Synthesis and Water Absorbency of Crosslinked Superabsorbent Polymers

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ABSTRACT: A series of novel copolymer superabsorbents based on monomer acrylamide (AM), potassium methacrylate (KMA), and 2-hydroxyethyl methacrylate (HEMA) were prepared by copolymerization using ammonium persulfate (APS) as an initiator and *N,N*-methylenebisacrylamide (MBA) as a crosslinking agent. The synthetic variables (the monomer concentration, crosslinker concentration, and initiator concentration) were also studied. The experimental results of superabsorbent polymers (SAPs) show a better absorbency in both water and NaCl solutions. The copolymers were characterized by IR spectroscopy. The water retention in the soil was enhanced using the above superabsorbents. The use of SAPs for the growth of groundnut plants was also investigated. SAPs can be considered for water-managing materials for agriculture and horticulture purposes in desert and drought-prone areas. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1795–1801, 2002

Key words: superabsorbent polymer; acrylamide; *N,N*-methylenebisacrylamide; water absorbency; crosslinking agent; water retention

INTRODUCTION

Superabsorbents[1] can absorb a large amount of water compared with general water-absorbing materials, in which the absorbed water is hardly removable even under some pressure. Because of their excellent characteristics, these superabsorbents are widely used in many products such as in disposable diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water-blocking tapes, medicine for the drug-delivery systems, and absorbent pads, where water absorbency or water retention is important.[1–8] Their use for agricultural applications[9] has shown encouraging results as they have been observed to help reduce irrigation water consumption, lower the death rate of plants, improve fertilizer retention in the soil, and increase plant growth rate. Their use for additional applications, that is, in communication cables, industrial absorbents, antiredecomposition agents for detergent formulations, artificial snow for winter sports, absorption/release of humidity, toys, cosmetics, and prevention of moisture ingress into walls and ceilings is in the experimental stage.[1,10,11] In such applications, water absorbency and water retention are essential. Some workers have modified these superabsorbent copolymers (SAPs) with a view to enhance their absorbency, gel strength, and absorption rate.[12–18] The influences of various reaction parameters on the water-absorption capacity of the SAPs have been investigated by various workers.[19,20] The dependence of water absorbency of SAPs on particle size and salinity were also investigated by Omidian et al.[21] The investi-

gation revealed that as the particle size became smaller the rate of absorption and ultimate degree of absorption both increased.

In our previous reports,[22,23] novel SAPs were investigated for improved growth of beans and croton plants in small pots and showed that absorbent-treated soil retained more moisture for a longer time and that both beans and croton plants live longer after germination. Here, we report on the synthesis of SAPs by polymerizing acrylamide (AM) with potassium methacrylate (KMA) and 2-hydroxyethyl methacrylate (HEMA). The swelling behavior of the above SAPs was studied, corresponding to the crosslink density, initiator concentration, and monomeric ratios. The water retention of the above SAPs in soil was also studied by growing groundnut plants.

EXPERIMENTAL

Materials

AM was purified by recrystallization from benzene. HEMA was distilled under reduced pressure. Ammonium persulfate (APS) was recrystallized from water. *N,N*-methylenebisacrylamide (MBA; chemically pure) was used as purchased. Ethylene glycol dimethacrylate (EGDMA) and diallyl phthalate (DP) were used as crosslinking agents after removing the stabilizer with a 2% NaOH solution. All solutions were prepared with double-distilled water. All the solvents were distilled before use. KMA was prepared in the laboratory.

Preparation of KMA

A potassium carbonate (0.5 mol) solution was prepared in distilled water and titrated against methacrylic acid (0.1 mol) put in a conical flask in dry ether. The white solid that separated was filtered under a vacuum pump and dried in a vacuum:

$$2CH_2\!\!=\!\!C\ (CH_3)\ COOH + K_2CO_3 \rightarrow$$

$$[CH_2\!\!=\!\!C\ (CH_3)\ COO]_2]K + H_2O + CO_2$$
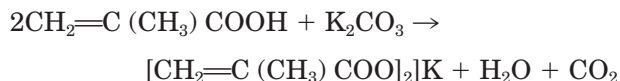
Synthesis Procedure

A series of the copolymer superabsorbents were prepared by the following procedure: The reactions were conducted in a three-necked flask equipped with a mechanical stirrer, condenser, and nitrogen line. A weighed quantity of monomers along with a crosslinking agent dissolved in distilled water was put in the reaction vessel under nitrogen flushing. After 15 min, APS was added to the reaction mixture and then the temperature was slowly increased to 80°C ± 1 with effective stirring. After 2 h of the reaction, a gel was formed. The resulting product was washed with ethanol and water and then dried in a vacuum oven at 60°C to a constant weight. The gel was dried, reweighed, and milled through a screen. All the SAPs were transparent.

Water-absorbency Measurement[24]

A sample (1 g) of the SAP was immersed in water (or a 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). Water absorbency was calculated using the following formula:

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

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

IR Spectra

The IR spectra of the copolymers were recorded on a Bio-Rad WIN FTIR using KBr pellets. The IR spectrum of the copolymer shows peaks corresponding to the functional groups attached to the monomeric units. The copolymer having acrylamide, KMA, and HEMA as monomeric units shows peaks at 3460 cm^{-1}, corresponding to NH stretching of the acrylamide unit, and at 1741 cm^{-1}, corresponding to the C=O of the ester group of acrylate unit, and a broad peak in the region 2362 cm^{-1}, corresponding to the O—H of the HEMA unit. Further, the spectrum also shows a peak at 1660 cm^{-1}, corresponding to the carbonyl group of the amide moiety of the acrylamide unit. In addition to the above peaks, peaks at 1243 and 1171 cm^{-1}, corresponding to the C—O—C coupling interaction of ester groups, are also observed. From the above IR data, it is observed that all the monomeric units are incorporated into the copolymer chain. Figure 1 repre-
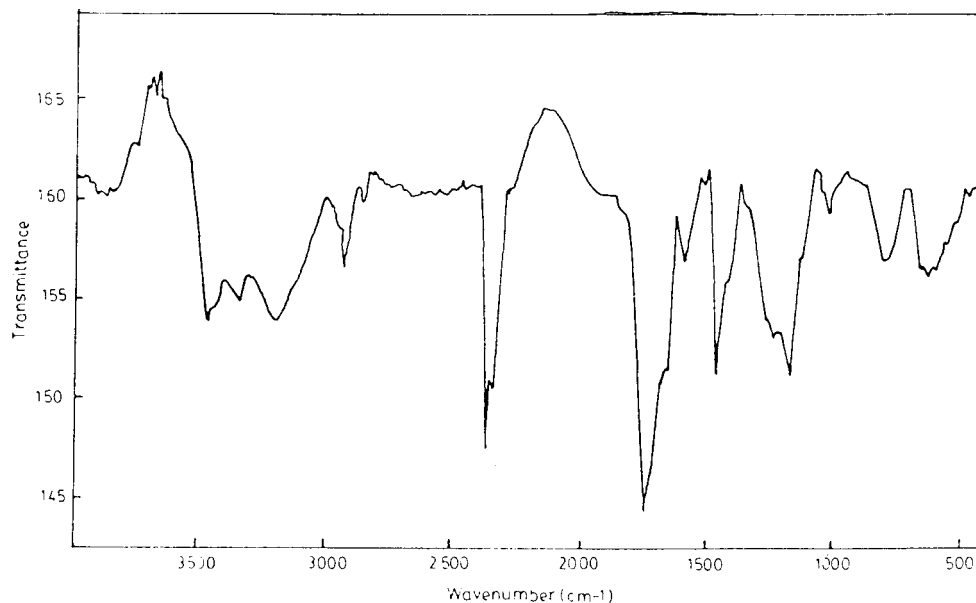
Figure 1   Infrared spectroscopy of poly(AM–KMA–HEMA) (S_{11}).

sents the IR spectra of the copolymer (S_{11}) having maximum absorbency.

Thermal Analysis

The thermostablity of the dry sample was determined using a Universal V1. 12E thermogravimetric analyzer (TGA) instrument. The temperature range in the experiment covered is 50–800°C at a heating rate of 20°C/min using dry nitrogen at a flow rate of 50 mL/min.

The TGA of the sample (S_{11}) is presented in Figure 2. The completely dried powder sample was taken for thermogravimetric analysis. Due to the high water-absorbing capacity, during the
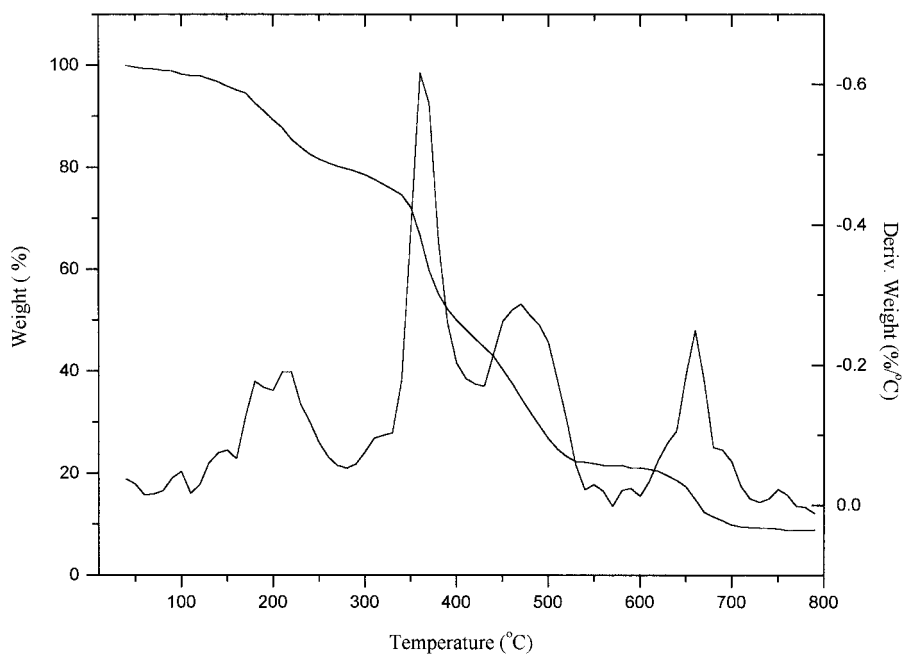

Figure 2   TGA curve of poly(AM–KMA–HEMA) (S_{11}).

procedure there may be moisture present in the sample, which will give a moisture weight loss below 100°C. The initial weight loss of the sample started at 200°C (16.5%). The sample has a significant weight loss at 300°C (27.0%) and at 400°C (52.13%) and continued to have a weight loss up to 500°C, with a weight loss of 70%. Therefore, this particular sample had an initial decomposition temperature of 339°C (32.64%).

RESULTS AND DISCUSSION

Table I illustrates the absorbability of copolymers as a function of monomeric units in the copolymer network. Swelling increases with increase in the KMA units (COOK) in the polymer backbone chain, but an excess of KMA units leads to an increase in the solubility of the copolymer at a fixed crosslinker concentration and a decreasing absorbing capacity of water.

Influence of Parameters on Water Absorbency

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

Effect of Crosslinking Agent
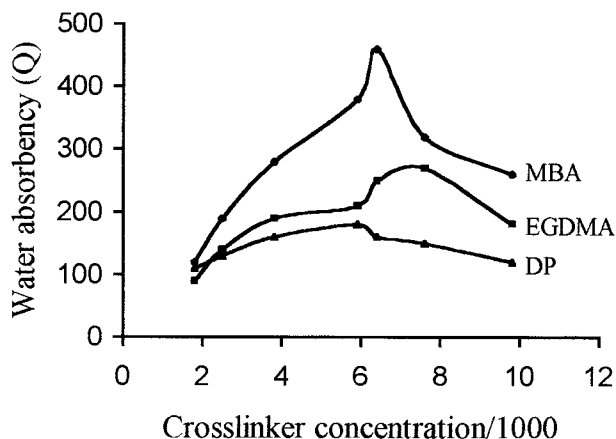
Figure 3 shows the water absorbency of cross-

Figure 3 Influence of crosslinker concentration on water absorbency (Q) in deionized water of poly(AM–KMA–HEMA) (S_{11}).

linked poly(AM–KMA–HEMA) as a function of the crosslinker concentration. The water absorbency increases as the MBA concentration increases from 1.8×10^{-3} to 6.4×10^{-3} mol/L and decreases considerably when the MBA concentration is higher than 6.4×10^{-3} mol/L. This is due to a decrease in the space between the copolymer chains as the crosslinker concentration increases. The swelling capacity increases as the EGDMA concentration increases from 1.8×10^{-3} to 7.6×10^{-3} mol/L and decreases considerably when

Table I Influence of Monomeric Ratios on Swelling Capacity of Crosslinked Poly(AM–KMA–HEMA) Superabsorbents

Polymer Code	Monomer in the Feed (mol/L)			Water Absorbency (Q)
	AM	KMA	HEMA	
S_1	0.80	0.06	—	95
S_2	0.80	0.12	—	120
S_3	0.80	0.18	—	180
S_4	0.80	0.26	—	240
S_5	0.80	0.30	—	194
S_6	0.80	—	0.06	75
S_7	0.80	—	0.12	90
S_8	0.80	—	0.18	120
S_9	0.80	—	0.22	84
S_{10}	0.80	0.26	0.18	350
S_{11}	**0.80**	**0.30**	**0.18**	**460**
S_{12}	0.80	0.32	0.18	380
S_{13}	0.80	0.36	0.18	290

Reaction conditions: Crosslinker [MBA]: 6.4×10^{-3} mol/L; initiator [APS]: 3.5×10^{-3} mol/L; temperature: ±80°C; reaction time: 2 h.
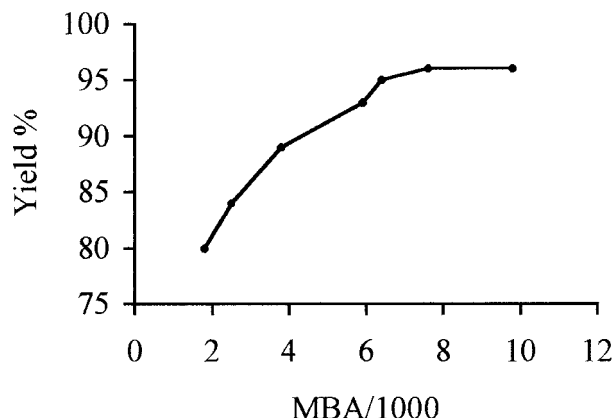
Figure 4 Influence of MBA concentration on yield of poly(AM–KMA–HEMA) (S_{11}).

Figure 5 Influence of APS concentration on water absorbency in deionized water of poly(AM–KMA–HEMA) (S_{11}).

the EGDMA concentration is higher than 7.6 $\times$ 10^{-3} mol/L. The swelling capacity increases as the DP concentration increases from 1.8×10^{-3} to 5.9×10^{-3} mol/L and decreases considerably when the DP concentration is greater than 5.9 $\times$ 10^{-3} mol/L. The maximum absorbency of the copolymer depends upon the nature and concentration of the crosslinking agent. From Figure 3, it is clearly evident that the maximum absorbency is found when the concentration of MBA reaches 6.4×10^{-3} mol/L, whereas the absorbency is maximum at a concentration of 7.6×10^{-3} mol/L and 5.9×10^{-3} mol/L in the case of EGDMA and DP, respectively. Further, it is also noticed that the maximum absorbency is found when MBA is used as a crosslinking agent. This can be due to the more polar nature of MBA as a crosslinking agent. The polarity of the crosslinking agent increases the swelling capacity due to polar end groups. The polar end groups attract water molecules quickly. As the concentration of the crosslinking agent increases, the swelling capacity of the copolymer increases up to a certain level, and with a higher crosslinker concentration, the swelling capacity decreases drastically.

The yield of the crosslinked copolymer poly-(AM–KMA–HEMA) as a function of the crosslinker concentration is presented in Figure 4. The yield of the copolymer was calculated after measurement of the equilibrium swelling. All soluble fractions were removed by repeated washings with water and methanol. As the crosslinker concentration increases, the yield of the copolymer increases since a greater number of repeating units are crosslinked.
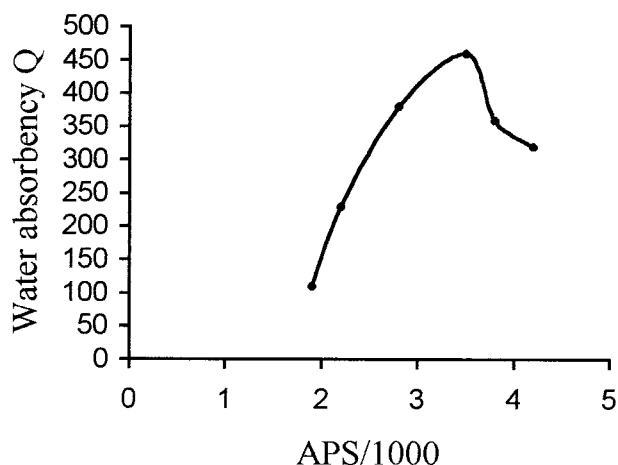
Effect of Initiator

The effect of the initiator (APS) concentration on the swelling properties of the copolymer and the copolymerization rate was also studied, and the results are presented in Figures 5 and 6. The swelling ratio increases as the APS concentration increases from 1.9×10^{-3} to 3.5×10^{-3} mol/L and decreases slowly with a further increase in the concentration of APS. This is due to an increase in the number of radicals produced as the concentration of APS increases. The increase in the production of radicals increases the rate of polymerization, thereby lessening the crosslinking density, and is further responsible for a decrease in the swelling capacity.
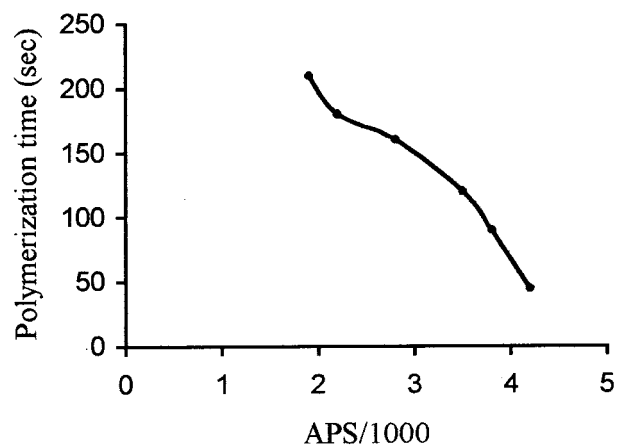

Figure 6 Influence of APS concentration on polymerization time of poly(AM–KMA–HEMA) (S_{11}).
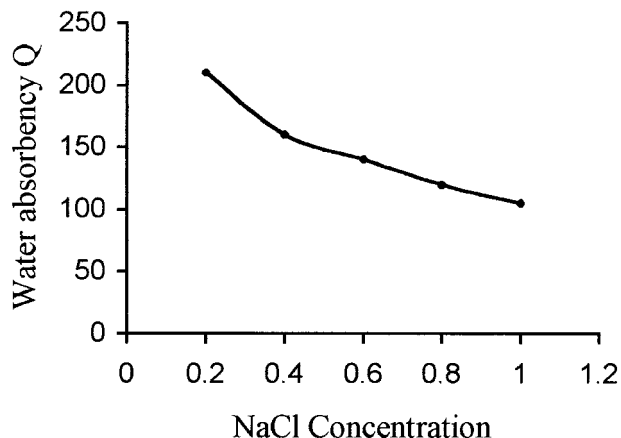
Figure 7 Influence of NaCl concentration on water absorbency (Q) in deionized water of poly(AM–KMA–HEMA) (S_{11}).

Figure 7 shows the effect of the NaCl concentration on the water absorbency of the copolymers. As the NaCl concentration increases, the absorbency decreases. This study was undertaken to determine the behavior of absorbency in salt solutions.

The time required to reach the maximum swelling capacity of the copolymers was studied and the results are presented in Figure 8. As the size of the sample increases, the time taken for the maximum absorbency for the gel also increases. The copolymer was obtained in gel form. This gel was washed with water and methanol to remove soluble fractions. The gel was cut into small pieces and dried in a vacuum oven. SAP, 0.1 g, was immersed in 200 mL of deionized wa-
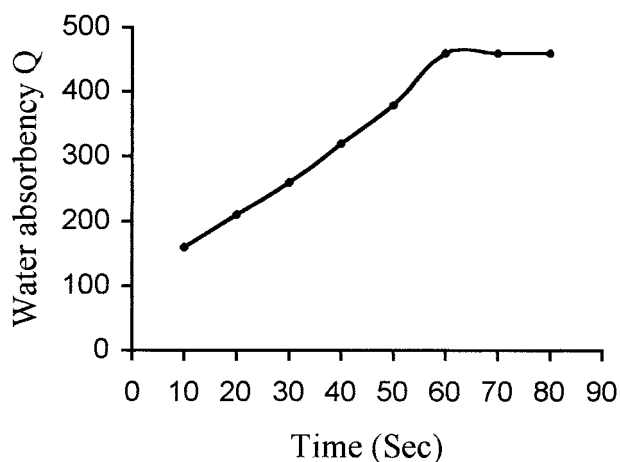

Figure 8 Water absorbency versus swelling time of poly(AM–KMA–HEMA) (S_{11}).
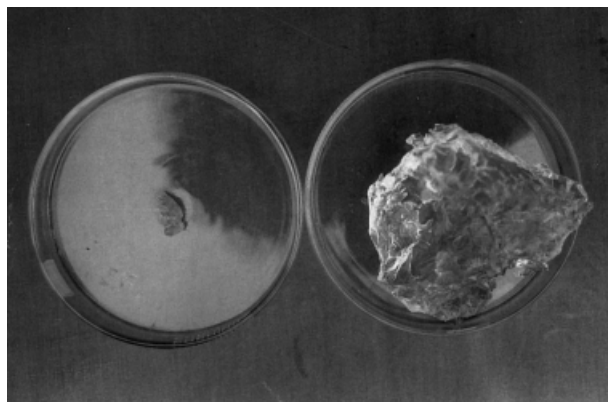

Figure 9 Dry and swollen SAPs (S_{11}).

ter, and the water absorbency was measured for every 10 min. The results indicate that the SAPs absorbed the maximum amount of water within 45 min. All the gels have good absorbency. The shape of the dry and swollen states of an SAP is presented in Figure 9.

Water Retention of SAPs

One of the most important applications of SAPs is for agricultural and horticultural purposes, especially for effective utilization of water in dry and desert regions and to transform "these dry and desert regions into green fertile lands." In this regard, the preliminary testing of these SAPs for water retention was carried out in small polyethylene bags by growing the seeds of groundnuts into plants with and without using SAPs. Equal amounts of soil (2 kg) was put into two polyethylene bags (A and B) and a 0.5% (w/w) superabsorbent copolymer (S_{11}) was thoroughly mixed with the soil in the polyethylene bag A. Ten healthy seeds were placed into two bags and equal amounts (400 mL) of water were added initially. Germination was observed after 6 days in both bags. The growth pattern of the plants was observed and care was taken to see that no pests or other diseases affected the plants. There was no considerable difference in the growth of the plants in both bags to 15 days. After 15 days, the plants in bag B started wilting, whereas the plants in bag A were fresh. At this juncture, an additional amount (400 mL) of water was added to bag B. Even after 30 days' growth, the plants in bag A were still fresh, whereas the plants in bag B started wilting, although an additional amount of water (400 mL) was added to bag B. After 30 days, further growth of the plants was observed

up to 40 days in both bags (A and B). At this stage, the plants were wilting in both bags. Now, an equal amount of water (400 mL) was added to both bags (A and B). Using the above SAPs, the moisture content of the soil can be retained up to 1 month. The plants in bag A were sustained up to 1 month without any additional water by adding SAPs to the soil. The SAPs have a good water-retention capacity in the soil. The water that can be saved by using the above SAPs is 800 mL for 40 days. From this study, it can be inferred that water can be saved and managed in dry and desert regions and SAPs can be used for the growth of the plants with less water, thereby making drought and desert regions into green fertile lands.

CONCLUSIONS

Novel superabsorbents were synthesized in an aqueous solution by copolymerization of the respective monomers with MBA as the crosslinking agent and APS as the initiator. The synthetic variables (monomer feed ratios, crosslinker concentrations, and initiator concentration) were also studied. The copolymers were characterized by IR spectroscopy. The absorbency of the SAPs was measured in water and NaCl solutions. The S_{11} superabsorbent has a high water absorbency [Q_{max} = 460 g H_2O/g (g/L)]. These SAPs also have a fast swelling capacity. The water retention of the soil was also enhanced using the above SAPs. This was studied by growing groundnut seeds. The results of the present work indicate that SAPs have a good water-retention capacity and found applications in agriculture, especially in drought-prone areas where the availability of water is less.

REFERENCES

1. Buchhloz, F. L. In Superabsorbent Polymers: Science and Technology; Buchholz, F. L.; Peppas, N. A.; Eds.; ACS Symposium Series 38; American Chemical Society: Washington, DC, 1994; p 573.
2. Sakiyama, T.; Chu, C. H.; Fujii, T.; Yano, T. J Appl Polym Sci 1993, 50, 2021.
3. Yoshida, M.; Asano, M.; Kumakura, M. J. Eur Polym J 1989, 25, 1197.
4. Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. J Appl Polym Sci 1992, 44, 249.
5. Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. J Appl Polym Sci 1993, 47, 113.
6. Advances in Superasorbent Polymers; Hogari, K.; Ashiya, F., Eds.; American Chemical Society: Washington, DC, 1994.
7. Erichksen, P. H.; Nguyen, H. V.; Oczkowski, B.; Olejinik, T. A. Eur. Patent 40 087, 1981.
8. Kobayashi, T. Kobunshi 1987, 36, 612.
9. Shimomura, T. Polym Mater Sci Eng 1993, 69, 485.
10. Figuly, G. D.; Royce, S. D.; Khasat, N. P.; Schock, L. E.; Wu, S. D.; Davidson, F.; Campbell, G. C., Jr.; Keating, M. Y.; Chen, H. W.; Shimshik, E. J.; Fisher, R. T.; Grimminger, L. C.; Thomas, B. E.; Smith, L. H.; Gillies, P. J. Macromolecules 1997, 30, 6174.
11. Po, R. J. Macromol Sci Rev Macromol Chem Phys C 1994, 34, 607.
12. Kobayashi, T. Kobunshi 1987, 36, 612.
13. Taylor, N. W.; Fanta, G. F.; Doane, W. M.; Russell, C. R. J Appl Polym Sci 1978, 22, 1343.
14. Burr, R. C.; Fanta, W. F.; Doane, W. M.; Russell, C. R. J Appl Polym Sci 1979, 24, 1384.
15. Burr, R. C.; Fanta, W. F.; Doane, W. M.; Russell, C. R. J Appl Polym Sci 1982, 27, 2313.
16. Kejun, K.; Benlian, W. J Appl Polym Sci 1990, 41, 3079.
17. Burr, R. C.; Fanta, W. F.; Doane, W. M.; Russell, C. R. J Appl Polym Sci 1979, 24, 2015.
18. Yoshinobu, M.; Morita, M.; Sakata, I. J Appl Polym Sci 1992, 45, 2031.
19. Kiatkamjorwong, S.; Pphunchareon, P. J Appl Polym Sci 1999, 72, 1349.
20. Wen-fu, L; You-min, T. J Appl Polym Sci 1999, 72, 1221.
21. Omidian, H.; Hashemi, S. A.; Sammes, P. G.; Meldrum, I. J. Polymer 1999, 40, 1753.
22. Padmanabha Raju, M.; Mohana Raju, K. J Appl Polym Sci 2001, 80, 2635.
23. Padmanabha Raju, M.; Mohana Raju, K. J Polym Mater 2001, 19, 149.
24. Yao, K. J.; Wang, B. L. J Appl Polym Sci 1990, 41, 3079.