

Synthesis and Absorbency of a Superabsorbent from Sodium Starch Sulfate-*g*-Polyacrylonitrile

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ABSTRACT: A sodium starch sulfate-based superabsorbent was synthesized to improve water and saline absorbencies. A sodium starch sulfate with high degree of substitution was synthesized by the reaction of starch gelatinized with dimethyl acetamide (DMAc)/lithium chloride (LiCl) and a dimethyl formamide-sulfur trioxide (DMF-SO₃) complex. The sodium starch sulfate was then graft-polymerized with acrylonitrile and the nitrile groups of the sodium starch sulfate-*g*-polyacrylonitrile were converted to a mixture of hydrophilic carboxamide and carboxylate groups by alkaline hydrolysis. The hydrolyzed sodium starch sulfate-*g*-polyacrylonitrile copolymer exhibited improved water and saline absorbencies compared with that of existing starch-based superabsorbents, resulting from the presence of sulfate groups. The maximum water and saline absorbencies of the sodium starch sulfate-based superabsorbent were 1510 and 126.4 g/g, respectively. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1423–1430, 2001

Key words: sodium starch sulfate; superabsorbent; DMAc/LiCl; DMF-SO₃ complex; acrylonitrile; polyacrylonitrile

INTRODUCTION

Superabsorbents can absorb tremendous amounts of water without dissolving in water because they contain considerable amounts of hydrophilic groups and have a three-dimensional structure. They are used in such varied fields as hygiene, food, cosmetics, and agriculture. Research on superabsorbents was initiated by the development of a starch-based superabsorbent, Superslurper, by the U.S. Department of Agriculture, Northern Regional Research Center, in the late 1960s.¹ Since then, modification of natural raw materials such as starch,² cellulose,^{3,4} and protein⁵ and direct synthesis from hydrophilic monomers such as

acrylamide^{6,7} and acrylic acid^{8,9} with crosslinkers have been utilized to prepare superabsorbents.

Among the superabsorbents, starch-based superabsorbents prepared by hydrolyzing starch graft-polymerized with acrylonitrile (AN) have been studied extensively and water absorbency greater than 1000 g/g has been reported. Contrary to the very high water absorbency, saline absorbency is much lower, at around 40 g/g, a phenomenon that is common to all superabsorbents, resulting from a reduction in the swelling of the absorbent by the charge-screening effect of the mobile ions in the liquid being absorbed. Thus, improvement in the saline absorbency, rather than water absorbency, is more critical in the development of superabsorbents.

The absorbency of a superabsorbent depends not only on the nature and the density of the hydrophilic groups but also the density of

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crosslinks forming the three-dimensional network.¹⁰ Higher absorbency can be obtained by introducing hydrophilic groups that have a greater tendency than commonly employed carboxylic acid groups to ionize. The higher degree of ionization results in greater swelling and thus higher absorbency, an effect that is more pronounced when there is an abundance of positively charged ions in the liquid being absorbed. The absorbency decreases with the increase in ionic strength of the liquid being absorbed as the excess mobile ions associate with the ionized hydrophilic groups. Because sulfate groups ionize more readily than do carboxylic acid groups, which are normally employed, it was thought that the degree of association with the mobile ions would be much less than that of carboxylic acid groups. Consequently, the effect on absorbency of the ionic strength of the liquid being absorbed would be less significant. Thus improvement of both the saline absorbency and the water absorbency of a starch-based superabsorbent was attempted by introducing sulfate groups into starch prior to graft polymerization and hydrolysis.

A number of methods for synthesizing starch sulfate have been suggested: tertiaryamine-SO₃ complex,¹¹⁻¹³ dimethyl sulfoxide (DMSO)-SO₃ complex,¹⁴ chlorosulfonic acid in organic solvent,¹⁵ and sulfuric acid¹⁶ were used to synthesize starch sulfate. However, these methods have some disadvantages: (1) the distribution of substituted SO₃ groups on starch sulfate is not even, (2) the degree of substitution (*DS*) cannot be easily controlled, and (3) degradation of a starch chain may occur when substitution is carried out to high *DS*. Since a high *DS* without a significant decrease in the molecular weight of starch is favorable for high absorbency, a new method for the synthesis of starch sulfate was required.

Thus a new method for synthesizing starch sulfate was developed and the starch sulfate prepared by this method was graft-polymerized with AN then hydrolyzed to obtain a superabsorbent with both high saline absorbency and high water absorbency.

EXPERIMENTAL

Materials

Acrylonitrile (AN; Yakuri Pure Chemicals Co., Ltd., Osaka, Japan) was purified with 5 wt % NaOH solution before use. Corn starch (Duksan Pharma-

ceutical Co., Ltd., Kyong Kido, Korea), lithium chloride (LiCl; Junsei Chemicals Co., Ltd., Tokyo, Japan), sulfuric acid fuming 65% SO₃ (Merck, Darmstadt, Germany) dimethyl acetamide (DMAc; Shinyo Pure Chemicals Co., Ltd., Osaka, Japan), dimethyl formamide (DMF; Duksan Pharmaceutical Co., Ltd., Kyong Kido, Korea), ceric ammonium nitrate (CAN; Aldrich Chemical Co., Inc., Milwaukee, WI), and other reagents were used as received without further purification.

Synthesis of Sodium Starch Sulfate

A DMF-SO₃ complex was prepared according to Schweiger's method.¹⁷ A γ -type sulfur trioxide (SO₃) obtained by heating sulfuric acid fuming 65% SO₃ at 45°C was dissolved in a cold DMF and additional DMF was added to prepare a DMF-SO₃ complex, whose composition was 1 g SO₃ /10 mL DMF-SO₃ complex.

Prior to sulfation, starch was gelatinized with DMAc/LiCl according to the following procedure. A 200-mL aliquot of DMAc was added to 20 g of starch in a four-neck flask equipped with a mechanical stirrer, dropping funnel, thermometer, and calcium chloride (CaCl₂) tube. After stirring the mixture for 20 min at 90°C, 8 g of LiCl was added, after which stirring continued for an additional 5 min. The gelatinized starch was then cooled to 5°C in an ice bath.

To synthesize starch sulfuric acid, the DMF-SO₃ complex was slowly added to the gelatinized starch and stirred for 1 h at 5°C. The synthesized starch sulfuric acid was fully dissolved by adding 100 mL of deionized ultrafiltered (DIUF) water. It was then precipitated with excess acetone. The precipitate was washed three times with methanol to remove the remaining DMAc and LiCl. The washed starch sulfuric acid was then dissolved in DIUF water and neutralized with a saturated sodium carbonate (Na₂CO₃) solution to prepare the sodium starch sulfate (SSS), which was precipitated with excess acetone, then stored in methanol overnight to remove moisture, and dried in vacuum at 40°C for 2 days.

Graft Polymerization

Graft polymerization of AN onto SSS was carried out with CAN radical initiator. SSS (2 g) and DIUF water (40 mL) were added to a four-neck flask equipped with a mechanical stirrer, dropping funnel, nitrogen bubbler tube, and reflux condenser. The solution was purged for 1.5 h with

a slow stream of nitrogen to remove oxygen. Then, CAN dissolved in 10 mL of 1*N* nitric acid solution was added, after which 4 g of AN was added to carry out the graft polymerization with nitrogen purge at different temperatures for 2 h. The amount of CAN and polymerization temperatures studied were 50, 75, 100, 125, 150, and 200 AGU/CAN (mol anhydroglucose unit in SSS/mol of CAN) and 20, 25, 30, 35, 40, 45, and 50°C, respectively. The synthesized sodium starch sulfate-*g*-polyacrylonitrile (SSS-*g*-PAN) was twice washed with methanol to remove remaining monomers, CAN, and nitric acid, then dried in vacuum at 50°C for 2 days. Homopolymers were extracted with DMF. SSS-*g*-PAN (2 g) was added to 200 mL of DMF, stirred at room temperature for 24 h, then filtered and washed with methanol, and finally dried in vacuum at 50°C for 2 days.

Alkaline Hydrolysis

The alkaline hydrolysis of the graft polymerization product was carried out without removing the homopolymers. The graft polymerization product was hydrolyzed by adding 1 g of SSS-*g*-PAN to 10 mL of NaOH solution in a 100-mL Erlenmeyer flask and heating. The NaOH concentrations of 1.2, 1.6, 2.4, 3.2, and 4.0*N*; hydrolysis temperatures of 80, 90, 100, 110, and 120°C; and hydrolysis times of 0.25, 0.5, 1.0, 1.5, and 2.0 h were studied. The hydrolyzed sodium starch sulfate-*g*-polyacrylonitrile (HSSS-*g*-PAN) was placed in methanol for 3 h to remove moisture, then ground to obtain HSSS-*g*-PAN particles of various sizes. These superabsorbent particles were then placed in an 80 vol % aqueous methanol solution and stirred overnight to remove the hydrolysis by-products such as Na₂SO₄ and other water-soluble materials. The washed particles were then stirred in methanol for 3 h to remove moisture, filtered, dried in vacuum at 50°C for 2 days, and stored in a desiccator.

Water Absorbency Using the Filtration Method

Approximately 20 to 30 mg of dried HSSS-*g*-PAN with average particle sizes of 215 μm was dispersed in 60 mL of DIUF water for 30 min. Then, excess water was allowed to drain through a 300-mesh wire gauze. The weight of the superabsorbent containing absorbed water was measured after draining for 1 h, and the water absorbency was calculated according to the following equation:

$$\text{Absorbency (g/g)} = \frac{W_2 - W_1}{W_1} \quad (1)$$

where W_1 and W_2 are the weights of dry superabsorbent and swollen superabsorbent, respectively.

Saline Absorbency Using the Filtration Method

Approximately 30 to 40 mg of dried HSSS-*g*-PAN with average particle sizes of 215 μm was dispersed in 40 mL of 0.9 wt % NaCl solution for 30 min. Then, excess solution was allowed to drain through a 300-mesh wire gauze. The weight of the superabsorbent containing absorbed saline solution was measured after draining for 1 h, and the saline absorbency was calculated according to eq. (1).

Water Retention Value

Approximately 20 to 30 mg of dried HSSS-*g*-PAN with average particle size of 215 μm was dispersed in 50 mL of DIUF water for 30 min. The swollen particles were placed on a 300-mesh wire gauze fixed in centrifuge tubes, then centrifuged at 700 *G* for 1 h and weighed, after which the water retention value (WRV) was calculated using eq. (1).

Sulfur Content and Degree of Substitution

To estimate the *DS* of SSS, the sulfur content of SSS was determined by the combustion flask method.¹⁸ *DS* was calculated from the sulfur contents using the following equation:

$$DS = \frac{162S}{3200 - 102S} \quad (2)$$

where *S* is the sulfur content (%) of SSS.

Evaluation of Graft Yield

Graft yield was calculated using the following equation:

$$\text{Graft yield(\%)} = \frac{A - B}{B} \times 100 \quad (3)$$

where *A* is the weight of SSS-*g*-PAN after removing homopolymers (g) and *B* is the weight of SSS (g).

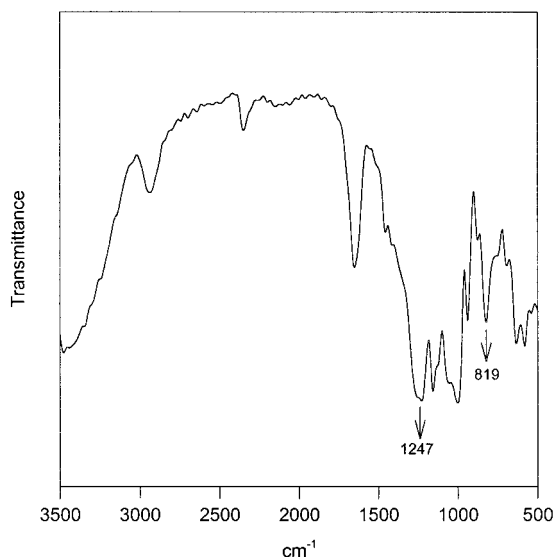


Figure 1 IR spectrum of SSS ($DS = 0.81$).

IR Analysis

To verify the synthesis of SSS, the graft polymerization of AN onto SSS, and the conversion of nitrile groups to hydrophilic groups on alkaline hydrolysis, infrared analysis was carried out on a Perkin-Elmer 1725X FTIR Spectrophotometer.

RESULTS AND DISCUSSION

Synthesis of Sodium Starch Sulfate

Introduction of sulfate groups to starch will result in an increase in the number of negatively charged groups when water is absorbed. Thus, the degree of swelling of an SSS-based superabsorbent can be expected to be higher and the resulting absorbency will be superior compared with that of existing starch-based superabsorbents. Although various methods for the preparation of highly substituted starch sulfate are known, degradation of the starch chain may be the result nonetheless. Therefore, a new method for synthesizing SSS of a high DS without extensive degradation was developed.

Schweiger¹⁷ developed a method for the synthesis of cellulose sulfate of a high DS with minimal degradation through the reaction of cellulose with DMF-SO₃ complex in DMF. However, when this method was used for the synthesis of SSS, a low DS was obtained. This may be the result of the differences in the reactivity of cellulose and starch. Starch consists of amylose and amylopec-

tin, which has a lower reactivity than amylose because of its dense network structure.¹⁹ Therefore, it was necessary to increase the reactivity of amylopectin by relaxing the network structure. The common method is to gelatinize the starch in an aqueous system at about 90°C. However, DMF-SO₃ complex is unstable in aqueous medium and produces sulfuric acid, which can degrade the starch chain and decrease DS . Therefore, a nonaqueous solvent system compatible with the DMF-SO₃ complex was required.

The DMAc/LiCl solvent system, also used in solvating cellulose, was selected for the synthesis of SSS, because it is compatible with the DMF-SO₃ complex and can gelatinize starch. Penetration of DMAc into the starch network was enhanced by increasing the temperature up to 90°C, after which LiCl was added to disrupt the hydrogen bonds that limit the accessibility of the hydroxyl groups to reactants in starch molecules. The DMAc/LiCl-gelatinized starch was then reacted with DMF-SO₃ complex to obtain SSS. Sulfur trioxide, with its electron-deficient sulfur atom adds onto the negatively charged oxygen atom of the polar mesomer of DMF, forming the DMF-SO₃ complex capable of reacting with the hydroxyl groups of starch.

In the IR spectrum of the synthesized SSS shown in Figure 1, bands resulting from S=O and S-O stretching can be observed at 1247 and 819 cm⁻¹, respectively, verifying the synthesis of SSS. Figure 2 shows the increase in DS with the

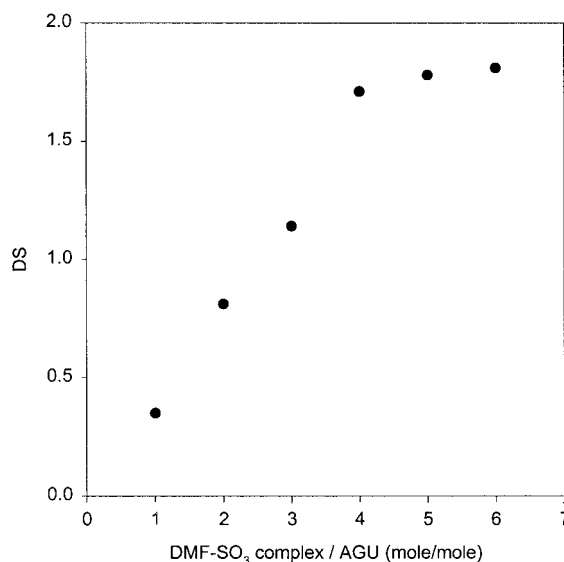


Figure 2 Effect of the amount of DMF-SO₃ complex on DS .

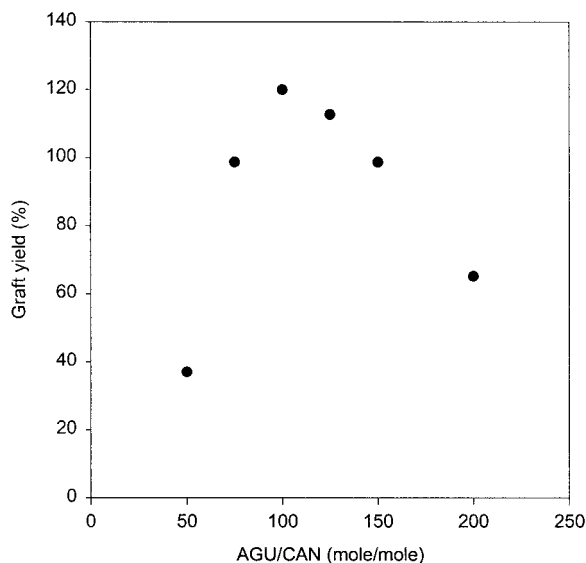


Figure 3 Effect of the amount of CAN on graft yield.

amount of DMF-SO₃ complex introduced to gelatinized starch. *DS* increased proportionally up to the DMF-SO₃ complex/AGU mole ratio of 4, then leveled off. *DS* was 1.71 when the DMF-SO₃ complex/AGU mole ratio was 4.

SSS with a *DS* of 0.81 was selected for the preparation of superabsorbents. Although SSS of a higher *DS* will exhibit higher charge densities, *DS* exceeding 1 will result in the substitution of the hydroxyl groups at C₂ or C₃ positions as well as those at C₆ position, which will obstruct the initiation of starch by CAN.

Effect of Graft Polymerization Conditions on Graft Yield

The changes in graft yield with the amount of CAN are shown in Figure 3. The polymerization temperature and time were 30°C and 2 h, respectively. The graft yield increases to 120% at a mole ratio of 100 AGU/CAN, then decreases to 65% at 200 AGU/CAN. The significant decrease in the graft yield above 100 AGU/CAN may possibly result from the decrease in starch radical concentration resulting, in turn, from the oxidation reaction of starch radicals with excess Ce⁴⁺ present at high CAN concentrations.²⁰ Figure 4 shows the effect of reaction temperature on graft yield. The amount of CAN and polymerization time were 100 AGU/CAN and 2 h, respectively. The graft yield increased from 65% at 20°C to 120% at 30°C, then decreased. This appears to be the result of the lower stability of the radicals at higher tem-

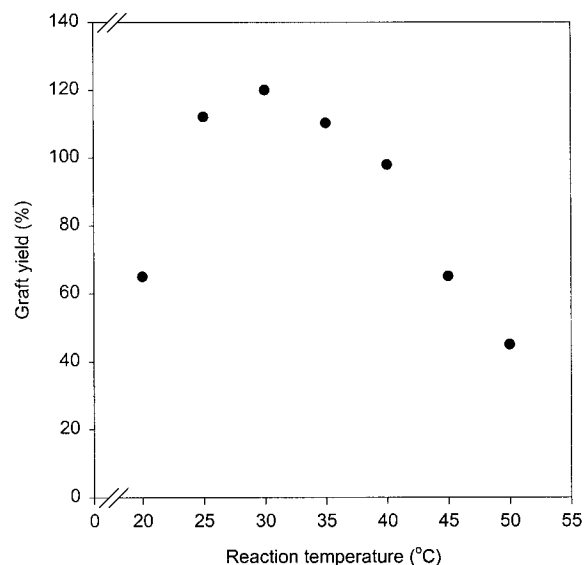


Figure 4 Effect of polymerization temperature on graft yield.

peratures. It is well known that the optimal initiation temperature of CAN is approximately 30 to 40°C.²¹

Effect of Alkaline Hydrolysis Conditions on Absorbency

The nitrile groups in the PAN graft chains were converted to the hydrophilic carboxylate and carboxamide groups through alkaline hydrolysis. Figure 5 shows the IR spectra of SSS-*g*-PAN and

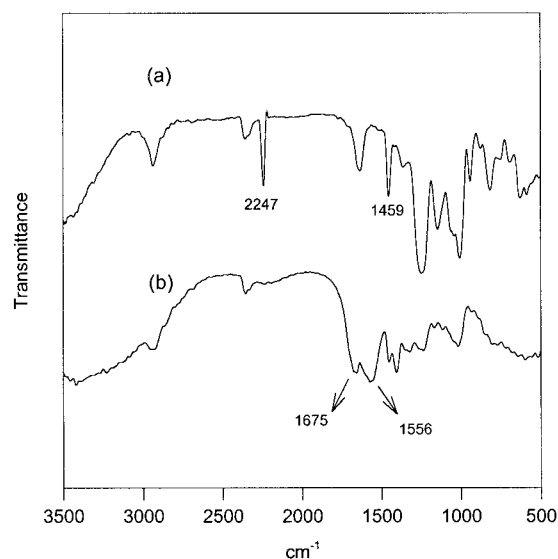


Figure 5 IR spectra of (a) SSS-*g*-PAN and (b) HSSS-*g*-PAN.

Table I Effect of the Concentration of NaOH Solution in Hydrolysis on the Absorbency and Sulfur Content of HSSS-*g*-PAN

| Concentration of NaOH Solution (<i>N</i>) | Water Absorbency (g/g) | Saline Absorbency (g/g) | Sulfur Content (%) |
|---|------------------------|-------------------------|--------------------|
| 1.2 | 789 | 83.7 | 1.31 |
| 1.6 | 987 | 93.8 | 1.30 |
| 2.4 | 1296 | 110.9 | 1.28 |
| 3.2 | 1510 | 126.4 | 1.24 |
| 4.0 | 1385 | 111.6 | 1.18 |

HSSS-*g*-PAN. The SSS-*g*-PAN and HSSS-*g*-PAN used for IR analysis were prepared by graft-polymerizing 4 g of AN onto 2 g of SSS with 100 AGU/CAN of CAN at 30°C for 2 h and hydrolyzing the graft copolymers in 3.2*N* NaOH solution at 100°C for 1 h, respectively. The C≡N stretching and CH₂ scissoring peaks of PAN at 2247 and 1459 cm⁻¹, respectively, confirm the graft polymerization of AN onto SSS (Fig. 5a). The alkaline hydrolysis of the SSS-*g*-PAN could be verified by the disappearance of the C≡N stretching band and appearance of the carboxamide and carboxylate bands at 1675 and 1556 cm⁻¹, respectively (Fig. 5b). SSS-*g*-PAN did not show appreciable absorbency because of the presence of hydrophobic PAN graft chains.

The alkaline hydrolysis behavior of SSS-*g*-PAN depends on such experimental conditions as the concentration of NaOH solution, hydrolysis temperature, and hydrolysis time. Table I shows the effect of the concentration of NaOH solution on the absorbency and sulfur content of HSSS-*g*-PAN hydrolyzed at 100°C for 1 h. Table II shows the effect of hydrolysis temperature on the absorbency and sulfur content of HSSS-*g*-PAN hydro-

Table II Effect of Hydrolysis Temperature on the Absorbency and Sulfur Content of HSSS-*g*-PAN

| Temperature (°C) | Water Absorbency (g/g) | Saline Absorbency (g/g) | Sulfur Content (%) |
|------------------|------------------------|-------------------------|--------------------|
| 80 | 1101 | 89.0 | 1.30 |
| 90 | 1313 | 109.4 | 1.29 |
| 100 | 1510 | 126.4 | 1.24 |
| 110 | 1499 | 106.5 | 1.10 |
| 120 | 1321 | 81.6 | 0.98 |

Table III Effect of Hydrolysis Time on the Absorbency and Sulfur Content of HSSS-*g*-PAN

| Time (h) | Water Absorbency (g/g) | Saline Absorbency (g/g) | Sulfur Content (%) |
|----------|------------------------|-------------------------|--------------------|
| 0.25 | 1361 | 89.7 | 1.34 |
| 0.5 | 1450 | 109.2 | 1.27 |
| 1.0 | 1510 | 126.4 | 1.24 |
| 1.5 | 1351 | 114.7 | 1.23 |
| 2.0 | 1288 | 106.3 | 0.96 |

lyzed in 3.2*N* NaOH solution for 1 h. Table III shows the change in absorbency and sulfur content with hydrolysis time in 3.2*N* NaOH solution at 100°C. These tables show that water and saline absorbencies depend strongly on hydrolysis conditions. Water and saline absorbencies increased up to 3.2*N*, 100°C, and 1 h, respectively, as a result of the increase in number of hydrophilic groups, then dropped significantly. This can be attributed to the degradation of the polymer chains and crosslinks resulting from the higher concentration of NaOH, higher temperatures, or long hydrolysis times. Castel et al.²² reported that the water-soluble parts in hydrolyzed starch-*g*-PAN increased with an increase in OH⁻/AN mole ratio in alkaline hydrolysis because excess OH⁻ degraded polymer chains and crosslinks. The sulfur content of HSSS-*g*-PAN decreased negligibly with increasing concentration of NaOH, hydrolysis temperature, or hydrolysis time. This indicates that sulfate groups of SSS-*g*-PAN are stable under the hydrolysis conditions, and that the S—O bond is not significantly hydrolyzed.

Effect of *DS* on Absorbency

Table IV shows the effect of the *DS* of SSS used to prepare the superabsorbent on the absorbency. The samples in Table IV were prepared by graft-polymerizing 4 g of AN onto 2 g of SSS with 100 AGU/CAN of CAN at 30°C for 2 h and hydrolyzing the graft copolymers in 3.2*N* NaOH solution at 100°C for 1 h. To compare the amount of grafted PAN per AGU, *g*-PAN/AGU was calculated using the following equation:

$$g - \text{PAN/AGU (g/mol)} = \frac{G(162 + 102DS)}{100} \quad (4)$$

where *G* and *DS* are graft yield (%) and degree of substitution, respectively. The *g*-PAN/AGU on

Table IV Effect of DS on the Absorbency of HSSS-*g*-PAN

| DS | Graft Yield (%) | <i>g</i> -PAN/AGU (g/mol) | Water Absorbency (g/g) | Saline Absorbency (g/g) | WRV (g/g) |
|------|-----------------|---------------------------|------------------------|-------------------------|-----------|
| 0 | 131.5 | 213.0 | 820 | 61.5 | 625 |
| 0.35 | 126.9 | 250.9 | 1442 | 114.4 | 1213 |
| 0.81 | 118.8 | 290.6 | 1510 | 126.4 | 1325 |
| 1.14 | 82.3 | 229.0 | 1616 | 122.2 | 1192 |
| 1.71 | 64.5 | 217.0 | 1750 | 113.4 | 1125 |

graft polymerization of AN onto SSS exhibited a maximum at the *DS* of 0.81, which may be the result of the higher accessibility of SSS with increasing solubility in water. The *g*-PAN/AGU decreased at *DS* values greater than 0.81, which is probably the result of the decrease in the number of sites that can be initiated. As *DS* increases, the hydroxyl groups at C₂ and C₃, which interact with Ce⁴⁺ to form radicals, are also sulfated, blocking the graft polymerization of AN onto SSS.

The water absorbency was higher for superabsorbents prepared from SSS of higher *DS*, whereas WRV increased with the *DS* up to 0.81, then decreased. This is thought to be the result of the decrease in the *g*-PAN/AGU and increase in the amount of homopolymers formed when SSS of *DS* above 0.81 is the starting material. When absorbency is evaluated using the filtration method, the swollen hydrophilic homopolymers cannot escape the superabsorbent network, resulting in a continuous increase in the value of water absorbency with *DS* values. However, when WRV is evaluated using the centrifugal filtration method, the swollen hydrophilic homopolymers are not chemically bound to the network and appear to escape through the wire mesh. Thus lower WRVs are obtained when the amount of homopolymers increases significantly, that is, when SSS of *DS* values greater than 0.81 are used in the preparation of superabsorbents. The saline absorbency increased with an increase in the *DS* of SSS used in the preparation of the superabsorbent up to 0.81, then decreased. It seems that grafted hydrophilic chains are more advantageous than independent hydrophilic homopolymers for higher saline absorbency.

The saline and water absorbencies of HSSS-*g*-PAN prepared from SSS of *DS* 0.81 were 126.4 and 1510 g/g, respectively, compared with 61.5 and 820 g/g for a hydrolyzed starch-*g*-PAN prepared for comparison. This study clearly shows that higher charge densities, obtained by sulfa-

tion of starch within *DS* of 0.81, results in significant enhancement of the water and saline absorbencies.

CONCLUSIONS

Starch was sulfated to enhance the absorbency of a starch-based superabsorbent by increasing the charge density of the starch network. A new method was developed for the sulfation of starch, in which high *DS* can be obtained with minimal degradation. By fully gelatinizing starch with DMAc/LiCl, a maximum *DS* of 1.71 could be obtained.

The SSS-based superabsorbent prepared by graft polymerization of AN onto SSS and alkaline hydrolysis exhibited improved water and saline absorbencies. The enhanced absorbency appears to be the result of the increase in charge density and ionization tendency brought about by the introduction of sulfate anions, in addition to the carboxylate anion in starch-based superabsorbents. The maximum water and saline absorbencies for this superabsorbent were 1510 and 126.4 g/g, respectively.

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