

Synthesis and Water Absorbency of the Copolymer of Acrylamide with Anionic Monomers

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SYNOPSIS

A series of novel copolymer superabsorbents based on acrylamide, sodium allylsulfonate, sodium acrylate, and *N,N'*-methylenebisacrylamide were prepared by copolymerization. The resulting superabsorbents have a fast swelling rate. The experimental results show that absorbency increases to a maximum as the cross-linking increases, but an excess of cross-linking leads to a swelling decrease. Their water retention was observed at pressures of 1–10 kg/cm² and temperatures of 60 and 100°C, respectively. The water retention of soil has been enhanced by using the poly(acrylamide–sodium allylsulfonate–sodium acrylate) superabsorbent; its use for bean growth was also investigated. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Superabsorbent compositions are valuable in various areas, such as agriculture,¹ industry,^{2,3} medicine,⁴ and other advanced technologies^{5,6} where water absorbency and water retention are important.

In recent years, an increasingly large number of synthetic superabsorbents have been investigated. In this article, we report on the copolymer superabsorbent prepared from acrylamide, sodium allylsulfonate, sodium acrylate, and *N,N'*-methylenebisacrylamide in aqueous solution by using potassium persulfate and *N,N,N',N'*-tetramethylethylenediamine as the redox initiator. The relation between the composition of the copolymer superabsorbents and their swelling behavior in water is studied, and this article also deals with the kinetics of the swelling of the gels, which, in addition, can give an impetus to an increasing water-retention capability of soil.

EXPERIMENTAL

Materials

Acrylamide (AM) was purified by recrystallization from benzene, mp 84–85°C. Sodium allylsulfonate

(SAS), commercial grade, was purified from 90% ethanol twice and vacuum-dried to constant weight. Potassium persulfate (KPS) was recrystallized from water. Sodium acrylate (AA), *N,N,N',N'*-tetramethylethylenediamine (TMEDA), and *N,N'*-methylenebisacrylamide (Bis) (chemically pure) were used as purchased. All solutions were prepared in distilled water.

Synthesis Procedure

A series of the copolymer superabsorbents were prepared by the following procedure:

The reactions were conducted in a flask equipped with a mechanical stirrer, condenser, and nitrogen line. A weighed quantity of monomers and KPS were dissolved in water, and the reaction medium was deaerated with nitrogen while stirring for 20 min and TMEDA was added. After 2.5 h of reaction at 35°C, the resulting product was precipitated in ethanol, washed, and vacuum-dried at 50°C to constant weight. The copolymer was reswollen in an excess of water to remove the solubles. The gel was dried, reweighed, and milled through a 40-mesh screen.

Water Absorbency Measurement⁷

A sample (1 g) of the superabsorbent was immersed in water (or saline solution) at room temperature

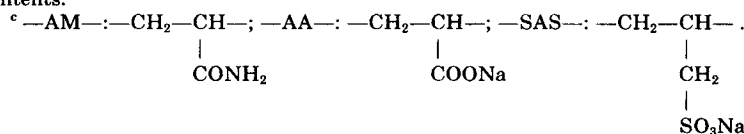
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Table I Influence of the Ionic Unit Content on the Swelling of Cross-linked Poly(AM-SAS-AA) Superabsorbents^a

No.	Composition of the Copolymer									
	Monomer in the Feed (mol/L)			Element Content ^b		Repeating Unit ^c (Mol %)			Soluble wt %	Q g/g
	AM	ASA	AA	N	S	—AM—	—SAS—	—AA—		
S1	0.97	0.04	—	17.21	1.16	93.33	6.67	—	10	108
S2	0.97	0.06	—	16.11	1.18	90.10	9.90	—	20	142
S3	0.97	0.08	—	16.00	1.40	89.76	10.24	—	30	176
A1	0.97	0.04	0.053	14.28	1.00	78.69	2.42	18.90	15	170
A2	0.97	0.04	0.112	11.39	0.97	65.29	2.42	32.88	25	250
A3	0.97	0.40	0.265	9.51	0.92	55.45	2.35	42.20	35	437

^a Reaction condition: [Bis] = 6.40×10^{-3} mol/L; [TMEDA] = 3.00×10^{-3} mol/L; [KPS] = 2.67×10^{-3} mol/L, at 35°C, 2.5 h.

^b The composition of the copolymer was determined from nitrogen and sulfur contents obtained by the Kjeldahl method and the oxygen flask method, respectively. The repeating units (mol %) of the copolymers were calculated from their nitrogen and sulfur contents.



until equilibrium was reached. Absorbability was determined by weighing the swollen gel (the gel was allowed to drain on a sieve 10 min). The water absorbency was calculated using the following equation:

$$\text{Water absorbency } Q(\text{g H}_2\text{O/g sample}) = \frac{M - M_0}{M_0}$$

Absorbency is expressed in grams of water retained in the gel by a gram of dried gel, and M and M_0 denote, respectively, the weight of the water swollen gel and the weight of the absorbent.

In addition, the water retention of the swollen gel was determined by a heating oven test at 60 or 100°C and by a ZNS-2 Model fluid-loss meter at various pressures (1–10 kg/cm²).

RESULTS AND DISCUSSION

Ionic Unit Content and Cross-linking

It is well known that the swelling of hydrogel is induced by the electrostatic repulsion of the ionic charges of its network. The ionic charge content is concerned with the ratio of the feed monomers. Table I illustrates the swelling absorbability as a function of ionic units (containing —CO₂Na and —SO₃Na groups) of the copolymer network. The swelling increase is due to an increase of the anionic units, but an excess of ionic units leads to an increase in the soluble material. On the other hand, the

swelling decreases drastically with the degree of cross-linking (Fig. 1).

IR Spectra and SEM Observation

The IR spectra were recorded with a Nicolet FT-20 SX spectrophotometer using KBr discs. In the spec-

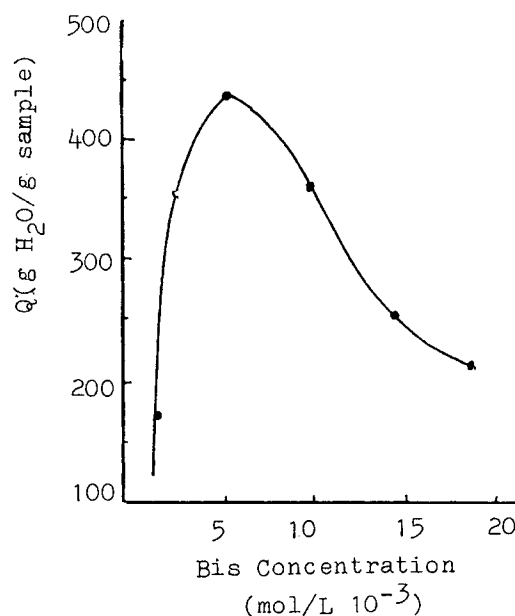


Figure 1 Absorbency of cross-linked poly(AM-SAS-AA), A3 sample, as a function of the concentration of the cross-linking agent (Bis).

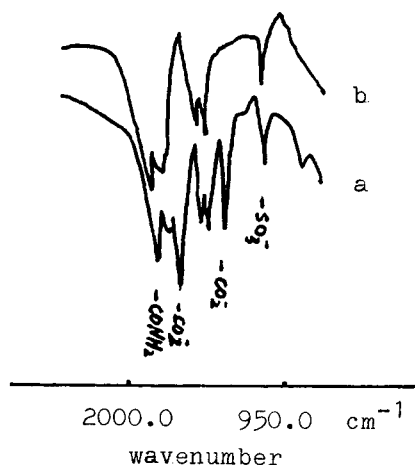


Figure 2 IR spectra for A3 and S1 sample: (a) A3; (b) S1.

tra (Fig. 2), the absorbance at 1667 and 1646 cm^{-1} , attributed to the amide group ($-\text{CONH}_2$) absorption, is present in $-\text{AM}-$ units. Similarly, the absorbances at 1311, 1585 ($-\text{CO}_2\text{Na}$), and 1048 ($-\text{SO}_3\text{Na}$) cm^{-1} were characteristic peaks for $-\text{AA}-$ and $-\text{SAS}-$ units, respectively.

Figure 3 shows the SEM of the morphology of cross-linked copolymers, (a) A3 and (b) S1. It is apparent from the photographs that A3 shows a broad network structure whereas S1 is a fine network. This observation is found to be in good agreement with A3 and S1 water absorbency as mentioned previously.

Swelling Kinetics

The water is absorbed by the superabsorbent and the swelling rate is described by the following experimental equation:

$$Q/dt = K(Q_{\max} - Q) \quad (1)$$

where Q_{\max} is the maximum absorbency; Q , the characteristic absorbency; and K , the swelling kinetic constant.

Integration from (1) gives

$$-\ln(Q_{\max} - Q) = KT + C \quad (2)$$

or

$$-\log(Q_{\max} - Q) = \frac{K}{2.303} T + C \quad (3)$$

where T is the characteristic swelling time, and C , the integration constant. As a consequence of $T = 0$, $Q = 0$, and $-\log Q_{\max} = C$, therefore,

$$\log \frac{Q_{\max}}{Q_{\max} - Q} = \frac{K}{2.303} T \quad (4)$$

For an example, the swelling rate of sample A3 is given in Figure 4. It is found that A3 is characterized by a high swelling rate: It can absorb up to a half-part maximum in 30 min. The K is determined to be 2.49×10^{-2} .

Influence of External Parameters on Absorbency

The swelling capacity of the superabsorbent is very dependent on pH, temperature, and composition of the absorbed liquid. Figure 5 shows that the absorbency reaches a maximum at pH 6 and decreases drastically with increasing pH. Figure 6 shows the water absorbency as a function of NaCl composition for the poly(AM-SAS-AA) superabsorbent; e.g., sample A3 decreases with increasing concentration of NaCl, and a late transition is observed between

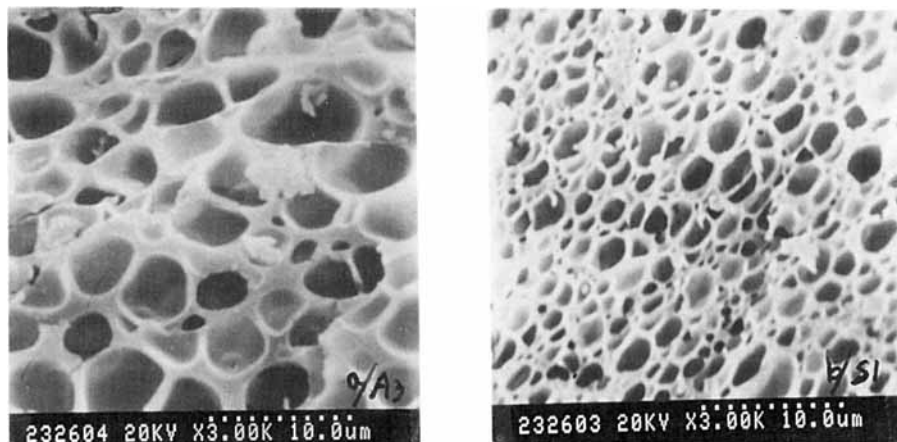


Figure 3 SEM graphs for A3 and S1 samples: (a) A3; (b) S1.

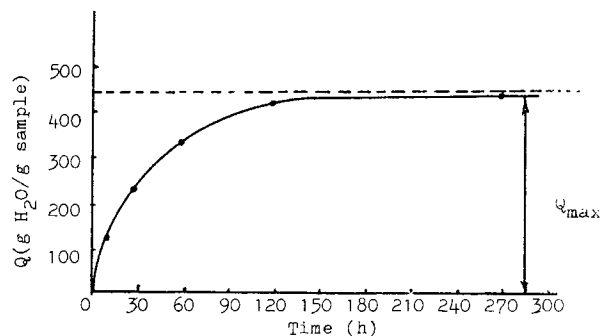


Figure 4 Swelling rate for the A3 superabsorbent, $Q_{max} = 437$ g/g.

0.5×10^{-2} and 10^{-3} mol/L NaCl concentration, whereas Q is determined to be 100–160 (g/g). On the other hand, the water retention of the swollen gel is sensitive to temperature (Fig. 7) but is stable at varied pressures (1–10 kg/cm²) (Fig. 8) and sample A3 is superior to S1.

In summary, the water absorbency is not only influenced by the ionization degree of the swollen gel but also by external parameters.

Water Retention in Soil

Figure 9 shows the water retention of soil that has been enhanced by using the poly(AM-SAS-AA)

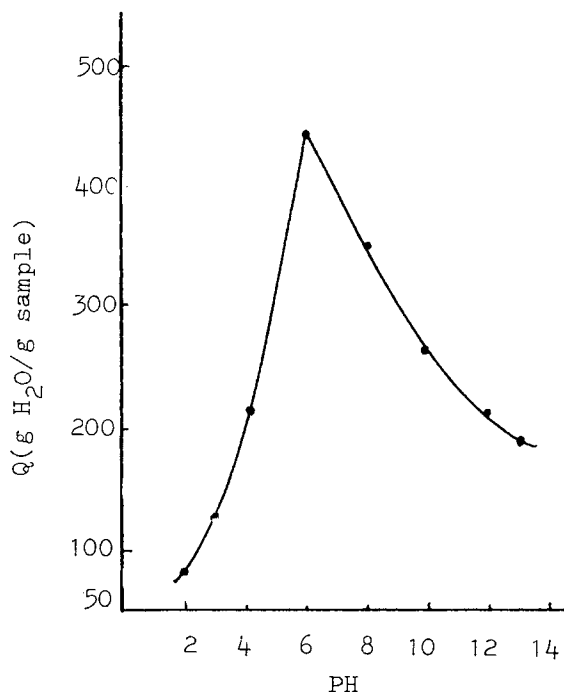


Figure 5 Influence of pH on the absorbency of the A3 sample.

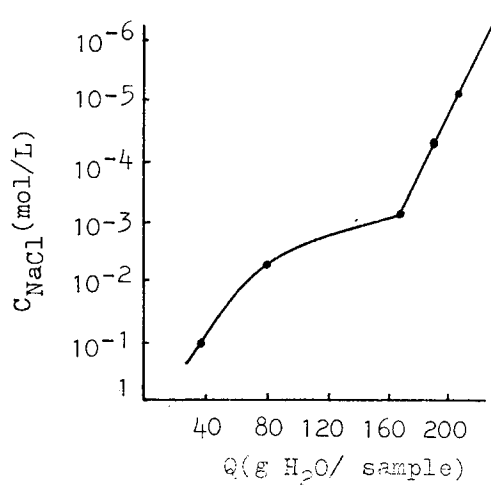


Figure 6 Influence of NaCl concentration on the absorbency of the A3 sample.

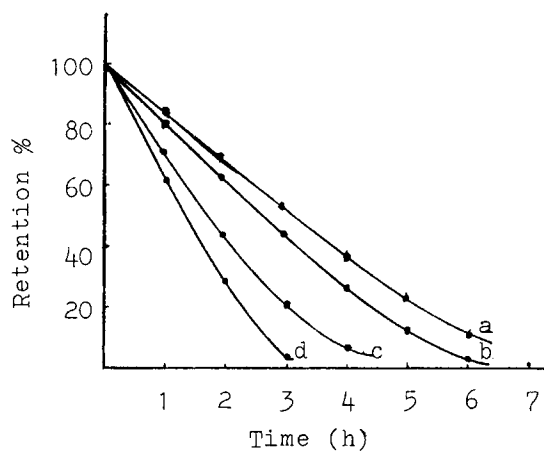


Figure 7 Water retention of the swollen gel at temperatures 60 and 100°C. 60°C: (a) A3; (b) S1; 100°C: (c) A3; (d) S1.

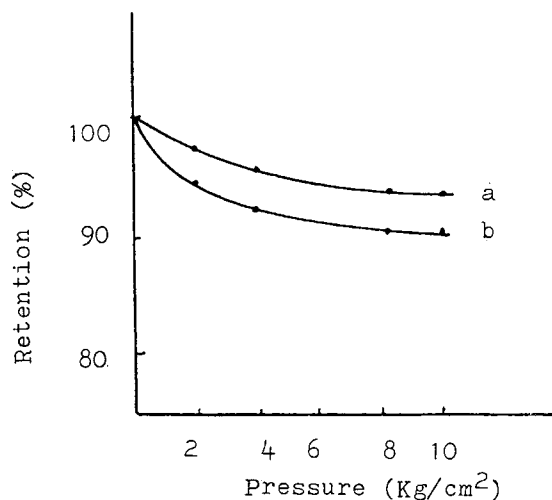


Figure 8 Water retention of the swollen gel at varying pressures (1–10 kg/cm², for 30 min): (a) A3; (b) S1.

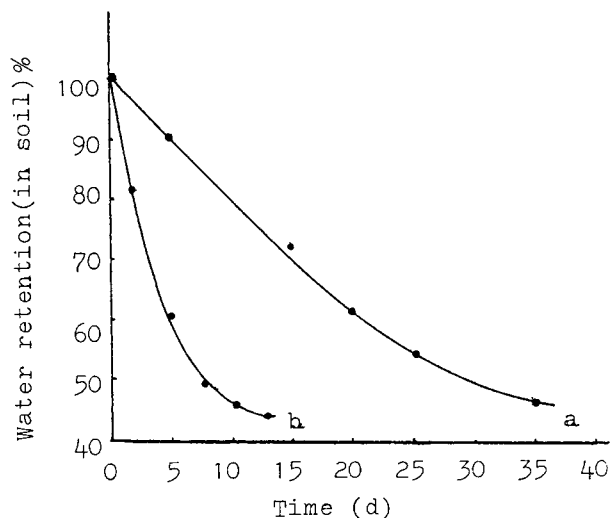


Figure 9 Water retention of soil, A3 content: (a) 0.3% (based on soil wt); (b) 0%.

superabsorbent (e.g., A3). The water retention was determined by drying the soil in the air and weighing over it time.

Figure 10 illustrates sample A3 for use as a soil conditioner. It is found that the bean has grown sturdier because the A3 superabsorbent was used.

Thermal Stability

The thermal stability of the copolymer superabsorbent is studied by using thermogravimetric analysis. Figure 11 is the thermogravimetric curve for samples A3 and S1. A3 shows a significant weight loss below 100°C, implying a loss of moisture. These samples were stored at the same ambient temperature and pressure. Because A3 contained hydrophilic groups (—CO₂Na), its moisture regain and retention is

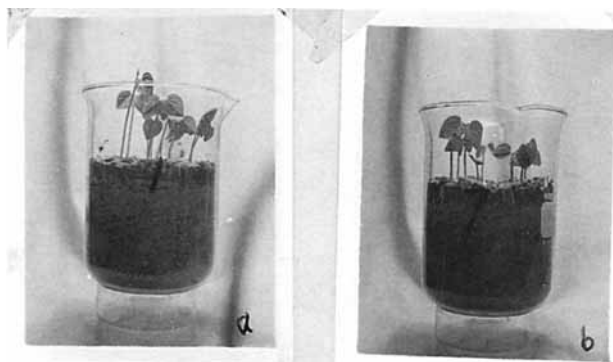


Figure 10 Use A3 superabsorbent for use as a soil conditioner for bean growth: (a) 0.3% (based on soil wt); (b) 0%.

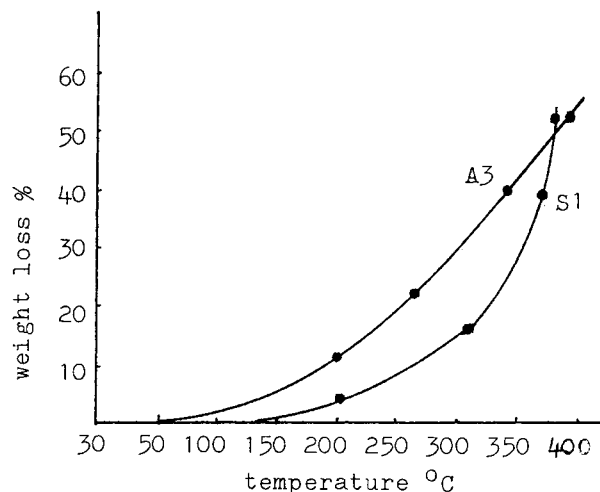


Figure 11 Thermogravimetric curve for A3 and S1 samples.

higher than those of S1 (which has non such groups). According to the following linear equation,⁸

$$\ln \ln \frac{1}{r} K - 0.457 \ln 10 \frac{E}{R\theta}$$

where *r* is the weight loss %; *θ*, the absolute temperature; and *E*, the pyrolysis activation energy.

Figure 12 is derived by plotting

$$-\ln \ln \frac{1}{r} \text{ vs. } \frac{1}{\theta}$$

From the slope (Fig. 12), the pyrolysis activation

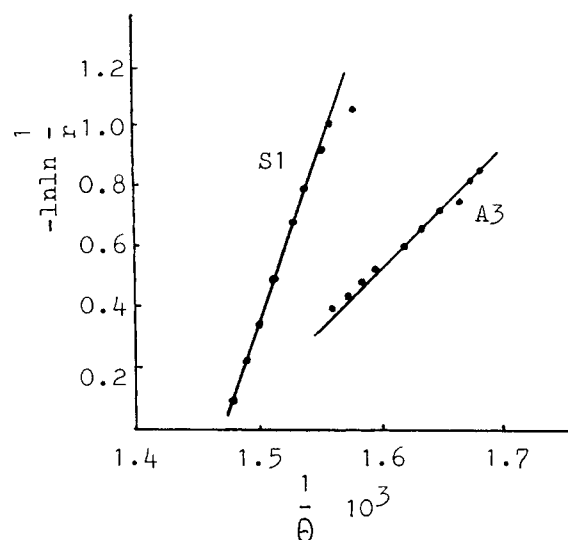


Figure 12 Pyrolysis activation energy for A3 and S1 samples.

energies for A3 and S1 are determined to be 32.5 and 101.6 kJ/mol, respectively. This illustrates that when the carboxyl group is introduced into the structural unit of the copolymers it results in a decrease in thermal stability, but the A3 sample is still stable at 150°C (wt % change is less than 5%), which means that A3, poly(AM-SAS-AA), is satisfactory for practical needs.

CONCLUSION

1. The novel copolymer superabsorbents, cross-linked poly(AM-SAS-AA), were synthesized in an aqueous solution by copolymerization of their respective monomers and N,N' -methylenebisacrylamide and initiated by using potassium persulfate with N,N,N',N' -tetramethylethylenediamine. In addition, the synthetic copolymers were characterized by elemental analysis and IR absorption spectroscopy.
2. It was found that the A3 sample has a high water absorbency and water retention. The $Q_{\max} = 437$ g/g in water and the swelling rate constant (K) were determined to be 2.49×10^{-2} .
A late transition was observed between 0.5

$\times 10^{-2}$ and 10^{-3} mol/L NaCl solution, whereas Q was determined to be 100–160 g/g.

3. The pyrolysis activation energies (E) for A3 and S1 were determined to be 32.5 and 101.6 kJ/mol, respectively.
4. The water retention of soil was enhanced by using the poly(AM-SAS-AA) superabsorbent (A3), and sturdy bean shoots grew when the A3 sample was used.

REFERENCES

1. G. Gilbert, Belg. Pat. 853,170 (1977).
2. D. J. Veal, U.S. Pat. 3,247,176 (1966).
3. S. Daniel, U.S. Pat. 4,384,988 (1983).
4. K. Ishihara, *Kobunshi Ronbunshu*, **46**(10), 591 (1989).
5. T. Motohashi, Tadakazu, *Chem. Ind.* **7**, 43–49, 62 (1979).
6. T. Kobayashi, *Kobunshi*, **36**(8), 612–615 (1987).
7. K.-J. Yao and B.-L. Wang, *J. Appl. Polym. Sci.*, **41**, 3079 (1990).
8. J. Wang, Y. Jiao, and S. Li, *J. Chem. Ind. Eng.*, **2**, 127 (1984).

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