

# Synthesis and Characterization of Reinforced Acrylic-Based Superabsorbents Crosslinked with Divinylbenzene

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**ABSTRACT:** A series of superabsorbent polymers were synthesized by an inverse suspension polymerization, with potassium persulfate as the initiator, Span60 as the dispersant, and *N,N'*-methylene bisacrylamide (BIS) and divinylbenzene (DVB) as multiple crosslinkers. The synthesis conditions, including the amount of dispersant, concentration of crosslinkers, oil-to-water phase ratio (*O/W*) of the polymerization system, total monomer concentration, and acrylamide (AM) content were studied. The results indicated that there were optima for the following properties: BIS crosslinker concentration (0.075 wt %), *O/W* (3 : 1), total monomer concentration (37.5 wt %), and AM content (5 wt %). In addition, the particle size had a significant influence

on the absorption speed, and the absorption speed increased with decreasing particle size. In comparison with the conventional sample crosslinked only by BIS, the superabsorbent with the same particle size but crosslinked by multiple crosslinkers had the higher absorption rate because of surface crosslinking. It also showed that the salt resistance and antihydrolyzing property of the superabsorbent crosslinked by multiple crosslinkers (BIS and DVB) were enhanced, which was also attributed to surface crosslinking by DVB. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1594–1600, 2006

**Key words:** synthesis; water absorption; surface-crosslinking

## INTRODUCTION

Superabsorbent polymers (SAPs) are slightly crosslinked copolymers that have the ability to absorb a lot of water. They have been extensively investigated and widely applied in the last 30 years.<sup>1–10</sup> Most SAPs have a three-dimensional network structure, and the water absorption (*Q*) process is an expansion course of this three-dimensional network. So the crosslinker and the crosslinking method are important factors affecting the properties of SAPs.

Among recently developed superabsorbents, acrylic acid (AA) based SAPs have been extensively studied and used, and *N,N'*-methylene bisacrylamide (BIS) has commonly been used to synthesize AA-based SAPs.<sup>11,12</sup> However, the disadvantages of a low absorption rate, poor salt resistance, and a lower mechanical strength of the swollen superabsorbents of these conventional SAPs have impeded their wide applications. Thus, many efforts<sup>13–18</sup> have been made to improve the properties of SAPs. Chen et al.<sup>13</sup> introduced interconnected pores to SAPs to increase their absorption rate, and these SAPs were synthesized by crosslinking polymerization in the presence of gas

bubbles formed by the chemical reaction of acid and NaHCO<sub>3</sub>. Kabiri et al.<sup>14</sup> prepared porous SAPs through a rapid, convenient solution polymerization of partially neutralized AA with acetone and sodium bicarbonate as porosity generators, which resulted in a faster absorbing rate. Suda and Rattana<sup>15</sup> also synthesized porous SAPs through foam polymerization. Ma et al.<sup>16</sup> enhanced the water-absorbing properties of AA-acrylamide (AM) copolymer SAPs by treating them in supercritical CO<sub>2</sub>. Philippova et al.<sup>17</sup> invented a way of reinforcing the mechanical properties of swollen SAPs without a loss of swelling ability by filling them with stiff-chain linear polyelectrolyte. Ren and Ha<sup>18</sup> improved the wet strength of poly(diallyldimethyl-ammonium chloride) SAPs by preparing the interpenetrating polymer network with a natural macromolecule,  $\kappa$ -carrageenan.

According to the gel swelling kinetics theory derived by Tanaka and Fillmore,<sup>19</sup> the cooperative diffusion coefficient is proportional to the osmotic longitudinal modulus and to the reciprocal of the friction coefficient describing the viscous interaction between the polymer chains and the solvent. Hence, for a given gel, the swelling rate can be represented by the cooperative diffusion coefficient of the network. The enhancement of the surface crosslinking of SAP particles is an effective way to increase the swelling rate of SAPs because the modulus of the swelling SAP increases, whereas the friction coefficient hardly in-

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TABLE I  
Materials and Reagents

Material	Function	Source
AA	Monomer	Wulian Chemical Factory, Shanghai, China Purification under reduced pressure
AM	Monomer	Linhai Chemical Agent Factory, Linhai, Zhejiang, China Purification by recrystallization in acetone
Potassium-persulfate	Initiator	Shanghai No. 2 Chemical Agent Factory Purification by recrystallization in water
BIS	Crosslinker	Fluka Co., Ltd., Switzerland
DVB (analytical pure)	Crosslinker	Jiangsu Niansha Chemical Reagent Factory, Suzhou, China
Sorbitan monostearate (Span60)	Dispersant	Zhejiang Longyou Chemical Reagent Factory, Longyou, China
Cyclohexane (analytical pure)	Solvent	Zhejiang Shuanglin Chemical Reagent Factory, Hangzhou, China
NaOH (analytical pure)	Neutralization agent	Zhejiang Hangzhou Chemical Reagent Factory, Hangzhou, China
Methanol (analytical pure)	Washing agent	Zhejiang Juhua Group, Quzhou, China
Sodium chloride (NaCl, analytical pure)	Testing agent	Zhejiang Hangzhou Chemical Reagent Factory, Hangzhou, China

creases. Ma et al.<sup>20</sup> prepared SAPs by solution polymerization in the presence of BIS; the SAPs were subsequently surface-crosslinked by ethylene glycol diglycidyl ether and were then modified with inorganic salt to obtain superabsorbents with high performances in areas such as strength and salt resistance. However, this process was more complicated.<sup>21</sup>

In this study, an inverse suspension polymerization process was applied to prepare AA-AM copolymer superabsorbents. The water-soluble crosslinker was added before the start of polymerization, whereas a hydrophobic crosslinker, divinylbenzene (DVB), was added after the start of polymerization. The effects of the polymerization parameters, including crosslinker concentration, oil-to-water phase ratio (*O/W*), monomer concentration, and AM content on *Q* were investigated. The particle morphology, absorption kinetics, salt resistance, and antihydrolyzing properties were also investigated.

## EXPERIMENTAL

### Materials

The chemicals used in the experiment are shown in Table I.

### Polymerization

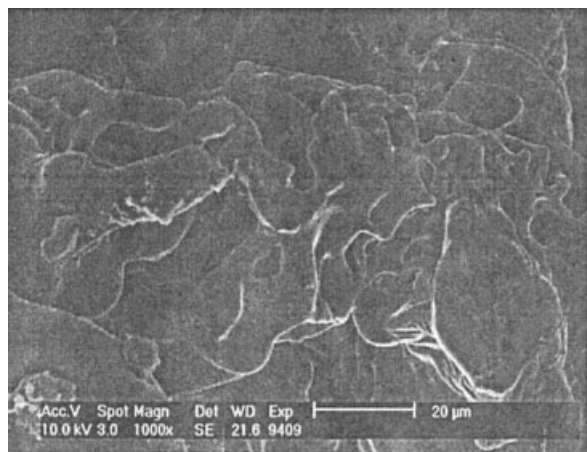
Polymerization was carried out through an inverse suspension process. First, AA was partially neutralized by NaOH solution under ice-water cooling. Then, a mixture of the monomers, initiator, BIS, and distilled water at a given mass ratio was introduced into a 500-mL, five-necked, jacketed glass reactor fitted with

a mechanical stirrer, nitrogen inlet, condenser, drop funnel, and thermometer. The dispersant (Span60) was added to cyclohexane to form the continuous phase and poured into the reactor. Then, the polymerization was run in the temperature range 55–65°C for 3 h. A predetermined amount of DVB was introduced into the reactive mixture, and the reaction lasted for 0.5 h at 65°C. The SAP was dehydrated through an azeotropic process and was obtained as beads. These beads were washed by methanol several times and was dried *in vacuo* for 24 h at 60°C.

### Characterization

The morphology of superabsorbents was observed with a scanning electron microscope (Philips XL30; Tokyo, Japan). We prepared the specimens by freeze-drying the swollen gels to avoid shrinkage in the drying process. First, the swollen specimens were immersed in liquid nitrogen (−196°C) to freeze both the superabsorbents and water. Then, they were put into the freezing-drying instrument (Thermo Savant, ModulyoD-230; Waltham, MA), in which the temperature was increased to −50°C and the pressure was decreased to 10<sup>−7</sup> bar. Under these conditions, the water vapor was eliminated through sublimation. Water elimination in this way can prevent the formation of an open macroporous structure in the particles and prevent them from collapsing. At last, the specimens were coated with gold and observed with scanning electron microscope (SEM).

A microscope (Olympus BH-2, Tokyo, Japan) was used to observe the shape and particle size of the SAPs.



**Figure 1** SEM micrograph of conventional SAP crosslinked only by BIS.

In  $Q$ , about 0.5 g of the dry sample was immersed in 500 g of distilled water for at least 24 h to reach the swelling equilibrium at room temperature. The completely swollen gel was filtered through a 100-mesh nylon pocket, and the remaining swollen gel was weighed.  $Q$  (g/g) was calculated as follows:

$$Q = (W_s - W_d)/W_d \quad (1)$$

where  $W_s$  and  $W_d$  are the swollen and dried weights of the sample (g), respectively.

The liquid absorption ( $Q_L$ ) was carried out in NaCl solutions with various concentrations.  $Q_L$  was calculated with eq. (1).

The swelling kinetics of the superabsorbents were measured gravimetrically in water at room temperature. After they were filtered with a 100-mesh nylon pocket, the weight changes of samples were recorded at the courses of swelling at regular time intervals. Water uptake (WU) was calculated as follows:

$$WU = (W_t - W_d)/W_d \quad (2)$$

where  $W_t$  is the weight of the sample at a regular time interval and  $W_d$  is the dried weight of the sample.

The antihydrolyzing properties of the superabsorbents were tested in distilled water and the calculation of  $Q$  was the same as eq. (1). The swollen sample was desiccated *in vacuo* at 95°C for at least 12 h after  $Q$  of sample was measured at its absorption equilibrium. Then, the dry sample was immersed in excessive water to reach equilibrium again. The procedure was repeated several times, and  $Q$ 's were tested in sequence. The repetitive water retention ( $R_n$ ) was calculated as follows:

$$R_n = Q_n/Q \times 100\% \quad (n = 1,2,3,\dots) \quad (3)$$

where  $Q_n$  is the  $n$ th water absorption and  $Q$  is the water absorption of the sample.

## RESULTS AND DISCUSSION

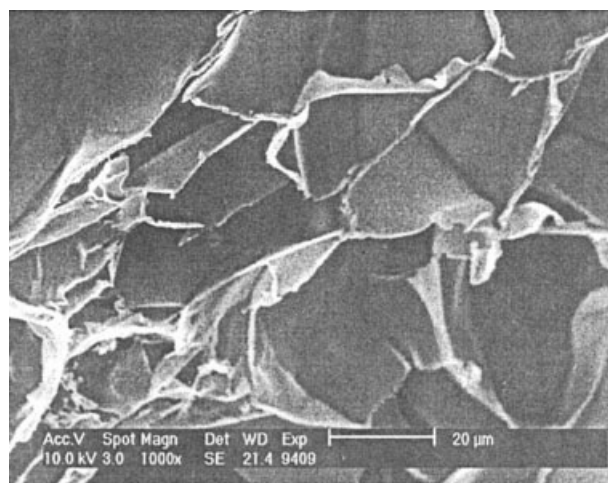
### Morphology of conventional and reinforced surface-crosslinking SAPs

The conventional SAP sample crosslinked only by BIS and the reinforced surface-crosslinking SAP sample crosslinked by BIS and DVB were prepared. Their corresponding SEM micrographs are shown in Figures 1 and 2, respectively.

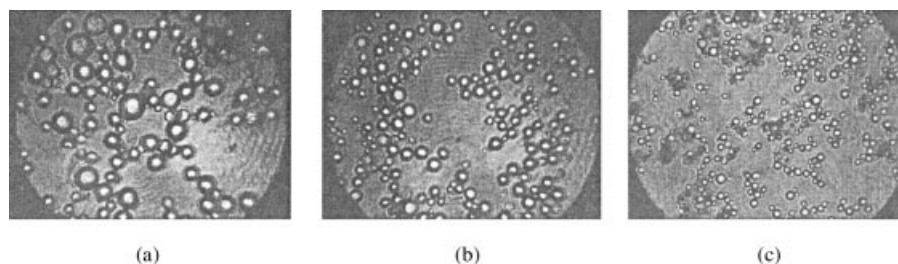
Figures 1 and 2 show that the surface morphology of the reinforced SAP crosslinked by BIS and DVB was different from that of the conventional SAP. The conventional SAP had a rather compact structure (Fig. 1), whereas the reinforced SAP had a distinct shell structure and a hollow inside (Fig. 2), which showed that surface crosslinking had occurred. During the freeze-drying process, water contained in SAP particles diffused from inside to outside, and the particles shrank. For SAP particles with no enhanced surface crosslinking, this shrinkage became more pronounced, and the resulting SAP exhibited a compact structure. However, the shrinkage of the SAP with enhanced surface crosslinking was hindered by their surface layers with enhanced crosslinking. As a result, the inside of particle was relatively empty, and the surface area became a shell.

### Influence of the polymerization parameters on the properties of the SAPs

The concentrations of the dispersant and crosslinkers,  $O/W$ , monomer concentration, and monomer mass feed ratio can affect the particle size and  $Q$  of SAPs.



**Figure 2** SEM micrograph of the reinforced SAP crosslinked by BIS and DVB.



**Figure 3** Micrographs of samples prepared with (a) 5.5, (b) 6.7, and 8.3 wt % dispersant.

Thus, the effects of these parameters on the characteristics are discussed in this section.

#### Effect of dispersant

Figure 3 shows the photographs of SAP particles synthesized with different concentrations of dispersant (Span60) in the inverse suspension polymerization.

The particles were well established in spherical forms, and the particle size of the SAP decreased with increasing amount of Span60. In the suspension/inverse suspension polymerization process,<sup>22</sup> dispersant can decrease the surface tension of a droplet and protect it from aggregation. So, more droplets were formed and stabilized in the polymerization system when more dispersant was added, which caused the decrease in particle size.

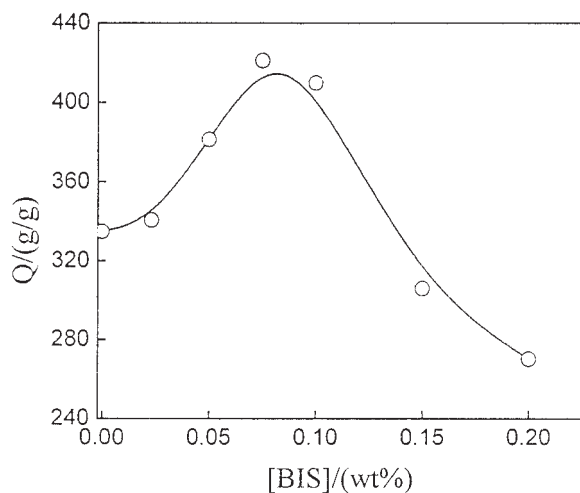
#### Effect of crosslinker concentrations

Because of its hydrophilicity, BIS diffused into the droplet and took part in the crosslinking reaction mostly inside particle, whereas DVB participated in the crosslinking reaction only in the vicinity of the

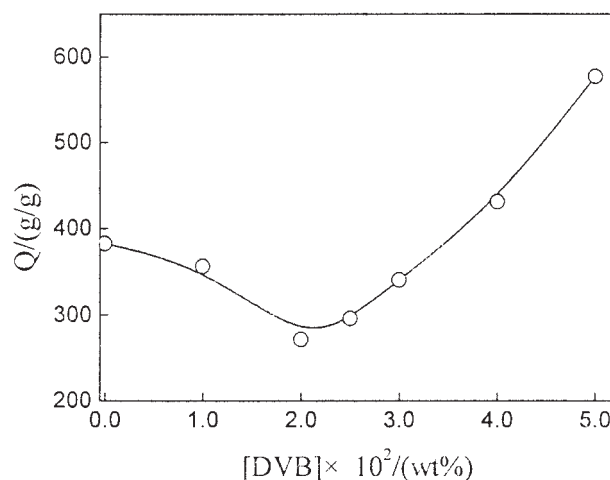
particle surfaces due to its hydrophobicity. The variation of  $Q$  with the amount of BIS and DVB are depicted in Figures 4 and 5, respectively.

As shown in Figure 4,  $Q$  increased with increasing BIS concentration when the BIS concentration was lower than a critical concentration, and  $Q$  decreased with increasing BIS concentration when the BIS concentration was greater than the critical concentration. The critical BIS concentration was 0.075%, and the reason for this behavior was explained in a previous article.<sup>23</sup>

In comparison with the results shown in Figure 4, the effect of DVB concentration on  $Q$  was different (Fig. 5).  $Q$  decreased first, passed through a minimum, and then increased with increasing DVB content. When DVB was introduced, the surface crosslinking layer was formed through the surface crosslinking. On the one hand, the surface crosslinking shell layer might have become a barrier to water penetration for its hydrophobic properties, which would have resulted in the lower  $Q$ . On the other hand, the sol fraction inside the SAP particles might have been difficult to diffuse out in the swelling process due to the existence of the enhanced surface crosslinking shell



**Figure 4** Effect of BIS concentration on  $Q$  ([DVB] = 0.025%).



**Figure 5** Effect of DVB concentration on  $Q$  ([BIS] = 0.025%).

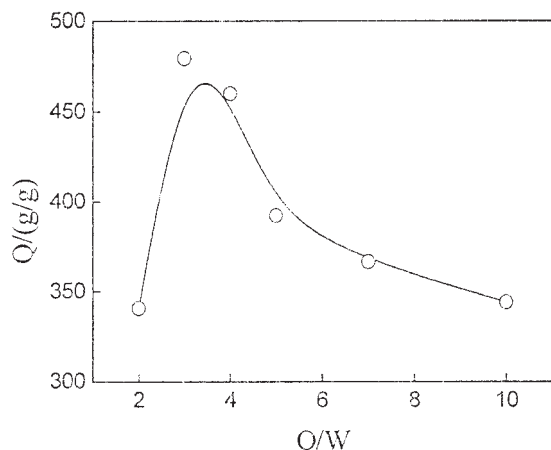


Figure 6 Effect of  $O/W$  on  $Q$ .

layer, which would have caused the higher  $Q$ . When the amount of DVB was low ( $<0.02\%$ ), the first aspect was dominant, so the absorption decreased with increasing DVB. However, as the DVB concentration increased ( $>0.02\%$ ), the second factor became the main one; thus, the absorption increased as the DVB concentration increased.

#### Effect of $O/W$

$O/W$  is defined as the volume ratio of cyclohexane to water. Because the surface crosslinking occurred in the vicinity of the oil/water interphase,  $O/W$  seriously influenced the surface crosslinking reaction and the properties of the resulting SAPs. The effect of  $O/W$  on  $Q$  is shown in Figure 6.

$Q$  increased to a maximum point and then decreased with increasing  $O/W$ . When  $O/W$  was extremely low, the reacting polymer particles expanded to a great extent, and more crosslinker molecules might have diffused into the particles to participate in the crosslinking reaction, which resulted in the higher crosslinking density and lower  $Q$ . When  $O/W$  was high, the reacting particles swelled a small amount. So the carboxylic groups on the particle surface extended with difficulty, which resulted in more difficulty for DVB to take part in the surface crosslinking reaction. Furthermore, if  $O/W$  was excessively high, the reacting particles shrank to a great degree, and the crosslinking reaction hardly took place, which resulted in an unfavorable increase in soluble polymer (sol) percentage. As a result,  $Q$  decreased.

#### Effect of monomer concentration

Figure 7 shows the effects of the total monomer concentration on the absorption ability of SAP. Lower or higher monomer concentrations were disadvanta-

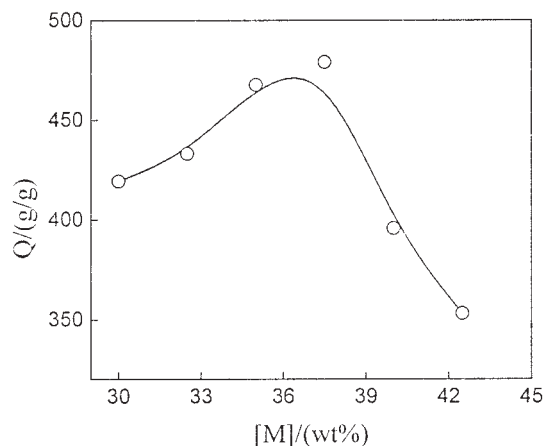


Figure 7 Effect of monomer concentration ( $[M]$ ) on  $Q$ .

geous for improving  $Q$ , and the optimal value for monomer concentration was 37.5 wt % in this study.

When the monomer concentration was relatively low, the polymerization rate was too low to bring about the crosslinking reaction,<sup>23</sup> which induced a more unfavorable percentage of soluble polymers. However, as the total monomer concentration became higher, chain transfer to polymers increased, especially at a high extent of conversion, and these resulted in increasing branching and reduced the product absorption capacity.<sup>4</sup>

#### Effect of AM concentration

To enhance the SAP properties, a nonionic monomer (AM) was introduced and copolymerized with the partially neutralized AA. The relationship between absorption ability and AM content is shown in Figure 8.

$Q$  increased to a peak value and then decreased with increasing AM content. When a small amount of AM was copolymerized with partially neutralized

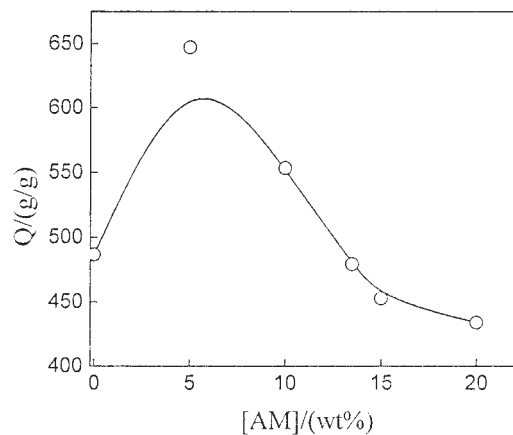
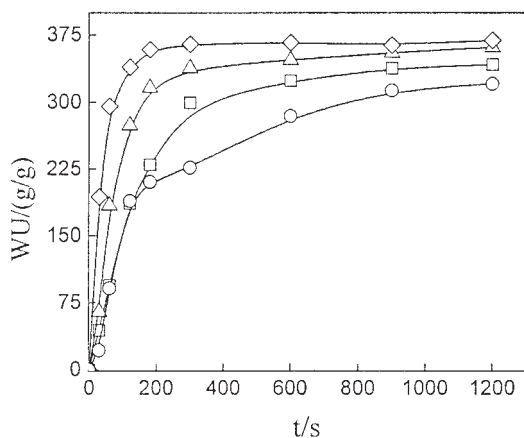


Figure 8 Effect of AM concentration on  $Q$ .



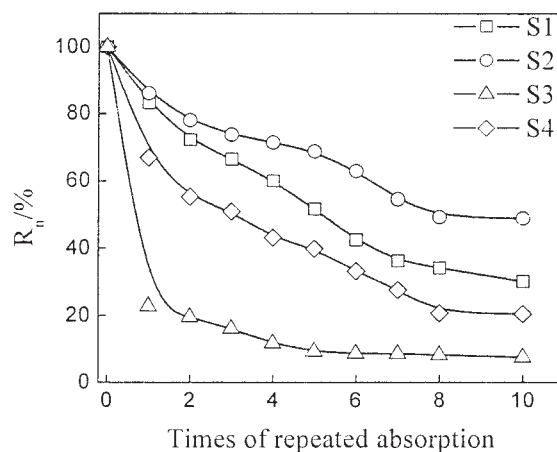
**Figure 9** Swelling curves of different SAPs (where  $t$  is the time for SAPs swelling). Conditions: (○) [BIS] = 0.05% and 20–40 mesh; (□) [BIS] = 0.025% and 20–40 mesh; (△) [BIS] = 0.025%, [DVB] = 0.025%, and 60–80 mesh; and (◇) [BIS] = 0.025%, [DVB] = 0.025%, and 100–120 mesh.

AA, it not only weakened the hydrogen bond between water and carboxyl groups but also exerted an influence on absorbency because of the synergistic effect of different hydrophilic groups.<sup>23</sup> However, as the AM concentration became greater,  $Q$  decreased, which was attributed to the low dissociation degree of AM.<sup>24</sup>

### Swelling kinetics of the SAPs

The particle size dependence of the swelling behavior and a comparison of swelling kinetics between the conventional SAP crosslinked only by BIS and SAPs crosslinked by both BIS and DVB are shown in Figure 9.

As shown in Figure 9,  $Q$  increased with decreasing particle size. The reason was that the surface area per SAP mass increased with decreasing particle size, which resulted in more rapid  $Q$  on the particle surfaces.<sup>25</sup> In comparison with the swelling curves of the conventional and enhanced surface-crosslinking SAPs in the same size range, we concluded that the sample prepared with enhanced surface crosslinking had a higher absorption rate than the conventional one.



**Figure 10** Comparison of the antihydrolyzing properties of different SAP samples.

### Antihydrolyzing properties and salt resistance of the SAPs

The enhancement of the antihydrolyzing properties of the SAPs will prolong the use-life of SAPs. Here, four SAP samples were compared, and their preparation conditions are listed in Table II.

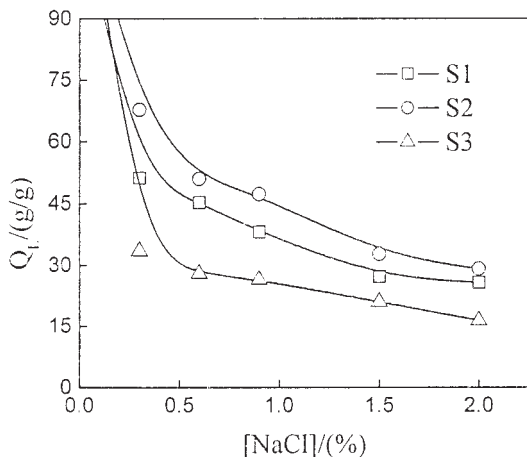
Figure 10 shows the comparison of the antihydrolyzing property for these samples (S1~S4).

Water retention decreased as expected with repeated absorption. In comparison with these SAPs, the sample with enhanced surface crosslinking (S2) had better antihydrolyzing properties than the others. The antihydrolyzing properties of the SAPs were affected by the percentage of soluble polymers (sol) and the stability of the chemical bonds, especially the crosslinking bonds. In general, better antihydrolyzing properties were achieved when the sol percentage of the SAP was lower and the chemical bonds were more stable.

For the conventional SAP (S1) crosslinked only by BIS, the amide bond ( $\text{-C(=O)-NH}_2$ ) from BIS degraded through the repeated absorption process. On the contrary, the alkyl bond from DVB remained stable in the course of circle absorbing. Thus, sample S2 had better antihydrolyzing properties because of the enhanced

**TABLE II**  
Synthesis Parameters of the Superabsorbents

Sample	Initial concentration of the added crosslinker (wt %)		O/W (v/v)	Monomer concentration (wt %)	AM content (wt %)
	BIS	DVB			
S1	0.05	0			
S2	0.025	0.025	3.1	37.5	5
S3	0	0.05			
S4	0.025	0			



**Figure 11** Effect of NaCl concentration on  $Q_L$ .

surface crosslinking by DVB. Because of its interior self-crosslinking network and large percentage of soluble polymers, the antihydrolyzing properties of sample S3 were very poor. As shown in Figure 10, the antihydrolyzing properties could be improved by the increase in the concentration of the BIS crosslinker. This was attributed to a decrease in the sol percentage.

The salt resistance of SAPs is characterized by absorption in NaCl solutions. The results for different SAPs are shown in Figure 11.

Sample S2 exhibited better salt resistance than samples S1 and S3. As hydrophobic DVB was introduced into the polymerization system, the resulting SAPs became more hydrophobic. Therefore, intermolecular hydrophobic associations were formed when the polymer was immersed in the aqueous solution because the aqueous solution containing salt increased the polarity of the solution and the effect favored the intermolecular association, which led the hydrodynamic size of chains to increase.<sup>26</sup> As a consequence, the SAP with amphiphilic properties (S2) had better salt resistance. However, sample S3 had poor salt resistance because of its slight self-crosslinking network and the higher sol percentage.

## CONCLUSIONS

Enhanced surfaced-crosslinking AA-AM SAPs were prepared through an inverse polymerization with BIS and DVB as multiple crosslinkers. On the basis of the effects of the reaction variables (crosslinker concentra-

tion,  $O/W$ , monomer concentration, and monomer feed ratio) on  $Q$ , the recipe was optimized as follows: [BIS] = 0.075 wt %,  $O/W$  = 3 : 1, [M] = 37.5 wt %, and [AM] = 5 wt %. The swelling kinetics studies of the SAPs indicated that the absorption rate of SAPs crosslinked by multiple crosslinkers was indeed improved in comparison with that of the conventional sample crosslinked by BIS only. Further, the antihydrolyzing properties and salt resistance of the SAPs were improved by the introduction of DVB.

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