Ds 12 (\square) Ca^{2+} , Ds 12 (\triangle) Fe^{3+} , Ds 12 (\star) Al^{3+} , Ds 12.

Table III Water Absorbency for Various Gels in Different Salt Cation Solutions

Sample	Ionic Strength			
	$< 2 \times 10^{-4}M$	$2 \times 10^{-4} \sim 5 \times 10^{-3}M$	$2 \times 10^{-3} \sim 5 \times 10^{-2}M$	$> 2 \times 10^{-2}M^a$
Ds 7	$Na^+ > Fe^{3+} > Ca^{2+} > Al^{3+}$	$Fe^{3+} > Ca^{2+} > Al^{3+} > Na^+$	$Na^+ > Fe^{3+} > Al^{3+} > Ca^{2+}$	$Na^+ > Fe^{3+} = Ca^{2+} = Al^{3+} = 0$
Ds 12	$Na^+ > Fe^{3+} > Ca^{2+} > Al^{3+}$	$Fe^{3+} > Ca^{2+} > Al^{3+} > Na^+$	$Na^+ > Fe^{3+} > Al^{3+} > Ca^{2+}$	$Na^+ > Fe^{3+} = Ca^{2+} = Al^{3+} = 0$
Ds 8	$Na^+ > Ca^{2+} > Al^{3+} > Fe^{3+}$	$Fe^{3+} > Al^{3+} > Ca^{2+} > Na^+$	$Na^+ > Fe^{3+} > Al^{3+} > Ca^{2+}$	$Na^+ > Fe^{3+} = Ca^{2+} = Al^{3+} = 0$

^aThe water absorbencies for sample Ds 7, Ds 8, and Ds 12 are reduced to zeros in ionic strength, for Ca^{2+} , Fe^{3+} , and Al^{3+} at $2 \times 10^{-2}M$, $3 \times 10^{-2}M$, and $3 \times 10^{-2}M$, respectively.

$\times 10^{-3} - 2 \times 10^{-2}M$, respectively. But water absorbency for DS8 has different tendency at the corresponding ionic strength, i.e., $Na^+ > Ca^{2+} > Al^{3+} > Fe^{3+}$; $Fe^{3+} > Al^{3+} > Ca^{2+} > Na^+$; and $Na^+ > Fe^{3+} > Al^{3+} > Ca^{2+}$ in the corresponding ionic strength's range. These results reveal that the same effect of multivalent cation solution on water absorbency is observed from higher ionic strength ($> 5 \times 10^{-3}M$). Similar results were also observed from our previous report and conformed to the formation constant of complexation.^{27,42} On the other hand, it is noted that the amount of water absorbency will influence the tendencies of the binding degree of multivalent cation to the carboxylate group on the gel in the lower ionic strength ($< 5 \times 10^{-3}M$, comparing DS8 with DS12).

Figures 9 and 10 also show the deswelling behavior of the polymeric gels (DS7, DS8, and DS12). The gel deswelling is apparently found to be in the range of the ionic strength of $2 \times 10^{-4} - 0.01M$ for the multivalent salt solution. This gel deswelling is more evident for the gel sample DS8 (Fig. 9). The phenomenon observed from our experiments is that the absorbents swelled first and then deswelled while the xerogels were immersed into high concentration multivalent cationic salt solution. This event can be explained by the fact that the swelling step corresponded to water entering the network fast by osmotic pressure difference and the deswelling step was related to the exchange of cations. The deswelling degree varied with exchange capacities of multivalent cations. In addition, the dried gel sample, which had once been immersed in high concentration multivalent cation solution, will never be reswelled in water. This occurrence can be attributed to the increase in crosslinking density arising from the complexation of the multivalent cations with the carboxylate groups. This behavior agrees with the consequence reported by Gugliemelli et al.⁴³ on the viscosity of hydrolyzed starch graft polyacrylonitrile dispersions in various salt solutions.

Effect of pH on Water Absorbency

The swelling behavior of the absorbent in various pH value solutions is investigated in this section. The absorbency keeps a rough constant from pH = 3 to pH = 11 and from pH = 4 to pH = 10 for poly(SA) gels and SA-DMAPS copolymeric gels, respectively (see Fig. 11). This behavior was explained by the buffer action of the sodium carboxylate group with acid or base in a previous pa-

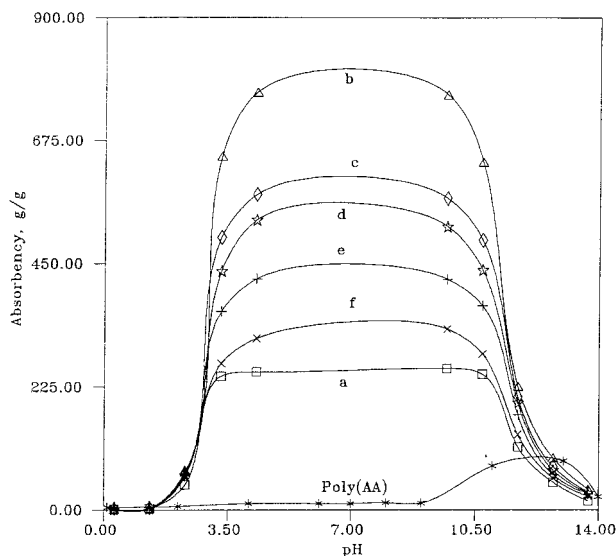


Figure 11 Retention between water absorbency and pH value.

per.²⁷ In our previous report, the SA-HEMA gel series revealed that the HEMA component (a non-ionic monomer) has no effect on the buffer action in various pH solutions. In contrast to the SA-DMAPS gel series, the DMAPS component exhibits some influence on the buffer action because the DMAPS monomer is a zwitterionic monomer. The buffer action disappears at the pH value < 4 and > 10 , and < 3 and > 11 for SA-DMAPS gel series and poly(SA), i.e., (DS7), respectively. As excess acid or base exists, their absorbency behaviors are confirmed by a crosslinked poly(acrylic acid). A scheme was presented in a previous paper.²⁷

Thermal Effect on Water Retention

The water retention for SA-DMAPS copolymeric gel series at 70°C is shown in Figure 12. The re-

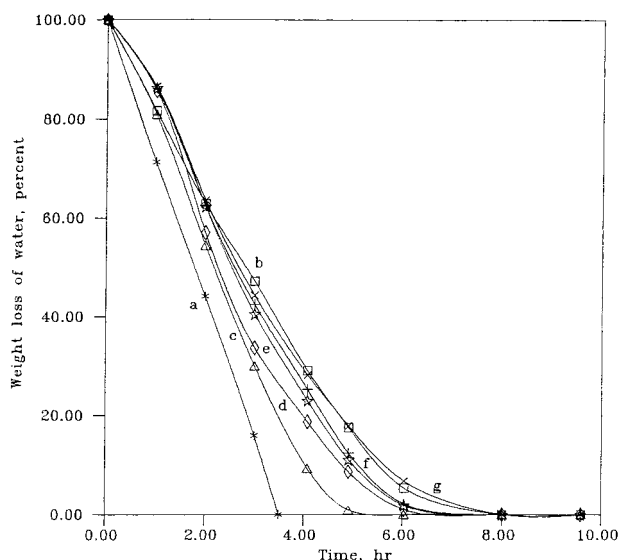


Figure 12 Water loss rate of swollen polymers at 70°C. (a) water; (b) Ds 7; (c) Ds 8; (d) Ds 9; (e) Ds 10; (f) Ds 11; (g) Ds 12.

sults show that the water retention capacity increases with an increase in the molar ratio of DMAPS (except DS7). This is because the DMAPS monomer has stronger hydrophilic ability induced by its hydrophilic groups. Meanwhile, the results also reveal that the loss rate of water is more rapid as water absorbency is higher. This is due to the a greater amount of free water on the interstice between the gel particles easily evaporized under thermal action. This interpretation is based on the DSC data.

Bound Water Determination

Three kinds of water (bounded water, half-bound water, and free water) identified from

Table IV Bound Water of Swollen Gels Determination. Parentheses Denote the Endothermic Peak under Saturated Absorbency

Sample No.	Contained Water, g/g Sample	ΔH , J/g	Pea, °C	FW + H-BW, g/g	BW, g/g
Ds7	4.06	660.1	3.68 (7.85)	1.98	2.08
Ds7.1	0.17	3.0	-9.44	0.01	0.16
Ds8	4.96	954.7	3.47 (7.66)	2.86	2.09
Ds9	4.03	675.5	4.61 (5.99)	2.05	2.00
Ds10	4.03	697.6	4.64 (7.75)	2.09	1.93
Ds11	4.90	976.9	5.11 (9.07)	1.93	1.97
Ds12	3.84	659.8	6.14 (8.88)	1.98	1.86

FW = Free water; H-BW = Half-bound water; BW = bound water.

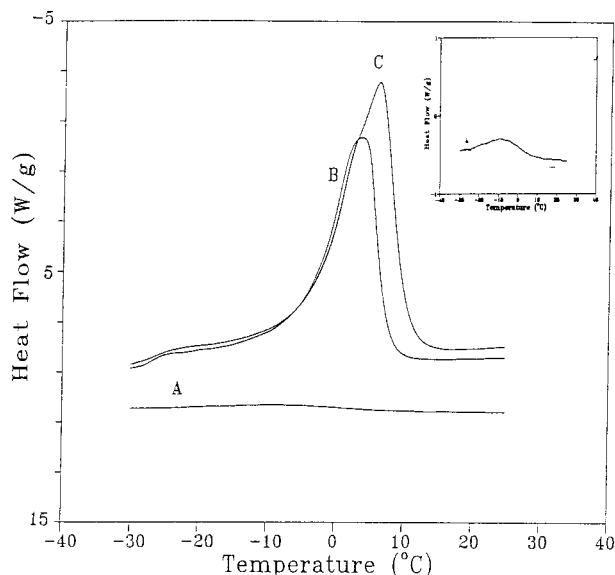


Figure 13 Typical DSC curves for (A) DS 7.1; (B) DS 7; and (C) DS 12.

NMR and DSC analysis were reported by Aisawa.⁴⁴ The partly DSC curves are shown in Figure 13 and the determined values are listed in Table IV. The information shown in Table IV demonstrates that the higher the water contained, the higher the temperature of endothermic peak (see Table IV, DS7 3.68°C and 7.85°C); and the decrease in the contained water of the gels will shift the endothermic peak to a lower temperature (comparing DS7.1 with DS7). The bound water is approximately equal to 2.0 g H₂O/g dried sample. This result apparently reveals that the bound water is not significantly affected by the introduction of the DMAPS into the SA gels, but the free water and the half-bound water may be affected (comparing DS7 with DS12).

CONCLUSIONS

The swelling behavior of these absorbents is related to their structure, their chemical composition, and the nature of external solutions. The water absorbency of poly(SA) series in deionized water or in 0.9 wt % NaCl solution would be effectively improved by copolymerizing SA with a small amount of zwitterionic monomer DMAPS. The deswelling behavior of these gels occurred as the ionic strength of the external salt solution increased, especially for the multivalent salt solutions. This deswelling behavior can be accounted for the complexation of multivalent cations with

the carboxylate group on the polymeric chain. The pH effect on water absorbency for this series of gels showed a narrower range of buffer action resulting from the addition of DMAPS into the gel. The bound water of poly(SA) gels is insignificantly affected by the introduction of DMAPS into the poly(SA) gels, as observed in DSC investigations.

Financial Support of this research by Tatung Institute of Technology, Taipei, Taiwan, ROC is gratefully acknowledged.

REFERENCES

1. F. L. Buchholz, *CHEMTECH*, September, 38 (1994). F. L. Buchholz and N. A. Peppas, Eds. *Superabsorbent Polymers: Science and Technology*, ACS Symposium Series 573.
2. T. Sakiyama, C. H. Chu, T. Fujii, and T. Yano, *J. Appl. Polym. Sci.*, **50**, 2021 (1993).
3. M. Yoshida, M. Asano, and M. Kumakura, *Eur. Polym. J.*, **25**, 1197 (1989).
4. T. Shiga, Y. Hirose, A. Okada, and T. Kurauchi, *J. Appl. Polym. Sci.*, **44**, 249 (1992).
5. T. Shiga, Y. Hirose, A. Okada, and T. Kurauchi, *J. Appl. Polym. Sci.*, **47**, 113 (1993).
6. K. Hogari and F. Ashiya, in *Advances in Superabsorbent Polymers*, American Chemical Society, Washington, D.C., 1994.
7. P. H. Ericksen, H. V. Nguyen, B. Oczkowski, and T. A. Olejnik, European Patent 40087 (1981).
8. T. Kobayashi, *Kobunshi* **36**, 612 (1987).
9. N. W. Taylor, G. F. Fanta, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **22**, 1343 (1978).
10. R. C. Burr, G. F. Fanta, and W. M. Doane, *J. Appl. Polym. Sci.*, **24**, 1384 (1979).
11. G. F. Fanta, R. C. Burr, W. M. Doane, and C. R. Russell, *J. Appl. Polym. Sci.*, **27**, 2713 (1982).
12. Y. Kejun and W. Benlian, *J. Appl. Polym. Sci.*, **41**, 3079 (1990).
13. G. F. Fanta, R. C. Burr, and W. M. Doane, *J. Appl. Polym. Sci.*, **24**, 2015 (1979).
14. M. Yoshinobu, M. Morita, and I. Sakata, *J. Appl. Polym. Sci.*, **45**, 805 (1992).
15. H. T. Lokhande, P. V. Varadarjan, and V. Iyer, *J. Appl. Polym. Sci.*, **45**, 2031 (1992).
16. D. Castel, A. Ricard, and R. Audebert, *J. Appl. Polym. Sci.*, **39**, 11 (1990).
17. I. Zoda, *Functional Materials*, **6**, 76 (1986).
18. K. Isomi, *Jpn. Kokai, Tokyo Koho JP*, 56,707 (1989).
19. K. Nagasuna, N. Suminaga, K. Kimura, and T. Shimomura, *Jpn. Kokai, Tokyo Koho JP*, 126,314 (1989).

20. H. Imada and M. Fujikawa, *Jpn. Kokai, Tokyo Koho JP*, 141,938 (1989).
21. A. Fujio, T. Komae, and Y. Yutaka, *Jpn. Kokai, Tokyo Koho JP*, 210,463 (1989).
22. S. Yada, T. Shibano, and K. Ito, *Jpn. Kokai, Tokyo Koho JP*, 215,801 (1990).
23. M. Sano, H. Mikamo, T. Suehiro, and N. Wakabayashi, *Jpn. Kokai, Tokyo Koho JP*, 258,839 (1991).
24. J. R. Gross, in *Absorbent Polymer Technology*, L. Brannon-Peppas and R. S. Harland, Eds., Elsevier Science Publishers, Amsterdam, 1990.
25. P. J. Flory, *Principle of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1953.
26. I. Ogawa, H. Yamano, and K. Miyogawa, *J. Appl. Polym. Sci.*, **47**, 217 (1993).
27. W. F. Lee and R. J. Wu, *J. Appl. Polym. Sci.*, **62**, 1099 (1996).
28. M. Ilavsky, *Macromolecules*, **15**, 782 (1982).
29. S. Kobayashi, K. D. Suh, Y. Shirokura, and T. Fujioka, *Polym. J.*, **21**, 971 (1989).
30. H. H. Hooper, J. P. Baker, H. W. Blanch, and J. M. Prausnitz, *Macromolecules*, **23**, 1096 (1990).
31. S. Kobayashi, H. Shirasaka, K. D. Suh, and H. Uyama, *Polym. J.*, **22**, 442 (1990).
32. N. Wada, Y. Yagi, H. Inomata, and S. Saito, *J. Polym. Sci. Part A: Polym. Chem.*, **31**, 2647 (1993).
33. D. Satyanarayana and P. R. Chatterji, *Polymer*, **34**, 3682 (1993).
34. D. G. Peiffer and R. D. Lundberg, *Polymer*, **26**, 1058 (1985).
35. D. J. Liaw and W. F. Lee, *J. Appl. Polym. Sci.*, **30**, 4697 (1985).
36. D. J. Liaw and W. F. Lee, *J. Appl. Polym. Sci.*, **34**, 999 (1987).
37. W. F. Lee and C. C. Tsai, *Polymer*, **35**, 2210 (1994).
38. W. F. Lee and C. C. Tsai, *Polymer*, **36**, 357 (1995).
39. W. F. Lee and C. C. Tsai, *J. Appl. Polym. Sci.*, **52**, 1447 (1994).
40. K. J. Buchanan, B. Hird, and T. M. Letcher, *Polym. Bull.*, **15**, 325 (1986).
41. J. J. Hermans, *Flow Properties of Disperse System*, Wiley Interscience, New York, 1953.
42. R. A. Day Jr. and A. L. Underwood, *Quantitative Analysis*, 6th ed., Prentice-Hall International, 1991, p. 64.
43. L. A. Gugliemelli, M. O. Weaver, C. R. Russell, and C. E. Rist, *J. Appl. Polym. Sci.*, **13**, 2007 (1969).
44. I. Aisawa, *Bull. Chem. Soc. Japan*, **44**, 2967 (1967).