# Design and Synthesis of Superabsorbent Polymers

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**ABSTRACT:** A series of novel copolymer superabsorbents based on the monomers acrylamide (AM), acrylic acid (AA), acrylonitrile, methacrylic acid, sodium acrylate (SA), and 2-hydroxyethyl methacrylate (HEMA) were prepared by copolymerization using ammonium persulfate as an initiator and *N,N*-methylenebisacrylamide as a crosslinking agent. The experimental results of superabsorbent polymers (SAPs) show that the absorbency in water and NaCl solutions is maximum for AM, SA, HEMA and AM, AA, SA combinations. The copolymers were characterized by IR spectroscopy. The water retention of soil was also enhanced using the above superabsorbents. Use of SAPs for the growth of the croton plant was also investigated. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2635–2639, 2001

**Key words:** superabsorbents; acrylamide; *N,N*-methylenebisacrylamide; ammonium persulfate; water absorbency

## INTRODUCTION

Superabsorbents are crosslinked networks of hydrophilic polymers with a high capacity for water uptake and have a variety of valuable applications.[1–4] Superabsorbents can absorb a large amount of water, and the absorbed water is hardly removable even under some pressure. Superabsorbent materials are valuable in various products such as disposable diapers, feminine napkins, and soil for agriculture and horticulture, gel actuators, water-blocking tapes, drug-delivery systems, and absorbent pads.[5–8] In such applications, water absorbency and water retention are essential. Some workers have modified these absorbent polymers with a view to enhance their absorbency, gel strength, and absorption rate.[8–15] The influence of various reaction parameters on the water-absorption capacity of the superabsorbent copolymers were investigated by various workers.[16,17] Further, the dependence of the water absorbency of superabsorbent copolymers on the particle size and salinity was also investigated by Omidian and coworkers.[18] The investigation revealed that as the particle size became smaller the rate of absorption and ultimate degree of absorption both increased. In this article, we report the synthesis of superabsorbent copolymers by polymerizing the comonomers acrylamide, acrylic acid, acrylonitrile, methacrylic acid, sodium acrylate, and 2-hydroxyethyl methacrylate. The swelling behavior and water retention of the above superabsorbent copolymers was studied in the laboratory and in soil.

## EXPERIMENTAL

### Materials

Acrylamide (AM) was purified by recrystallization from benzene. Sodium acrylate (SA) was pre-

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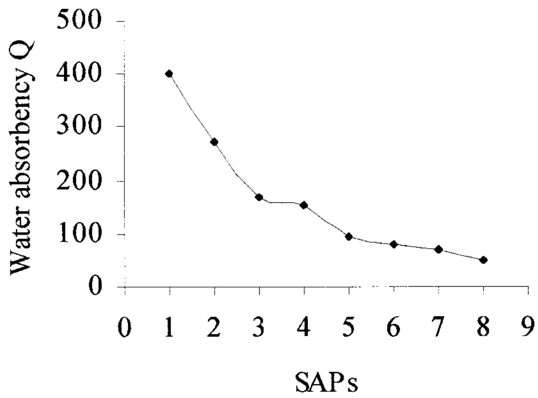


**Figure 1** Water absorbency versus SAPs.

pared in our laboratory. Acrylic acid (AA), acrylonitrile (AN), methacrylic acid (MAA), and 2-hydroxyethyl methacrylate (HEMA) were distilled under reduced pressure. *N,N*-methylenebisacrylamide (BisA) was used (chemically pure) as purchased. All solutions were prepared in double-distilled water.

### Synthesis Procedure

The reactions were conducted in a flask equipped with a mechanical stirrer, condenser, and nitrogen line. A weighed quantity of the monomers along with a crosslinking agent and ammonium persulfate (APS) were dissolved in water. After 1-h reaction at ±80°C, the resulting product was precipitated in ethanol, washed, and vacuum-dried at 50°C to a constant weight. The copolymer was reswollen in an excess of water to remove the soluble material. The gel was dried, reweighed, and milled through a 40-mesh screen.

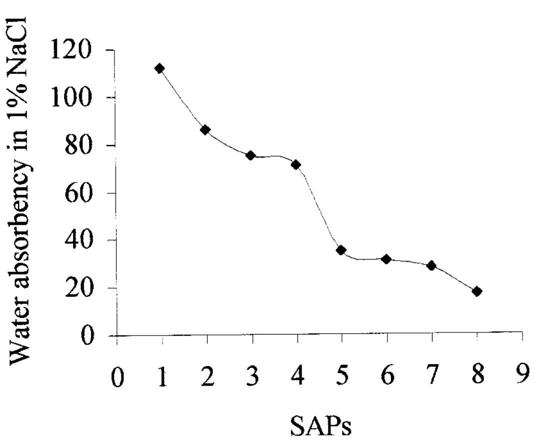


**Figure 2** Water absorbency in 1% NaCl versus SAPs.

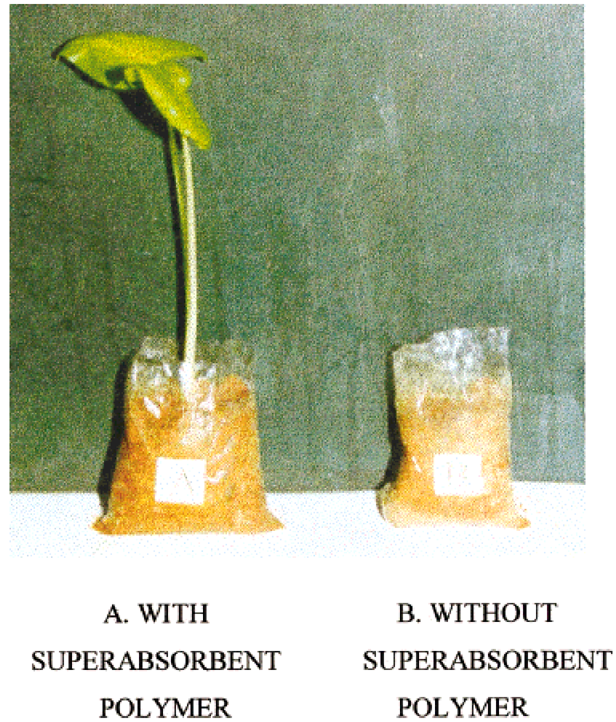


**Figure 3** Effect of SAP in soil. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

### Water-absorbency Measurement

A sample (1 g) of the superabsorbent was immersed in water (or saline solution) at room temperature until equilibrium was reached. Absorbability was determined by weighing the swollen gel (the gel was allowed to drain on a sieve for 10 min). The water absorbency was calculated using the following equation[19]:

$$\text{Water absorbency } Q \text{ (g } H_2O\text{/g sample)} = \frac{M - Mo}{Mo}$$

Absorbency is expressed in grams of water retained in the gel by a gram of dried gel. *M* and *Mo* denote the weight of the water swollen gel and the weight of the absorbent, respectively.

## RESULTS AND DISCUSSION

Various combinations of the monomers, crosslinker, and initiators were used to develop the superabsorbent polymers (SAPs). Table I illustrates the influ-

**Table I Influence of the Monomers on the Swelling Nature of Crosslinked SAPs**

| Sample No. | Monomers | Monomers in the Feed (mol/L) | Water Absorbency ($g/gH_2O$) | Water Absorbency in 1% NaCl |
|---|---|---|---|---|
| SAP-1 | AM | 0.5 | 400 | 112 |
| | SA | 0.2 | | |
| | HEMA | 0.3 | | |
| SAP-2 | AM | 0.38 | 272 | 86 |
| | AA | 0.33 | | |
| | SA | 0.22 | | |
| SAP-3 | AM | 0.33 | 170 | 75 |
| | AA | 0.23 | | |
| | HEMA | 0.12 | | |
| SAP-4 | AM | 0.60 | 152 | 71 |
| | AA | 0.30 | | |
| | MAA | 0.30 | | |
| SAP-5 | AA | 0.50 | 95 | 35 |
| | SA | 0.25 | | |
| | HEMA | 0.25 | | |
| SAP-6 | AM | 0.75 | 80 | 31 |
| | HEMA | 0.25 | | |
| SAP-7 | AM | 0.25 | 70 | 28 |
| | AN | 0.25 | | |
| | AA | 0.12 | | |
| SAP-8 | AM | 0.50 | 50 | 17 |
| | AN | 0.50 | | |

Reaction conditions: Initiator: APS $1.6 \times 10^{-3}$ (mol/L); crosslinking agent: BisA $1.2 \times 10^{-3}$ (mol/L); 1 h at ±80°C.

ence of monomers on the swelling nature of the copolymer network.

## IR Spectra

The IR spectra of superabsorbent copolymers were recorded in a Biorod WIN FTIR using KBr pellets. The IR spectrum of the copolymers are shown as peaks corresponding the groups attached to the monomeric units. In the case of the copolymer having AM, AN, and AA as monomeric units, the peaks observed in the IR spectrum are 3466 $cm^{-1}$, corresponding to NH stretching of the AM unit; 2929 $cm^{-1}$, corresponding to the associated COOH group of the AA unit; and 2362 $cm^{-1}$of the nitrile group of the AN unit. Further, the spectrum also showed peaks at 1700 and 1659 $cm^{-1}$, corresponding to the carbonyl group of acid moiety of the AA unit and the carbonyl group of the amide moiety of the AM unit.

In addition to the above peaks, peaks at 1454 and 1172 $cm^{-1}$corresponding to C—O—C and OH coupling interactions of the carboxylic group and C—N stretching vibrations are also observed. From the above observations made in the IR spectra of the copolymers, the presence of all the three monomeric units, that is, AM, AA, and AN, in the copolymer was confirmed. Similar observations show that the corresponding peaks of the monomeric units are also found in the copolymers of the other superabsorbents having different combinations of the other monomeric units. The IR data of the copolymers are presented Table II.

## Water Absorbency and Retention of SAPs

The key properties of SAPs are the swelling capacity and the elastic modulus of the swollen crosslinked gel. Both these properties are related to the crosslink density of the network. The wa-

**Table II IR Spectral Data of SAPs ($cm^{-1}$)**

| Polymers | νNH of AM Unit | νCOOH of AA Unit | νC≡N of AM Unit | νC=O of Amide Group of AM Unit | νC=O of Ester Group of SA Unit | νC—N Group of AN Unit | C—O—C Coupling Interactions of Carboxylic and Ester Groups |
|---|---|---|---|---|---|---|---|
| SAP-1 | 3410 | — | — | 1668 | 1729 | — | 1272 |
| SAP-2 | 3207 | 2979 | — | 1678 | — | — | 1183 |
| SAP-3 | 3470 | 2931 | — | 1608 | 1735 | — | 1173 |
| SAP-4 | 3460 | 2928 | — | 1660 | 1741 | — | 1173 |
| SAP-5 | — | 2952 | — | — | 1731 | — | 1275 |
| SAP-6 | 3205 | — | — | 1664 | — | — | 1278 |
| SAP-7 | 3466 | 3184 | 2362 | 1659 | 1700 | 1454 | 1172 |
| SAP-8 | 3203 | — | 2242 | 1668 | — | 1413 | — |

ter-absorption capacity is measured for these copolymers. Some SAPs have the capacity to absorb as high as 400 mL of water per gram of the copolymer (SAP-1). The water-absorption capacity of the various superabsorbent copolymers is presented in Table I. The specialty of these superabsorbent copolymers is the fast-absorbing capacity of water to get the required swollen polymer. The water absorbency of SAPs in a 1% NaCl solution is also presented in Table I.

One of the most important applications of SAPs is for agriculture and horticulture purposes, especially for effective utilization of water in dry regions and to transform these dry regions into green fertile lands. In this regard, the preliminary testing of these SAPs for water retention was also carried out in these laboratories by growing the seeds of croton into a plant with and without using SAPs.

The experiments indicate that the water retention in the soil is very high when SAP is added to the soil. The plant was sustained more than 1 month without adding any additional water when it was grown by adding SAPs and 400 mL water to the soil. The same plant was sustained only for 5–6 days without adding SAPs to the soil and using the same amount of water. The experimental result shows that the plant grew to a height of 150 cm using the SAP, where as the height of the plant without adding the SAP was only 50 cm.

## CONCLUSIONS

The novel copolymer superabsorbents were synthesized in an aqueous solution by copolymerization of the respective monomers with BisA as a crosslinking agent using APS as an initiator. The copolymers were characterized by IR absorption spectroscopy. The absorbency of the copolymers was measured in water and in a salt solution. These superabsorbents have a fast swelling rate. The water retention of the soil was enhanced using the superabsorbent copolymer. Use of SAPs for the growth of the croton plant was also investigated.

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