Influence of Reaction Parameters on Water Absorption of Neutralized Poly(acrylic acid-*co*-acrylamide) Synthesized by Inverse Suspension Polymerization

SUDA KIATKAMJORNWONG,¹ PATTAMA PHUNCHAREON²

¹ Department of Photographic Science and Printing Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

² Multidisciplinary Program of Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, Bangkok 10330, Thailand

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ABSTRACT: Highly water-absorbing polymers of neutralized poly(acrylic acid-*co*-acrylamide) were synthesized in an effort to investigate the influences of reaction parameters on water absorption. In addition, the extent of water absorption and the absorption rate were studied to determine their relationship with the reaction parameters. This article explains the synthesis technique, characterization of the water-absorbing copolymers, and their properties. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1349–1366, 1999

Key words: neutralized poly(acrylic acid-*co*-acrylamide); inverse suspension; water absorption

INTRODUCTION

Highly water-absorbing polymers have drawn much interest since Fanta et al. at the Northern Regional Laboratory of the United States Department of Agriculture succeeded in grafting monomers onto starch and other polysaccharides, which yielded products with water absorption of several hundred to thousand times its dried weight. Research and development of highly water-absorbing polymers from starchbased polymers to petrochemical-based polymers, which are nonbiodegradable with a long service life, has been carried out for more than two decades. To synthesize the highly waterabsorbing polymers in a bead form, an inverse suspension process is generally used. In an inverse suspension polymerization, the aqueous monomer mixture is suspended in a hydrophobic oil phase. The suspended droplets of monomer solution strongly depend on the chemical and physical properties of the dispersing agents or on nonionic steric stabilizers blended to achieve an overall HLB of between 4 to 6, used to stabilize the suspension. This article investigates the reaction parameters and their influences on the acrylic acid-to-acrylamide ratio in copolymers, bead size, and water absorption behavior.

A series of copolymer superabsorbents was prepared by the following procedure.

Correspondence to: S. Kiatkamjornwong.

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EXPERIMENTAL

Total Concentration and Molar Ratio of the Monomer Solution Preparation of the Dispersed Phase

A predetermined amount of aqueous potassium hydroxide solution (Merck) was carefully added to the acrylic acid (99%, Siam Resin & Chemical), which was thermally controlled not to be heated above 40°C in order to obtain a 100% neutralized acrylic acid salt. Exact amounts of acrylamide (AM) (99%, Siam Resin & Chemical) were dissolved in the above-mentioned monomer solution in various molar ratios and total monomer concentrations at a fixed amount of a crosslinking agent (N,N'-MBA, Fluka). A specified amount of a thermal initiator [(NH₄)₂S₂O₈, from Merck], freshly dissolved in 2 cm³ of distilled water, was added in the monomer solution and stirred until a homogeneous mixture was obtained.

Preparation of the Continuous Phase

Distilled *n*-hexane (commercial grade, Rungsap Chemical) was selected as an organic phase. The organic phase containing an appropriate proportion of water in an oil-suspending agent (Span 80: Sorbitan monooleate, Kao) was prepared in a 500cm³, four-necked, round bottle flask fitted with a mechanical stirrer, a nitrogen gas inlet, a spiral reflux condenser, a drip funnel, and a thermometer and was heated to $60 \pm 1^{\circ}$ C using a water bath, stirring at 200 rpm while bubbling nitrogen gas over for a 15-min period. To obtain suitable reaction conditions, the set amounts of each chemical needed for different formulations were as listed in Table I.

Copolymerization

The mixed monomer solution was added dropwise at a predetermined flow rate (10 cm³ min⁻¹ to obtain an isothermal polymerization) into the continuous phase while being agitated at 200 rpm. The reaction was allowed to proceed for 2 h to ensure complete consumption of the monomers. The reaction was then stopped, and water was removed from the copolymer by stirring the reaction mass in 300-cm³ distilled methanol (commercial grade, Rungsap) in a 1000-cm³ beaker. The methanol solution was decanted, and a further 700 cm³ of fresh methanol was added to the reaction mass. The mixture was stirred overnight with a mechanical stirrer at same speed (200 rpm). The mixture was filtered and dried in an air oven at 70°C for 6 h. The dried reaction mass was ground and was separated into portions by sieve analysis.

This reaction procedure will henceforward be called the base procedure, and other procedures in this work involving changing some of the reaction parameters of the base procedure will be called modified reaction, as listed in Table I. These are the concentration of the crosslinking agent, the degree of neutralization of acrylic acid, the concentration of the initiator and the concentration of the suspending agent, and the type of the suspending agent.

Characterization of the Copolymer

The synthesized copolymers were investigated for their properties as follows.

Identification of Functional Groups of the Copolymers

The functional groups of the copolymers were investigated using a Fourier-transform infrared (FTIR) spectrophotometer (Perkin–Elmer infrared (IR) spectrophotometer, model 1760 X). The copolymer was ground with the dried KBr powder. The KBr disc was dried again and subjected to FTIR spectrophotometry.

Determination of Thermal Properties of the Copolymers

The copolymers were investigated with a differential scanning calorimeter (Du Pont, model DSC 2100) to study their thermal properties. The measurements were carried out over a temperature range of 50 to 350°C with a heating rate of 10°C min⁻¹ under the N₂ flow rate of 10 cm³ min⁻¹ with a sensitivity of $100/R_g$ 500 μV . The weight of the sample used was 15 to 25 mg.

Determination of Surface Morphology of the Copolymers

The surface morphology of the copolymers was investigated using a scanning electron microscope (SEM; model JSM-T 220A JEOL) without crosssectioning. The thickness of gold coated on the copolymers was 25 nm, and the SEM was operated with a 15 or 20 kV accelerating voltage.

				Modified Reaction for		
Material and Condition	Reaction Range	Crosslinker	Degree of Neutralization	Initiator	Suspendir	ıg Agent
Dispersion medium Total monomer conc	n-hexane $5-10$	<i>n</i> -hexane 5, 7, 10	<i>n</i> -hexane 5	<i>n</i> -hexane 5	<i>n</i> -hexane 5	n-hexane 5
Molar ratio of KA :	10:90-90:10	10:90-90:10	40:60,30:	40:60	40:60	40:60
Neutralization of acrylic acid	40 - 100	100	100, 76, 59, 46	100	100	100
Water : n -hexane	1:15	1:15	1:15	1:15	1:15	1:15
Suspending agent, Type % $w v^{-1}$	Span 40, 60, 80; 0.5–2.0	Span 80; 1.0	Span 80; 1.0	Span 80; 1.0	Span 80; 0.5, 1.0, 1.5, 2.0	Span 40, 60, 80; 1.0
$(NH_4)_2 S_2 O_8, g dm^{-3}$ (M)	$\begin{array}{c} 0.5-3.0\ 2.19 imes10^{-3}-10^{-3}-110^{-3}-110^{-2}\end{array}$	$\begin{array}{c} 1.4 \\ 6.14 \times 10^{-3} \end{array}$	$rac{1.4}{6.14 imes 10^{-3}}$	$\begin{array}{c} 0.5,1.0,1.4,1.8,2.2,2.6\\ (2.19,4.39,6.14,7.89,\\ 9.65,11.4)\times10^{-3} \end{array}$	$1.4 \ 6.14 imes 10^{-3}$	$\frac{1.4}{6.14 \times 10^{-3}}$
N,N'-MBA, mol % of monomer	0-0.075	0, 0.025, 0.05, 0.075	$0, 0.025, 0.05, 0.05, 0.075^{a}$	0.025	0.025	0.025
Polymerization	60	60	60	60	60	60
Polymerization time	2	2	2	2	2	2
(n) Agitation rate (rpm)	200	200	200	200	200	200

Table I Feature of Base Reaction and the Influencial Parameters

 $^{\rm a}$ The molar ratio of 30 : 70 of KA : AM was used in the presence of 0.075 mol % of $N,N'\text{-}{\rm MBA}.$

Determination of Copolymerization Ratios of the Monomer Concentrations

The copolymerization ratios of monomers were determined by an elemental analyzer, (model PE 2400 series 2 of Perkin–Elmer), which measures the percentage ratio of C, H, and N. The ratio of acrylamide and potassium acrylate was calculated using the number of moles according to C, H, and N in the copolymer from the analysis results.

Determination of Rheological Properties of the Copolymers

Copolymers synthesized at various crosslinking agent concentrations were examined regarding flow properties using a Brookfield viscometer, model RVT, at 25°C with a number 14 spindle and a speed of 5 rpm. The shear moduli of copolymers were calculated using the viscosity of the swollen gel.

Sample Preparation

An amount of 300 g of distilled water was added to 0.3 g of dry copolymer in a 600 cm³ glass beaker, and this was allowed to swell for 30 min. The completely swollen copolymer was filtered through a 100-mesh aluminum screen for 2 h, and the viscosity of the remaining swollen copolymer was measured.

Water Absorbency of the Copolymers

In Distilled Water

An amount of 150 g of distilled water was added to 0.1 g of the dry copolymer (A) in a 250-cm³ glass beaker, and this was allowed to swell sufficiently for 30 min. The completely swollen copolymer was filtered through a 100-mesh aluminum screen for 3 h, and the remaining swollen copolymer was weighed (B). The water absorbency was calculated by the equation shown below:

Water absorbency of copolymer

(g of water/g of dry copolymer) = (B - A)/A (1)

This will henceforward be called the base procedure of absorption.

In Salt Solutions

The base procedure of absorption was carried out, replacing distilled water with a series of sodium chloride, potassium chloride, potassium bromide, magnesium chloride, and calcium chloride solutions of 0.005, 0.05, 0.1, 0.3, 0.5, and 0.9% wt v^{-1} , respectively, in order to measure the extent of water absorption.

In Buffer Solutions

The base procedure of absorption was carried out with a series of buffer solutions ranging from pH 2 to 12 in place of distilled water at room temperature. The two buffer solutions were prepared by mixing 0.20M boric acid, 0.05M citric acid, and 0.10*M* tri-sodium phosphate (Na₃PO₄ \cdot 12H₂O), respectively. Anhydrous boric acid (12.37 g) and 10.51 g of citric acid monohydrate were dissolved in distilled water and diluted to 1000 cm^3 in a volumetric flask to make a 0.200*M* boric acid and a 0.05M citric acid solution. This is called Solution 1. Solution 2 was prepared by dissolving $38.01 \text{ g of Na}_3 PO_4 \cdot 12H_2O$ in distilled water, and it was diluted to 1000 cm³ in a volumetric flask to give a 0.10M sodium phosphate solution. To prepare a specific buffer solution (pH, solutions 1 and 2) were mixed at a specific volume based on Shugar and Dean.¹

Aqueous Absorbing Speed of the Copolymer

The speed at which the copolymer absorbs aqueous fluid is an important property. It is characterized by a "vortex test."² This test was performed and reported in seconds by the following procedure.

50 g of physiological saline solution, 90% aqueous solution of sodium chloride, and a stirring rod were placed in a 100-cm³ beaker, and the solution was stirred with a magnetic stirrer at a rate of 600 rpm. Into the beaker was charged 2.0 g of the highly water-absorbing resin, which later gelled by hygroscopic swelling. The gellation subdued the fluidity, precluding the agitation from inducing a swirl. The water-absorbing speed was expressed in terms of the time taken from the addition of water-absorbent resin until the cessation of swirl.

RESULTS AND DISCUSSION

Characterization the Functional Groups of the Copolymer by FTIR

The functional groups of the synthesized copolymer were investigated by FTIR. The result shows

	Total Monomer Concentration (Molar)							
	5M		7M		10 <i>M</i>			
Molar Ratio of KA : AM	Water Absorbency (g g ⁻¹)	Vortex Time (s)	Water Absorbency (g g ⁻¹)	Vortex Time (s)	$\begin{array}{c} \hline \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\$	Vortex Time (s)		
10:90	soluble	> 200	766 ± 116	89.20	soluble	78.79		
20:80	soluble	> 200	778 ± 146	63.41	645 ± 111	71.20		
30:70	59 ± 9	> 200	778 ± 56	50.48	762 ± 59	50.25		
40:60	1484 ± 403	59.31	825 ± 88	41.26	743 ± 51	39.80		
50:50	673 ± 181	35.21	617 ± 75	26.52	762 ± 45	30.84		
60:40	725 ± 47	33.55	$541\pm~35$	52.91	840 ± 128	30.40		
70:30	769 ± 175	27.31	478 ± 90	43.83	$576\pm~60$	21.61		
80:20	956 ± 360	29.30	$420\pm~64$	29.24	618 ± 77	20.27		
90:10	834 ± 239	26.41	365 ± 40	27.10	619 ± 16	15.82		

Table IIEffect of the Total Monomer Concentration and Molar Ratio of the Monomers on the WaterAbsorbency and Water Absorption Speed of the Synthesized Copolymer, in the Absence of the
Crosslinking Agent

that the FTIR spectrum of the synthesized copolymer is similar to those of poly(acrylic acid) and polyacrylamide. The spectrum of the copolymer confirms the existence of the carboxylate and carboxamide functionalities evidenced by the absorption peaks at 1560 and 1400 cm⁻¹, and 1610, 1660, and 3200 cm⁻¹, respectively.

Total Concentration, Molar Ratio of Monomer Solution, and Crosslinking Agent Concentration

Tables II–V show the results of the water absorbency test and the vortex test of the copolymer

beads synthesized by inverse suspension polymerization with various total concentrations of monomer solutions, molar ratios of monomer concentrations of potassium acrylate (KA), and acrylamide (AM), and the crosslinking agent concentrations.

The synthesized copolymers of AM and KA are swollen in water on account of the hydrophilic pendants (amide and carboxylate groups) in their structure. In particular, the synthesized copolymer with a 60 : 40 molar ratio of AM : KA and a total concentration of monomer solution of 5M at

Table III Effect of the Total Monomer Concentration and Molar Ratio of the Monomers on the Water Absorbency and Water Absorption Speed of the Synthesized Copolymer, in the Presence of the N,N'-MBA Crosslinking Agent, 0.025 mol % of Monomers

			Total	Monomer Conc	entration (M	Iolar)	
		5 <i>M</i>		7 <i>M</i>		10M	
Molar Ratio of KA : AM in Feed	Molar Ratio ^a of KA : AM in Copolymer	$\begin{array}{c} Water \\ Absorbency \\ (g \ g^{-1}) \end{array}$	Vortex Time (s)	$\begin{array}{c} Water \\ Absorbency \\ (g \ g^{-1}) \end{array}$	Vortex Time (s)	$\begin{array}{c} Water \\ Absorbency \\ (g \ g^{-1}) \end{array}$	Vortex Time (s)
10:90 20:80	10.76:89.24 19.06:80.95	456 ± 30 629 ± 22	39.38 35.13	232 ± 4 305 ± 9	44.28	201 ± 15 299 + 24	42.14
30:70 40:60	25.56:74.43 37 79 · 62 21	661 ± 78 775 ± 99	29.95 21.41	417 ± 20 429 ± 15	22.56 25.10	405 ± 11 499 ± 28	31.10 26.23
50:50 50:50 60:40	43.12:56.88 52.85:47.15	525 ± 28 612 ± 22	25.54 42.74	512 ± 25 487 ± 39	26.58 30.94	400 ± 20 410 ± 31 401 ± 46	23.19 19.93
70 : 30 80 : 20	63.25:36.75 77.57:22.43	575 ± 72 584 ± 31	23.07 20.17	457 ± 43 374 ± 21	34.84 24.52	375 ± 29 350 ± 24	18.65 19.93
80:20 90:10	77.57:22.43 87.89:12.10	$584 \pm 31 \\ 582 \pm 27$	$\begin{array}{c} 20.17\\ 18.24 \end{array}$	$\begin{array}{c} 374 \pm 21 \\ 356 \pm 19 \end{array}$	$\begin{array}{c} 24.52\\ 19.43\end{array}$	$350 \pm 24 \\ 342 \pm 14$	19.93 17.38

^a The molar ratio of KA : AM was checked by elemental analysis.

	Total Monomer Concentration (Molar)							
	5M		7M		10 <i>M</i>			
Molar Ratio of KA : AM	Water Absorbency (g g ⁻¹)	Vortex Time (s)	Water Absorbency (g g ⁻¹)	Vortex Time (s)	$\begin{tabular}{c} \hline & \\ \hline & \\ Absorbency (g \ g^{-1}) \end{tabular} \end{tabular}$	Vortex Time (s)		
10:90	335 ± 1	43.21	179 ± 4	44.85	97 ± 2	41.21		
20:80	447 ± 26	40.83	255 ± 9	40.21	169 ± 11	36.61		
30:70	537 ± 53	33.20	276 ± 31	39.86	185 ± 12	30.24		
40:60	568 ± 27	28.35	244 ± 4	17.81	159 ± 3	27.36		
50:50	558 ± 50	18.38	270 ± 19	11.48	$215\pm~2$	23.19		
60:40	544 ± 55	22.97	244 ± 2	37.71	145 ± 2	20.76		
70:30	519 ± 92	16.19	233 ± 1	14.96	170 ± 3	14.21		
80:20	386 ± 21	14.80	226 ± 3	11.31	143 ± 2	12.34		
90:10	319 ± 4	14.21	204 ± 4	10.76	133 ± 5	8.43		

Table IV Effect of the Total Monomer Concentration and Molar Ratio of the Monomers on the Water Absorbency and Water Absorption Speed of the Synthesized Copolymer, in the Presence of the N,N'-MBA Crosslinking Agent, 0.05 mol % of Monomers

0.025 mol % crosslinking agent, N,N'-MBA, produced water-insoluble beads with the high waterabsorbency value of 775 times its dry weight and a high water absorption speed (21.41 s). The water absorption ability and the water absorption speed decreased with increasing total monomer concentration and crosslinking agent concentration because chain transfer to polymers was increased with the monomer concentration, especially at a high extent of conversion, and this results in increasing branching and selfcrosslinking reactions that affect product properties.³ Additionally, high monomer concentrations provide unfavorable percentages of soluble polymers. Although the reaction time was as long as 2 h, residual monomers in the final products were found by water extraction.

As mentioned above, the copolymers crosslinked with N,N'-MBA of 0.025 mol % gave a high absorbency of 775 g g⁻¹ along with a high gel strength by sacrificing water absorption; that is, the extent of water absorption is lower than for the water absorbing copolymers synthesized in the absence of the crosslinking agent (1484 g g⁻¹;

Table V Effect of the Total Monomer Concentration and Molar Ratio of the Monomers on the Water Absorbency and Water Absorption Speed of the Synthesized Copolymer, in the Presence of the N,N'-MBA Crosslinking Agent, 0.075 mol % of Monomers

	Total Monomer Concentration (Molar)						
	5M		7M		10M		
Molar Ratio of KA : AM	Water Absorbency (g g ⁻¹)	Vortex Time (s)	$\begin{tabular}{c} \hline & \\ & Water \\ & Absorbency \ (g \ g^{-1}) \end{tabular} \end{tabular}$	Vortex Time (s)	Water Absorbency (g g^{-1})	Vortex Time (s)	
$10:90 \\ 20:80 \\ 30:70 \\ 40:60 \\ 50:50 \\ 60:40 \\ 70:30 \\ 20$	269 ± 12 439 ± 9 476 ± 15 519 ± 32 471 ± 8 385 ± 7 484 ± 14 492 ± 5	28.19 23.59 21.89 16.70 23.51 18.53 21.48	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$29.14 \\ 25.81 \\ 25.87 \\ 21.89 \\ 15.14 \\ 40.21 \\ 16.31 \\ 15.74$	$61 \pm 2 \\ 86 \pm 4 \\ 121 \pm 3 \\ 158 \pm 13 \\ 140 \pm 21 \\ 123 \pm 15 \\ 104 \pm 20 \\ 08 \pm 14$	27.23 26.28 24.17 20.93 21.11 18.37 15.21	
$80:20 \\ 90:10$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{c} 18.26\\ 13.41 \end{array}$	$\begin{array}{rrr} 296 \pm & 2 \\ 275 \pm 17 \end{array}$	$\begin{array}{c} 15.74 \\ 14.38 \end{array}$	$\begin{array}{c} 98 \pm 14 \\ 91 \pm 5 \end{array}$	$\begin{array}{c} 13.49 \\ 10.93 \end{array}$	

see Table II) because the formation of more crosslinks lowers the swelling of the gel. In general, crosslinking agents have been employed to help improve the gel strength of the swollen gel, but they are also very effective in reducing the water absorbency.

The critical molar ratio of AM : KA at 60 : 40 produced the optimum superabsorbent polymer; this indicates that one of the side reactions could be the crosslinking of the copolymer with an appropriate crosslinking agent, whose concentration is 0.025 mol % of monomers. The copolymerization reactivity ratios of KA and AM are 1.35 and 0.78, respectively;⁴ and the glass transition temperature of potassium acrylate is 194°C, which is higher than that of acrylamide, 165°C.^{4,5} When the copolymers contain higher amount of acrylate units, water absorption decreases, especially in the case of incorporating the crosslinking agent (Tables III–V).

The water absorbency ability of the all synthesized copolymers containing various ratios of monomers of KA and AM, in the absence of the crosslinking agent, was higher than those with the crosslinking agent because the former contained both soluble and insoluble beads with poor gel strength. The noncrosslinked portion dissolves in water. The insolubility of the copolymer is possibly due to the formation of a gel in the absence of any crosslinking monomer, which may be explained by the following side reactions.

- 1. Polymerizing highly concentrated solutions of acrylic acid may cause autocrosslinking through a hydrogen abstraction from the polymer backbone, followed by radical combination.^{6,7}
- 2. Chain transfer to polymer may occur during the polymerization.³
- 3. The occurrence of imidization that usually takes place in the polymerization of acrylamide in concentrated solution and at high temperature and pH.⁸ The imidization of the amide pendants in the copolymer is shown in eq. (2).

The absorbency of crosslinked polymers can be explained in term of swelling. Swelling is a diffusion phenomenon driven by the affinity of the molecules of the swelling material for the molecules of the contracting fluid. The swelling equilibria of ionized hydrogels are determined by a balance of three main forces,^{9,10} as follows:



- 1. The free energy of mixing of the network chains with solvent,
- 2. the net osmotic pressure within the network, resulting from the mobile counterions surrounding the fixed-charge groups (ion swelling pressure), and
- 3. the elastic retractile response of the network (elastic swelling pressure).

Forces (1) and (2) favor hydrogel swelling, while force (3) opposes it. A classical crosslinked network has a swelling limit controlled by a balance between the thermodynamic forces due to polymer-solvent interactions and the entropic force of coiled polymer chains.

The swelling equilibrium is dependent on the entropy of dilution, the heat of dilution, and the entropy of the polymer network. For a given polymer–solvent system, the equilibrium swelling is a function of the crosslink density. The relationship involving the equilibrium swelling ratio Q, defined as the ratio of the final swollen volume to the original unswollen volume of the network, was derived by Flory.¹¹ If the crosslink density is not too high and the solvent is a good solvent, the following approximate relationship was obtained:

$$Q^{5/3} = \frac{(1/2 - \chi_1)^2 \bar{M}_c}{\nu_1 \rho_0 v_{i,r}^{2/3} (1 - 3\bar{M}_c / \bar{M}_n)}$$
(3)

where χ_1 is the polymer-solvent interaction parameter, v_1 is the molar volume of solvent, $v_{\underline{i},r}$ is the polymer volume fraction at crosslinking, M_c is the molecular weight of the polymer chain between crosslinks, and \overline{M}_n is the initial molecular weight of the noncrosslinked polymer, and ρ_0 is the density of the polymer as prepared.

The parameter that describes the basic structure of the hydrogel is the molecular weight between crosslinks, \bar{M}_c . This parameter defines the average molecular size between two consecutive junctions regardless of the nature of those junctions. An additional parameter of importance in the structural analysis of hydrogels is the

	W	ater Absorbency Capacity (g g	g ⁻¹)
of Acrylic Acid (%)	0.025 mol % N,N'-MBA	0.05 mol % N,N'-MBA	0.075 mol % N,N'-MBA
100	775 ± 99	568 ± 27	476 ± 15
76	581 ± 18	557 ± 51	471 ± 42
59	570 ± 68	523 ± 39	428 ± 28
46	507 ± 59	476 ± 17	447 ± 14

Table VIEffect of the Neutralization Degree of Acrylic Acid at Various Crosslinking AgentConcentrations on Water Absorbency of the Synthesized Beads

crosslinking density ρ_x , which is related to M_c , as defined by eq. (4).

$$\rho_x = 1/(v\bar{M}_c) \tag{4}$$

where ν is the specific volume of the polymer. From eqs. (3) and (4), the equilibrium swelling ratio Q is inversely related with the crosslink density ρ_x .

Basically, increasing the molar percent of the crosslinking agent to the monomer, the crosslink density ρ_x (mol cm⁻³) increases. For the effects of N,N'-MBA on crosslinking behavior of the superabsorbent in terms of water absorbency, as increasing the crosslinking agent concentration, $v_{i,r}$ values are expected to become larger, and \bar{M}_c should also be higher. This will reduce the Qvalues, as shown by the water absorbency of the crosslinked superabsorbent at all ratios of KA : Am and at three monomer concentrations of Tables II-IV. At a certain degree of ionization, the molar percentage of the crosslinking agent to the monomer determines the equilibrium water-absorbing capacity of the absorbent. At a high total monomer concentration, such as at 10M, the solubility of crosslink agent is typically not very water soluble, often increasing with monomer concentration due to the increasing organic content of the monomer phase. In the absence of crosslinking agent at a certain total monomer concentration, soluble gel was obtained at a high ratio of acrylamide (80-90%; see Table II). Increasing the potassium acrylate concentration increases the gel fraction of the absorbent to retain high water absorbency; a higher crosslinking concentration (0.025 mol %) is thus needed. Such an increase in crosslinking agent concentration, to some extent, reduces the water absorption value due to higher crosslinking sites. The higher the total monomer concentration (7-10M), the lower the water absorption. This is due to many short kinetic chains leading to more concentrated low molecular weights of two homopolymers and copolymers. Buchholz and Burgert¹² elucidated the effect of the crosslinking agent on superabsorbent properties. The concentrations we used in the present work are less than 0.5 mol % of the monomer, and MBA is naturally a high relative reactivity that may lead to its early depletion during copolymerization. They concluded that the polymer chain formed in a later stage of the polymerization can then lack the crosslinking agent. This fact contributes to amount of soluble polymer. Some low-molecular-weight polymers can be extracted by water. For a Vortex time, the higher the KA, the lower the gel strength, and the shorter the vortex time. The higher the KA content in the copolymer, the lower the viscosity due to the better solubility in aqueous droplets.

Neutralization Degree of Acrylic Acid

Table VI shows the water-absorbing capacity of the crosslinked copolymers synthesized with a 60 : 40 molar ratio of AM : KA by 1.4 g L^{-1} (6.14 $\times 10^{-3}M$) (NH₄)₂S₂O₈, 1% w v⁻¹ of organic phase, and Span 80 at various neutralization degrees of acrylic acid and crosslinking agent concentrations. The crosslinked copolymer of potassium acrylate (KA) and acrylamide (AM) gave the optimum result for 100% neutralized poly(acrylic acid) with a water absorbing capacity of 775 g g^{-1} at 0.025 mol % N,N'-MBA. Higher degrees of neutralization increase the concentration of acrylic acid in the form of its salt in the aqueous phase, but simultaneously lower the solubility of the crosslinking agent in the organic phase, leading to less crosslinking sites on the chains. The waterabsorbing capacity decreased with decreasing neutralization degree of acrylic acid. The low neutralized poly(acrylic acid), having many free, nonneutralized carboxylic functionalities, cause au-

Initiator Concentration, $(g L^{-1})$ of Aqueous Phase	% Water Absorbency (g g ⁻¹)	Vortex Time (s)
	no reaction 701 ± 84 775 ± 99 678 ± 25 666 ± 29 661 ± 77	$\begin{array}{c}$

Table VIIEffect of the Concentration of theInitiator on Water Absorption Capacity ofSynthesized Copolymer Beads

tocrosslinking through hydrogen abstraction from the polymer backbone, followed by radical combination.^{6,7}

Concentration of the Initiator

The effect of $(NH_4)_2S_2O_8$ concentration for inverse suspension copolymerization of AM : KA on absorption properties is shown in Table VII.

The copolymers synthesized by 1.4 g L^{-1} (6.14 $\times 10^{-3}M$ (NH₄)₂S₂O₈ gave the optimum result, which has the highest water absorbency. Table VIII shows that the water-absorbing capacity of the copolymers increased with increasing initiator concentrations up to an optimum result at 1.4 g L⁻¹ (6.14 × 10⁻³M) (NH₄)₂S₂O₈, and then decreased with increasing initiator concentration. Based on general kinetics, the rate of polymerization depends on the concentration of monomers and initiators for a bimolecular termination. The persulphate ions $(S_2O_8^{2-})$ in aqueous solution, when heated alone or in the presence of a reducing agent, decompose to sulphate radical ions (SO^{4-}) . These primary radicals will initiate the monomers to form free radicals of monomers, which propagate monomer molecules in succession to form a large polymeric radical and a dead polymer in the termination step. The rate of polymerization at a low concentration of persulphate ions, that is, a low quantity of free radicals so produced, is slower than at a high concentration. At a high concentration of persulphate ions, high quantities of produced free radicals may cause a chain transfer to polymers,³ so the synthesized copolymer has a high crosslink density, which affects the water absorbency capacity.

Concentration of the Suspending Agent

The optimum conditions for synthesizing the copolymers, which were selected to study other effects on the water absorbency, are a 60 : 40 molar ratio of AM : KA, a total monomer concentration of 5*M* with the crosslinking agent concentration of 0.025 mol % of monomers, 1.4 g L⁻¹ (6.14 $\times 10^{-3}M$) (NH₄)₂S₂O₈, and 100% neutralization of acrylic acid. In this section, the synthesized copolymers were produced by the fixed conditions, as in the early section, but with various concentrations of the suspending agent (Span 80), as shown in Table VIII. The shape of particles produced in suspension processes can be affected by the viscosity of monomer phase, while the size of particles is controlled by the hydrophilic–lipophilic balance HLB values of each particular type of the suspending agent.

The optimum suspending agent concentration was $1.0\% w v^{-1}$ of the organic phase to give the copolymer, which has the highest water absorbency (775) with a shorter vortex time of 21 s. The results given in Table VIII show that the waterabsorbing capacity of copolymer beads is dependent on the concentration of the suspending agent. Two effects may be responsible for the following results:⁵ (1) The level of grafting reaction of the suspending agents onto the particle surface, and (2) the particle size. If the suspending agent was grafted onto the particle surface, then the hydrophobic polymeric layer might retard water penetration and reduce the water-absorbing capacity. For the effect of particle size on water absorption, the smaller average particles obtained by Span 80 (76 μ m) have a higher water absorption, the detail of which shall be described in the following section.

Type of the Suspending Agent

Table IX shows the water absorbency of the copolymer beads, synthesized by a 60 : 40 molar ratio of AM : KA with 1.4 g L^{-1} (6.14 × 10⁻³M)

Table VIII	Effect of t	the Sus	spending Ag	gent
Concentrat	ion on the	Water	Absorbency	of the
Synthesized	d Beads			

Suspending Agent, Span 80, % $w v^{-1}$ of Organic Phase	% Water Absorbency (g g ⁻¹ Dry Polymer)	Vortex Time (s)
0.5	607 ± 24	33.02
$1.0 \\ 1.5 \\ 2.0$	$775 \pm 99 \\ 570 \pm 65 \\ 606 \pm 25$	21.41 28.04 27.10

Type of Suspending Agent	Surface Tension in <i>n</i> -Hexane $(mN m^{-1})$ at 27°C	% Water Absorbency (g g ⁻¹)	Vortex Time (s)
Span 40	45	664 ± 40	20.34
Span 60	34	688 ± 52	27.02
Span 80	31	775 ± 99	21.41

Table IX Effect of the Type of Suspending Agent on Water Absorbency

 $(\mathrm{NH}_4)_2\mathrm{S}_2\mathrm{O}_8$, 1% $w~v^{-1}$ suspending agent, and 0.025 mol % *N*,*N'*-MBA for various types of suspending agents. The synthesized beads gave the optimum product properties with Span 80 surfactant as the suspending agent with a water absorbency value of 775 $g~g^{-1}$.

The type and concentration of the suspending agent affect the particle size of synthesized copolymer beads.⁵ While the HLB numbers of acryl-amide–potassium acrylate monomer mixtures were between 9 and 10, the HLB numbers of the suspending agents (Span series), which resulted in successful inverse suspension polymerization recipes, were in the range between 4 and 7. They are Span 80 (sorbitan monooleate), Span 60 (sorbitan monopalmitate) with the HLB values of 4.3, 4.7, and 6.7, respectively.

When different suspending agents were used in the inverse suspension polymerization, the particle size of the suspending beads varied with their stabilization efficiency, as shown in Figure 1. The average particle size increased with increasing HLB values of the suspending agents. This is related to the decreasing water absorbency capacity of synthesized copolymer beads, that is, Span 40 (133 μ m) < Span 60 (101 μ m) < Span 80 (76 μ m). This result is in contrast with the fact that the particle size of the suspending beads depends on their stabilization efficiency, from which we would expect the size to increase with decreasing HLB number due to decreasing stabilization efficiency. The effects that may be responsible for this result are considered to be chemical and physical properties and surface tension of suspending agents in *n*-hexane, as shown in Tables IX and X. From Table X, since Span 40 has the highest hydroxyl value, it might have an effect on the level of grafting of the suspending agent onto the particle surface, so the hydrophobic polymeric layer could retard water penetration.⁵ In addition, the solubility of Span 80 in *n*-hexane is better and insoluble in water, giving better drop properties than those of Span 40 and







Figure 1 SEM of copolymer beads, synthesized by (a) Span 80, (b) Span 60, (c) Span 40.

							Solubility ^b ((10% sol; 25°C)
Product Name	Chemical Name	Acid Value ^a	Sponification Value ^a	Hydroxyl Value	HLB	Water	Ethanol	N-Hexane	Xylene
Span 40	Sorbitan monopalmitate	7.5 max	140–150	275–305	6.7	Н	D	Н	S
Span 60	Sorbitan monostearate	5-10	147 - 157	235-260	4.7	Η	D	Н	S
Span 80	Sorbitan monooleate	5.5 - 7.5	149–160	193–209	4.3	Ι	S	S	S

Table X The Chemical and Physical Properties of Suspending Agents

^a Milligrams of KOH that react with 1 g of the sample.

^b Solubility: S, totally soluble; H, hazy; I, insoluble; D, slightly soluble.

Span 60, which is confirmed by the measured surface tension values, which are 31, 45, and 34 mN m⁻¹ at 27°C, respectively. Thus, the suspension droplet size of Span 80 suspending agent is smaller than others, giving more surface area and resulting in the high water absorbency capacity. Note that the present experiment uses a lower amount of dispersing agent (1% $w v^{-1}$ of the organic phase), whereas polymerizations carried out elsewhere used 2–5 wt % for an inverse microemulsion system, due to the stability problem.¹³

Buffer Effect on the Swelling Behavior

Table XI gives the preparative buffer solutions along with their ionic strengths.¹ Table XII shows the influence on the water absorbency of the solution pH (2–12) on the water absorption capacity of the synthesized copolymers produced by inverse suspension polymerization at a total monomer concentration of 5*M* and at various molar ratios of AM : KA with 0.025% *N*,*N'*-MBA, 1% $w v^{-1}$ Span 80, 1.4 g L⁻¹ (6.14 \times 10⁻³*M*)

Table XI Ionic Strength of Buffer Solution at Various pHs at 25°C

Desired pH	$\begin{array}{c} \text{Solution 1} \\ (\text{cm}^3) \end{array}$	$\begin{array}{c} \text{Solution 2} \\ (\text{cm}^3) \end{array}$	Ionic Strength (mol ion ^{-1} dm ^{-3})
2	97.5	2.5	0.1866
3	88.0	12.0	0.1762
5	67.0	33.0	0.1521
7	49.5	50.5	0.1243
9	34.5	65.5	0.1048
11	22.0	78.0	0.0886
12	8.5	91.5	0.0711

 $(\rm NH_4)_2S_2O_8$ and 100% neutralization of acrylic acid in a sodium salt of citrate–phosphate–borate buffer solution system.

The swelling capacity of the copolymer beads is very dependent on the pH and composition of the absorbed liquid. The table shows that the absorbency of synthesized copolymer beads of various molar ratios of AM : KA reaches a maximum at pH 5. The swelling of copolymer beads was found to increase significantly from pH 2 to 5, and remained relatively constant afterwards. Swelling in a high portion of phosphate buffer (a higher volume of solution 2 or higher pHs) is greater than swelling in a citrate buffer.

Normally, hydrogels are also classified into three categories by their ionic character.¹⁴ In particular, anionic hydrogels prepared by the copolymerization of acrylic acid are most important for industrial products that are used widely as superabsorbents. Cationic hydrogels, however, have not been developed much as industrial products. Nonionic hydrogels are also very useful since they can absorb water over a wide range of pH and there is no ionic interaction between the solutes in a water and gel matrix.

Sodium cations in a citrate-phosphate-borate buffer can interact with anions on the network, thus decreasing the charge density of anions on the network and retarding the ion exchange between H^+ ions from inside and outside the gel network. The water absorption is far below than that in distilled water because of the ionic content.

The theoretical framework developed to describe the equilibrium swelling characteristics of networks includes the Flory–Rehner model, the Peppas–Merrill model, and the Peppas–Luchy model.¹⁵ For the developed model for the anionic

	% Water Absorbency (g g^{-1})							
Molar Ratio AM : KA								
	pH 2	pH 3	pH 5	pH 7	pH 9	pH 11	pH 12	In Distilled Water
10:90	14	35	59	62	61	61	62	582
30:70	11	25	72	75	70	65	69	575
50:50	9	20	63	63	59	61	65	525
60:40	4	14	59	59	55	58	56	775
80:20	25	26	53	55	50	48	50	629
90:10	27	23	35	38	35	34	38	456

Table XII Effect of pH on Swelling Behavior of Copolymer Beads at 25°C

polymeric network interacting crosslinked with solvents present and exhibiting a non-Gaussian chain length distribution, the complete equilibrium expression is shown in eq. (5), as follows:

$$\begin{split} \frac{V_1}{4I} & \left(\frac{\upsilon_{2,s}}{\bar{\upsilon}}\right)^2 \left(\frac{K_a}{10^{\text{pH}} + K_a}\right)^2 \\ &= \left(\ln(1 - \upsilon_{2,s}) + \upsilon_{2,s} + \chi_1 \upsilon_{2,s}^2\right) \\ &+ \frac{(V_1/\bar{\upsilon}\bar{M}_c)(1 - (2\bar{M}_c/\bar{M}_n))\upsilon_{2,r}((\upsilon_{2,s}/\upsilon_{2,r}))^{1/3}}{-(1/2(\upsilon_{2,s}/\upsilon_{2,r})))(1 + (1/N(\upsilon_{2,s}/\upsilon_{2,r}))^{1/3})^2}{(1 - (1/N)\upsilon_{2,s}^{2/3})^3} \end{split}$$

$$(5)$$

where v_1 is the molar volume of the swelling agent; I, the ionic strength of the swelling solution; $v_{2,s}$, the polymer volume fraction in the equilibrium-swollen polymer; $v_{2,r}$, the polymer volume fraction in the so-called relaxed polymer state; χ_1 , the Flory polymer–solvent interaction parameter; K_a , the ionization of the ionizable group of the swellen polymer; pH, the acidity–basicity of the swelling solution; N, the effective number of bond vectors between consecutive crosslinks; \overline{M}_n , the number-average molecular weight before crosslinking; \overline{M}_c , the number-average molecular weight between crosslinks; and v, the specific volume of the polymer.

Based on eq. (5) the molar volume of the swelling agent should increase with increasing pH of the solution. As shown previously, the swelling equilibria of ionized hydrogels are determined by a balance of three primary forces. The main forces that favor hydrogel swelling are the free energy of mixing of the network chains with solvents and the ionic osmotic pressure generated from mobile counterions to charged ions in the network (Donnan equilibrium).¹⁶ For this result, the latter force is plausibly explained as follows.

The simplest of the theories attribute the ion swelling pressure to the difference between the osmotic pressure of free ions in the gel and the outer solution. The distribution of the ions between the gel and the outer solution forms the Donnan equilibrium. Within this theory, the ionic forces depend only on the ionic composition of the solvent and on the concentration of fixed ionizable groups in the gel but not on the properties of the neutral network.¹⁶

The external pH has a profound effect on the balance of forces that determine equilibrium swelling in these gels. The molar ratio of AM : KA in hydrogel, which gives the optimum swelling, should be 90 : 10. As the pH is lowered to the strongly acidic region, the carboxylate side chains of the potassium acrylate become hydrolyzed to be the carboxylic group, thus decreasing the charge density of anions on the network. The concomitant decreases in mobile counterion content of the network sharply decrease the internal osmotic pressure, which retards the observed swelling transitions.

The opposite behavior occurs in the weakly acidic and basic solutions in the pH range of 5–12. Upon increasing the pH, the concentration of the base cations in the outer solution and the concentration of the base anions inside the network will also increase. Those cations will be attracted into the gel to balance the osmotic pressure occurring from the anions of base-hydrolyzed acrylamide and carboxylate groups. Those cations will replace the mobile H^+ ions. The gel, of course, acts as an ion exchanger. New H^+ ions will be supplied by water. The concentration of mobile ions in the

Concentration of		Water Absorbency (g H_2O/g Dry Polymer)						
Salt Solution $(\% \ w \ v^{-1})$	NaCl	KCl	KI	KBr	MgCl_2	CaCl_2		
0.000 0.005 0.05 0.1 0.3 0.5 0.9	$\begin{array}{c} 775 \pm 99 \\ 570 \pm 20 \\ 212 \pm 7 \\ 154 \pm 5 \\ 93 \pm 4 \\ 75 \pm 0.6 \\ 60 \pm 0.2 \end{array}$	$\begin{array}{r} 775 \pm 99 \\ 551 \pm 42 \\ 244 \pm 10 \\ 178 \pm 5 \\ 109 \pm 4 \\ 87 \pm 2 \\ 68 \pm 0.9 \end{array}$	$\begin{array}{r} 775 \pm 99 \\ 562 \pm 20 \\ 334 \pm 17 \\ 244 \pm 5 \\ 154 \pm 4 \\ 123 \pm 2 \\ 98 \pm 0.9 \end{array}$	$\begin{array}{r} 775 \pm 99 \\ 548 \pm 34 \\ 299 \pm 22 \\ 208 \pm 3 \\ 132 \pm 0.4 \\ 105 \pm 3 \\ 81 \pm 2 \end{array}$	$\begin{array}{r} 775 \pm 99 \\ 547 \pm 13 \\ 109 \pm \ 0.7 \\ 80 \pm \ 2 \\ 37 \pm \ 1 \\ 25 \pm \ 2 \\ 19 \pm \ 1 \end{array}$	$\begin{array}{c} 775 \pm 99 \\ 477 \pm 12 \\ 87 \pm 11 \\ 52 \pm 3 \\ 22 \pm 1 \\ 16 \pm 1 \\ 12 \pm 1 \end{array}$		

Table XIII Effect of Different Salt Solution Concentrations on Water Absorbency of the Copolymer

gel will thus increase more rapidly than in the outer solution, and the ion swelling pressure will increase.

Swelling Behavior in Salt Solution

The salt effect is clearly evidenced as a result of the osmotic pressure differential between the internal solution in the gel and the external solution due to the different ion concentrations.¹⁷ The water intake by the gel reduced the osmotic pressure until an ion concentration equilibrium was reached.

The highly water-absorbing copolymer obtained earlier with water absorbency of 775 g g⁻¹ was selected to test the salt effect in various concentrations of NaCl, KCl, KI, KBr, MgCl₂, and CaCl₂ solutions. The influences of salt solutions upon water absorbency of the copolymer are summarized in Table XIII.

A water-absorbent system consists of a quantity of polymer network with a variable quantity of aqueous component. The osmotic pressure attributable to the polymer network is the driving force for the water absorption and, consequently, swelling. At swelling equilibrium, the chemical potential of water in the polymer equals that of water surrounding the polymer. Addition of a simple salt to the polymer solution leads to network contraction, as indicated by viscosity lowering and the decreasing chemical potential of the water surrounding a polyelectrolyte polymer. Therefore, absorbent polyelectrolyte polymers cannot imbibe as much salt water as pure water.¹¹

The result shows the tendency that the water absorbency decreases as the salt concentration increases due to the ionic strength (I) of the salt solution. At low ionic strength (large Debye lengths), repulsions are long-range interactions, and the gel expands to minimize the repulsion free energy; as the ionic strength rises (small Debye lengths), repulsions are shielded, and the gel is dewashed.¹⁷ The ion concentration and ionic strength of the salt solutions are calculated in Table XIV.¹⁸

Note that the water absorbency decreases even more with increasing $MgCl_2$ and $CaCl_2$ concentra-

Concentration of	Ionic Strength of Salt Solutions ^a (mol ion ⁻¹ dm ⁻³)							
Salt Solution $(\% \text{ wt } v^{-1})$	NaCl	KCl	KI	KBr	MgCl_2	CaCl_2		
0.005	$8.5558 imes10^{-4}$	$6.7060 imes10^{-4}$	$3.0119 imes10^{-4}$	$4.2017 imes10^{-4}$	$7.3779 imes10^{-4}$	$1.3515 imes10^{-3}$		
0.05	$8.5558 imes10^{-3}$	$6.7060 imes10^{-3}$	$3.0119 imes10^{-3}$	$4.2017 imes10^{-3}$	$7.3779 imes10^{-3}$	0.0135		
0.1	0.0171	0.0134	$6.023 imes10^{-3}$	$8.4034 imes10^{-3}$	0.0148	0.0270		
0.3	0.0513	0.0402	0.0181	0.0252	0.0443	0.0811		
0.5	0.0856	0.0671	0.0302	0.0420	0.0738	0.1351		
0.9	0.1540	0.1207	0.0542	0.0756	0.1329	0.2433		

Table XIV Ionic Strength of the Salt Solutions

 $^{a}I = \frac{1}{2}\Sigma(C_{i}Z_{i}^{2})$, where I, C_{i} , and Z_{i} are the ionic strength, the ionic concentration, and the charge on each individual ion, respectively.¹⁸

Buffer	Solution	Saline Solution			
Ionic Strength $(mol ion^{-1} dm^{-3})$	Water Absorption $(g g^{-1})$	Ionic Strength $(mol \ ion^{-1} \ dm^{-3})$	Water Absorption $(g \ g^{-1})$		
0.1521 (pH 5)	59	0.1540 (NaCl)	60		
0.1243 (pH 7)	59	0.1207 (KCl)	68		
0.0886 (pH 11)	58	0.0856 (NaCl)	75		
-		0.0811 (CaCl ₂)	22		
0.0711 (pH 12)	56	0.0756 (KBr)	81		
· *		$0.0738~(\mathrm{MgCl}_2)$	25		

Table XVComparison of Water Absorption of Poly(potassium acrylate-co-acrylamide) in pH andSaline Solutions

tions. This suggests that the equilibrium osmotic pressure is reached earlier in the presence of the divalent ion as a result of the higher ionic strength of the MgCl₂ and CaCl₂ solutions compared with that of other salt solutions at the same concentration, or the lower amount of divalent cations than monovalent cations needed to maintain the charge balance; so the drop will occur at lower salt concentrations in the divalent case. In addition, the divalent Mg²⁺ and Ca²⁺ ions may crosslink the gel by salt formation with the carboxylate groups on adjacent chains or chain segments of the copolymer. Consequently, the crosslink density of the network increases.^{17,19–20}

At the same ionic strength value, the water absorbency of copolymers in various salt solutions containing different cations and anions is shown in Table XIII. The water absorbency of copolymers is relatively constant, except for the results of MgCl₂ and CaCl₂ solutions, where the divalent salts differ because Mg²⁺ and Ca²⁺ can react with the free carboxylic sites of the gel by a chelate formation to give additional divalent carboxylate groups on the backbone. On the other hand, the counterion species was very important for the swelling equilibrium at the same type of cation and the same oxidation state.²¹ For the present work, the effect of the counterion of the pH-sensitive hydrogel seems to be independent of the type of anion at the same ionic strength.

Water Absorbency of the Buffering and Saline Solutions

The effects of ionic strength due to the pH solutions and saline solutions can be compared as follows. At a relatively close ionic strength, water absorbency of the superabsorbent copolymer (at 60: 40 KA/AM) in various pH solutions is relatively lower than those of the monovalent saline solutions but higher than those of divalent saline solutions, as shown in Table XV. The main attribute to the difference between pH and monovalent saline solution is the presence of different anions. The buffering solution contains borate, citrate, and phosphate anions with a charge of 3; whereas the saline solution has chloride, bromide and iodide anions with a charge of one, such as in the cases of pHs 5 and 7. The contribution of divalent cations of the saline solution is overwhelming the anion effects at high pH solutions (pH 11 and 12).²¹

Rheological Properties of the Copolymers

The viscometric properties of the synthesized copolymers produced by inverse suspension polymerization of total monomer concentration 5*M*, at a 60 : 40 molar ratio of AM : KA, with various crosslinking agent concentrations of N,N'-MBA, $1\% w v^{-1}$, Span 80, 1.4 g L^{-1} ($6.14 \times 10^{-3}M$), and 100% neutralization degree of acrylic acid, are shown in Table XVI.

Properties of the product are related to the crosslink density of the network, modulus increases, and swelling capacity decreases. The result shows that the water absorbency of copolymers decreases with increasing shear modulus of the swollen gel because the increasing crosslinking agent concentration (0 to 0.075 mol %) controls the crosslink density on networks of the synthesized copolymer. In addition, it increases the elastic retractile response of the network. From Table XVII, the viscosity of swollen gels synthesized with various crosslinking agent concentrations decreases with the increasing shear

Crosslinking Agent (mol % of Monomer)	Water Absorbency $(g \ g^{-1})$	Viscosity ^a (Pa s)	Shear Stress ^b (Pa)	Shear Strain	Shear Modulus ^c (Pa)
None	1484 ± 408	0.25	0.5	1200	$4.167 imes10^{-4}$
0.025	775 ± 99	5.5	11	1200	$9.167 imes10^{-3}$
0.050	568 ± 27	6.25	12.5	1200	$1.040 imes10^{-2}$
0.075	$519\pm~32$	7.75	15.5	1200	$1.290 imes10^{-2}$

Table XVI The Rheological Properties of the Copolymers

^a Calculated from $(N \times 2.5 \times 1000)/1000$ Pa.s, where N is the measured value from the viscometer.

^b Calculated from the equation $\eta = \pi/\nu$, where η is the viscosity, ν is the shear strain, and τ is the shear stress.

^c Calculated from equation $\tau = G\nu$, where G is the shear modulus.

rate because of a shear thinning effect of the material.²² The materials that have this behavior are called pseudoplastic materials. With increasing shear rates, matchstick-like particles suspended in the liquid will be turned lengthwise into the direction of the flow. Chain-type molecules in a melt or in a solution can disentangle, stretch, and orient parallel to the driving force. Particles or molecular alignments allow particles and molecules to slip past each other more easily in noncrosslinked polymers or low crosslinking density networks, and this shows up as reduced viscosity.

Thermal Properties of the Copolymer

The copolymers were investigated by differential scanning calorimetry (DSC) to identify the T_g and T_m of the copolymer. The DSC thermograms of the copolymers synthesized with Span 80, Span 60, or Span 40 as the suspending agent are shown in Figure 2. All DSC thermograms of the copolymers show two endothermic peaks. As such, the phase separation is anticipated to exist in the

copolymers. The T_{g1} , T_{m1} , T_{g2} , and T_{m2} of the copolymers are depicted in Table XVIII.

The T_{g1} and T_{g2} are characterized as the T_g of polyacrylamide and poly(potassium acrylate), respectively, whereas the reference T_g values are 165 and 194°C, respectively.^{4,23} As in Table XVIII, the T_{g1} and T_{m1} of the copolymers, synthesized with different types of suspending agents, are different, while the T_{g2} and T_{m2} of these copolymers are approximately equal. Thus, the type of suspending agents are essential to the thermal properties of the copolymers, especially at T_{g1} and $T_{m1}.$ The T_{g1} of the copolymer synthesized with Span 80 as a suspending agent is higher than those with Span 60 and Span 40, respectively, which are far lower (89-101°C) than the reference T_g value of the polyacrylamide (165°C), while the T_{g2} values of all copolymers are far higher than the reference T_g value of poly(potassium acrylate) (194°C). They are probably due to the interference coating of the suspending agent on the surface of the copolymer beads (241-244°C), imide polymer on acrylamide

 Table XVII
 Effect of the Shear Rate on the Viscosity and the Relationship Between the Shear Rate

 and Shear Stress of the Copolymers Synthesized with Various Crosslinking Agent Concentrations

C1	0.0 mol % N,N'-MBA		0.025 mol % N,N'-MBA		0.05 mol % N,N'-MBA		0.075 mol % N,N'-MBA	
Shear Rate (s ⁻¹)	Viscosity (Pa s)	Shear Stress (Pa)	Viscosity (Pa s)	Shear Stress (Pa)	Viscosity (Pa s)	Shear Stress (Pa)	Viscosity (Pa s)	Shear Stress (Pa)
1	0.50	0.50	9.50	9.50	10.50	10.50	11.00	11.00
2	0.25	0.50	5.50	11.00	6.25	12.50	7.75	15.50
4	0.313	1.252	3.00	12.00	3.75	15.00	4.13	16.52
8	0.313	2.504	1.81	14.48	2.13	17.04	2.50	20.00
20	0.188	3.76	0.95	19.00	1.03	20.60	1.13	22.60
40	0.156	6.24	0.575	23.00	0.625	25.00	0.50	20.00



Figure 2 DSC thermograms of copolymer synthesized with various types of span suspending agent and crosslinked with 0.025 mol % N,N'-MBA.

units, and the steric hindrance of the suspending agent molecules.

Surface Morphology of the Copolymer Beads

The copolymer beads were photographed by SEM to observe the surface appearance. The electron micrographs of the water-soluble and crosslinked

copolymers, are shown in Figures 3 and 4, respectively. From the SEM micrographs, lumps are observed on the water-soluble copolymer in Figure 3, whereas the crosslinked copolymer beads are rather round in appearance. The cellular structure found in the crosslinked copolymer is shown in Figure 4. The occurrence of the cellular structure may be due to the high molar ratio of

	Thermal Properties (°C)					
Suspending Agent	T_{g1}	T_{m1}	T_{g2}	T_{m2}		
Span 40	89.77	121.67	241.09	256.67		
Span 60	97.59	140.00	241.59	255.00		
Span 80	101.86	140.00	244.61	260.00		

Table XVIII The T_g and T_m Values of the Copolymers Synthesized with Different Suspending Agents

acrylamide and high pH used in polymerization to produce polyacrylamide and polyimide networks due to imidization. This structure increases the surface area of the copolymer beads, a requirement for high water absorbency.

CONCLUSIONS

Highly water-absorbing copolymers of poly(potassium acrylate-co-acrylamide) were synthesized by an inverse suspension copolymerization. Acrylamide and potassium acrylate were used as comonomers, and N,N'-methylenebisacrylamide as a crosslinker polymerized by ammonium persulphate in *n*-hexane, each emulsified by a series of sorbitan surfactants with a relatively lower concentration of 1.0% $w v^{-1}$ at 60°C for 2 h. The synthesized beads were collected by precipitation with excess methanol. The effects of influential reaction parameters on the water absorption of the newly synthesized copolymers were investigated. The reaction conditions are as follows: total monomer, 5M; ammonium persulfate, $6.14 \times 10^{-3} M$; volume ratio



Figure 3 SEM micrographs of the water-soluble copolymer without crosslinking agent.



Figure 4 SEM micrographs of crosslinked copolymer having a cellular structure on the surface.

of the aqueous phase to the organic phase, 1: 1.5; crosslinker concentration, MBA 0.025 mol % of the monomer concentration; stirring speed, 200 rpm. The water absorption at 40 : 60 mole ratios of potassium acrylate and acrylamide is 775 g g^{-1} (dry weight), having an high liquid absorption rate (21.41 s). The water absorption ability decreased with increasing crosslinker and salt concentrations due to the osmotic pressure differential between the inside and outside of the swollen gel. The water absorption depended highly on the pH of the buffer solution and the type and concentration of the saline solution. The copolymers exhibited a shearthinning behavior at both low and high shear rates. A cellular structure was found on the surface of hydrogel beads synthesized with the crosslinking agent. The superabsorbents of poly(potassium acrylate-co-acrylamide) exhibit the behavior of pH sensitivity.

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