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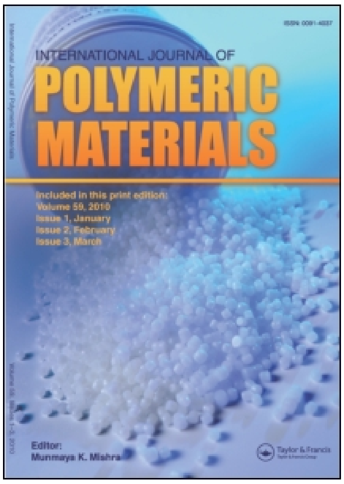

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SYNTHESIS AND SWELLING BEHAVIOR OF SUPERABSORBENT POLYMERIC MATERIALS

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SYNTHESIS AND SWELLING BEHAVIOR OF SUPERABSORBENT POLYMERIC MATERIALS

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A series of novel crosslinked copolymers based on the monomers acrylamide (AM), calcium acrylate (CA), and sodium methacrylate (SMA) were prepared by aqueous solution polymerization using ammonium persulfate (APS) as initiator and N, N-methylene-bis-acrylamide (MBA) as crosslinking agent. The synthetic variables monomer concentration, crosslinker concentration, initiator concentration were also studied. The experimental results of SAPs show good absorbency in both water and NaCl solutions. The copolymers were characterized by IR spectroscopy. The water retention of SAPs was studied in an oven at 60 and 100°C.

Keywords: Superabsorbent copolymers, acrylamide, crosslinking agent, swelling capacity, water retention

INTRODUCTION

Superabsorbents can absorb large amounts of water in a short time. The absorbed water can be retained even under pressure. Therefore, superabsorbents have great advantages over traditional water-absorbing materials such as cotton, pulp, sponge, etc., and found to have a variety of valuable applications [1–4]. Superabsorbents are used widely in sanitary goods such as disposable diapers, hygienic napkins, soil for agriculture and horticulture, gel actuators,

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water-blocking tapes; drug delivery systems and absorbent pads, etc. [5–8]. In such applications, water absorbency and water retention are essential. Some workers have modified these SAPs with a view to enhance their absorbency, gel strength and absorption rate [8–15]. In this direction the authors have done some work on the synthesis of superabsorbent copolymers and gels that have been tried for the growth of groundnut plants and crouton plants with and without superabsorbent polymers and reported the same in the literature [16–19].

In the present investigation, the authors report the synthesis of superabsorbent copolymers by polymerizing the acrylamide (AM) with calcium acrylate (CA) and sodium methacrylate (SMA). The copolymers are characterized by IR spectroscopy. The swelling behavior of the above superabsorbent copolymers (SAPs) was studied, corresponding to crosslink density, initiator concentration and monomer ratios.

EXPERIMENTAL

Materials

Acrylamide (AM) was purified by recrystallization from benzene. Ammonium persulfate (APS) was recrystallized from water. N, N-methylene bisacrylamide (MBA) (chemically pure) was used as purchased. Ethylene glycol dimethacrylate (EGDMA) and Diallyl Phthalate (DP) were used as crosslinking agents after removing stabilizer with 2% NaOH solution. All the solutions were prepared with doubly distilled water. All the solvents were distilled before use. Calcium acrylate (CA) and sodium methacrylate (SMA) were prepared in the laboratory.

Preparation of Calcium Acrylate (CA)

Calcium oxide (0.5 mole) was dispersed in methanol. Acrylic acid (0.1 mole) was taken up in a conical flask in dry ether and titrated with the calcium oxide suspension. A white solid separated out. The product was filtered under vacuum and dried in a vacuum desiccator.

$$2CH_2 = CHCOOH + CaO \rightarrow [CH_2 = CHCOO]_2Ca\downarrow + H_2O$$

Preparation of Sodium Methacrylate (SMA)

Sodium carbonate (0.5 mole) solution was prepared in distilled water and titrated against methacrylic acid (0.1 mole) taken in a conical flask in dry ether. The white solid separated was filtered under a vacuum pump and dried in a vacuum desiccator.

$$2CH_2 = C(CH_3)COOH + Na_2CO_3 \rightarrow 2CH_2 \\ = C(CH_3)COONa \downarrow + H_2O + CO_2 \uparrow$$

Synthesis Procedure

A series of superabsorbent copolymers were prepared by the following procedure.

All the reactions were conducted in a 3-necked flask equipped with a mechanical stirrer, condenser and nitrogen line. A weighed quantity of monomers, along with crosslinking agent dissolved in distilled water, was put in the reaction vessel. After 15 minutes of stirring, ammonium persulfate was added to the reaction mixture and then slowly the temperature raised up to 80°C with effective stirring. After 2 hrs of reaction, a gel was formed. The gel was washed with ethanol and water and then dried in a vacuum oven at 60°C to constant weight. The dried gel was reweighed and milled through a screen. All gels are transparent.

Water Absorbency Measurement

A sample (1 g) of the superabsorbent copolymer was immersed in water (or saline solution) at room temperature until equilibrium is reached. Absorbability is determined by weighing the swollen gel (the gel was allowed to drain on a sieve for 10 min). The water absorbency is calculated using the following equation[20].

$$\text{Water absorbency } Q(\text{g } H_2O/\text{g sample}) = \frac{m - m_0}{m_0}$$

Absorbency is expressed in grams of water retained in the gel by a gram for dried gel, m and m_0 denote the weight of the water swollen gel and the weight of the absorbent, respectively.

RESULTS AND DISCUSSION

Table 1 illustrates the absorbability of copolymers as a function of monomer distribution in the copolymer network. Swelling increases with the increase in ionic units (or monomer ratio) in the polymer back

TABLE 1 Influence of the Monomeric Ratios on the Swelling Capacity of Crosslinked Poly(AM-CA-SMA)

Polymer code	AM	Monomer in the feed (mole/L)CA	SMA	Water absorbency (Q)
S_1	0.80	0.10	–	110
S_2	0.80	0.16	–	130
S_3	0.80	0.20	–	190
S_4	0.80	0.22	–	120
S_5	0.80	–	0.12	160
S_6	0.80	–	0.20	190
S_7	0.80	–	0.24	280
S_8	0.80	–	0.18	210
S_9	0.80	0.20	0.24	370
S_{10}	0.80	0.22	0.24	500
S_{11}	0.80	0.25	0.24	450
S_{12}	0.80	0.28	0.24	390

Reaction Conditions: Crosslinking agent [MBA] $= 7.8 \times 10^{-3}$ mol/L; Initiator [APS] $= 3.8 \times 10^{-3}$ mol/L; Temp: 80°C ± 1, Reaction time: 2 h.

bone chain, but an excess of ionic units leads to an increase in the solubility of the copolymer at a fixed crosslinker concentration and decreasing the absorbing capacity of water.

IR Spectra

The IR spectra of the copolymers were recorded on a Bio-Rad WIN FTIR using KBr Pellets.

The IR spectra of the copolymers show the peaks corresponding to the functional groups attached to the monomer units. The peaks observed are 3454 cm^{-1} corresponding to the NH stretching of the acrylamide unit, 1735 cm^{-1} corresponding to $\nu C = O$ of the acrylate unit and 1658 cm^{-1} corresponding to the carbonyl group of the acrylamide unit. In addition to the above peaks, peaks are also observed at 1253 and 1172 cm^{-1} corresponding to C-O-C stretching interactions of ester groups. The above IR analysis indicates that all the monomeric units, i.e. acrylamide, sodium methacrylate and calcium acrylate are incorporated in the copolymer backbone. Figure 1 represents the IR spectra of the copolymer (S_{10}) having maximum absorbency.

Thermal Analysis

Thermostablity of the dry sample was performed using a Universal VI. 12E Thermogravimetric Analyzer (TGA) Instrument.

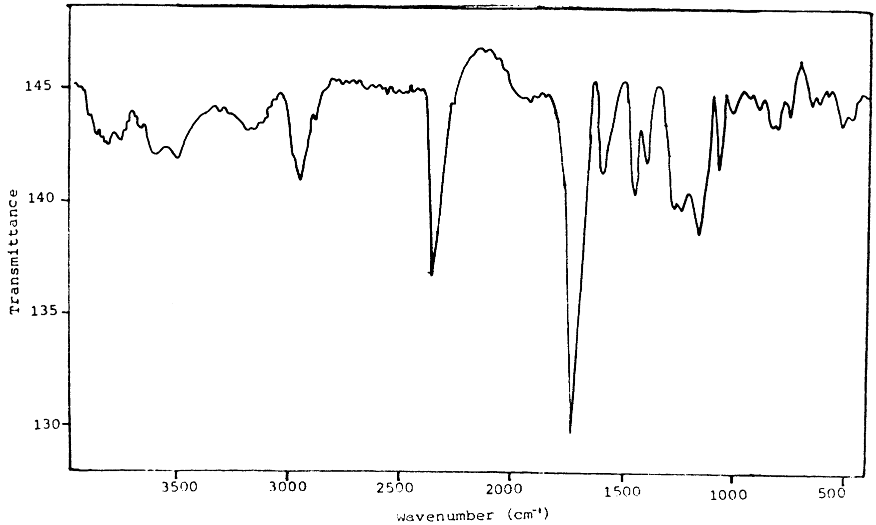

FIGURE 1 Infrared spectroscopy of Poly(AM-CA-SMA)(S_{10}).

The temperature range in the experiment covered was 50 to 800°C at a heating rate of 20°C/min using dry nitrogen at a flow rate 50 ml/min.

The TGA of the sample (S_{10}) is presented in Figure 2. The sample shows a very small weight loss below 100°C, implying loss of moisture. The sample has significant weight loss at 200°C (6.03%) and at 300°C (28.06%). The major weight loss started at 350°C (66%) and continued to lose weight up to 400°C, with a weight loss 88%. Therefore this particular sample have a major weight loss at 350°.

Influence of Parameters on Water Absorbency

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

Effect of Crosslinking Agent

Figure 3 shows the water absorbency of the crosslinked poly (AM-CA-SMA) as a function of crosslinker concentration. The water absorbency increases as MBA concentration increases from 1.5×10^{-3} to 7.8×10^{-3} mol/L and decreases considerably when MBA concentration is higher than 7.8×10^{-3} mol/L. This is due to decrease in space between the copolymer chains as crosslinking increases. The swelling capacity increases as EGDMA concentration increases from 1.5×10^{-3}

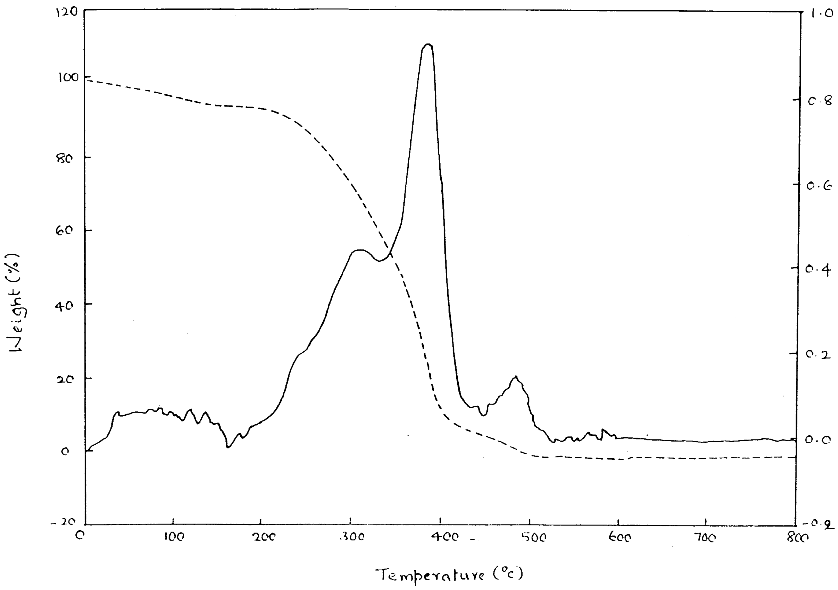

FIGURE 2 TGA curve of Poly(AM-CA-SMA)(S_{10}).

to 5.8×10^{-3} mol/L and decreases considerably when EGDMA concentration is higher than 5.8×10^{-3} mol/L. The swelling capacity increases as DP concentration proceeds from 1.5×10^{-3} to 9.0×10^{-3} mol/L and decreases considerably when DP concentration is higher than 9.0×10^{-3} mol/L. The concentration at the maximum

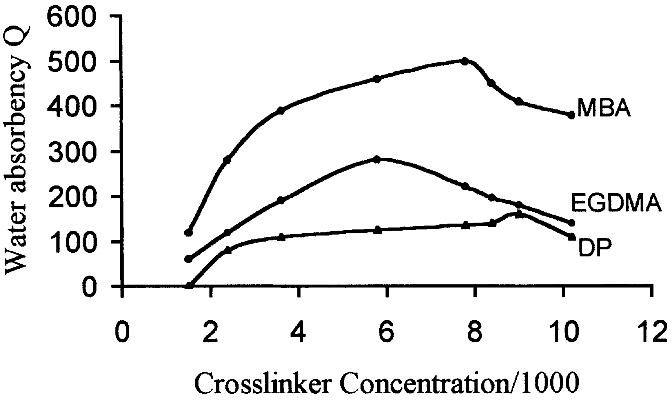

FIGURE 3 Influence of crosslinker concentration on water absorbency (Q) in deionized water of Poly(AM-CA-SMA)(S_{10}).

absorbency of the copolymer depends upon the nature of the crosslinking agent. Figure 3 shows that the maximum absorbency is found when the concentration of MBA reaches to 7.8×10^{-3} mol/L, whereas absorbency is maximum at concentration 5.8×10^{-3} mol/L in the case of EGDMA and DP, respectively. It is also noticed that maximum absorbency is found when MBA is used as crossliking agent. This may be due to the more polar nature of N, N-methylene-bis-acrylamide (MBA) as crosslinking agent. As the concentration of the crosslinking agent increases, the swelling capacity of the copolymer increases up to a certain level and with higher crosslinker concentration the swelling capacity decreases drastically. The effect of MBA crosslinker concentration on the yield of the copolymer poly (AM-CA-SMA) is presented in Figure 4. As crosslinker concentration increases the yield of the copolymer also increases due to increase in number of crosslinks.

Effect of Initiator

The effect of initiator (APS) concentration on swelling properties and polymerization rate of the copolymers was also studied and the results are presented in Figure 5 and 6. The swelling ratio increases as APS concentration proceeds from 2.0×10^{-3} to 3.8×10^{-3} mol/L and decreases slowly with further increase in 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 higher production of radicals at higher concentration of the initiator increases the rate of polymerization thereby drastically lessening the crosslinking density

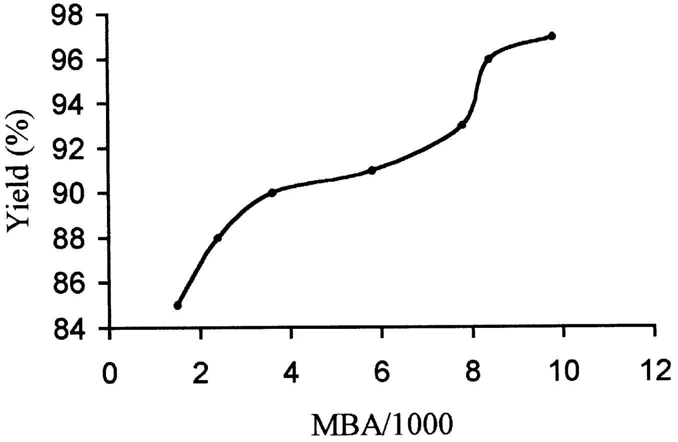

FIGURE 4 Influence of MBA concentration on yield of Poly(AM-CA-SMA) (S_{10}).

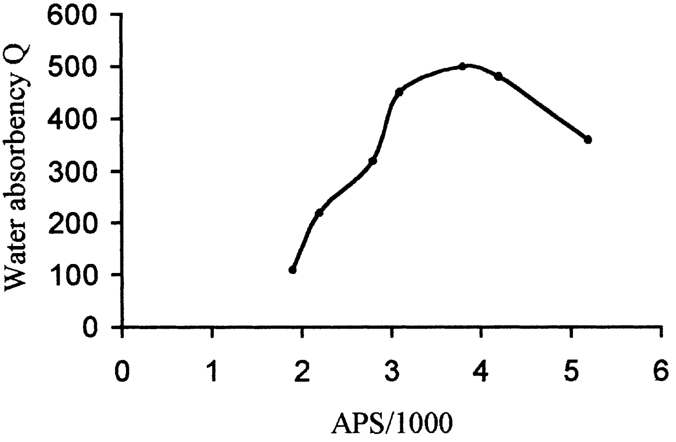

FIGURE 5 Influence of APS concentration on water absorbency in deionized water of Poly(AM-CA-SMA)(S_{10}).

and this is responsible for decrease in the swelling capacity of the copolymer.

Figure 7 shows the effect of NaCl concentration on water absorbency of the copolymer. As NaCl concentration increases the absorbency decreases. This study is important to know the behavior of absorbency in salt solutions.

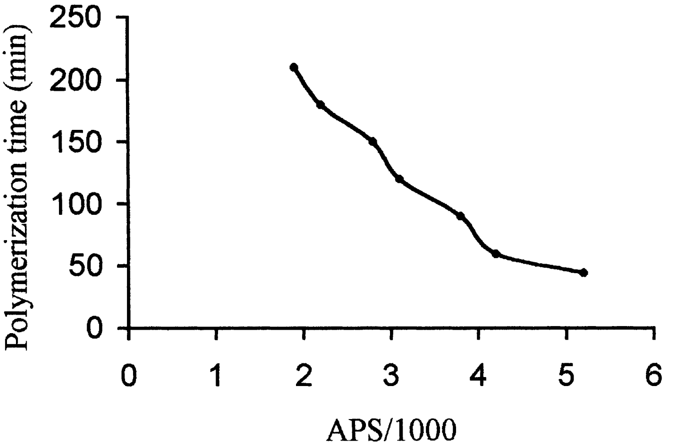

FIGURE 6 Influence of APS concentration of the polymerization time of Poly(AM-CA-SMA)(S_{10}).

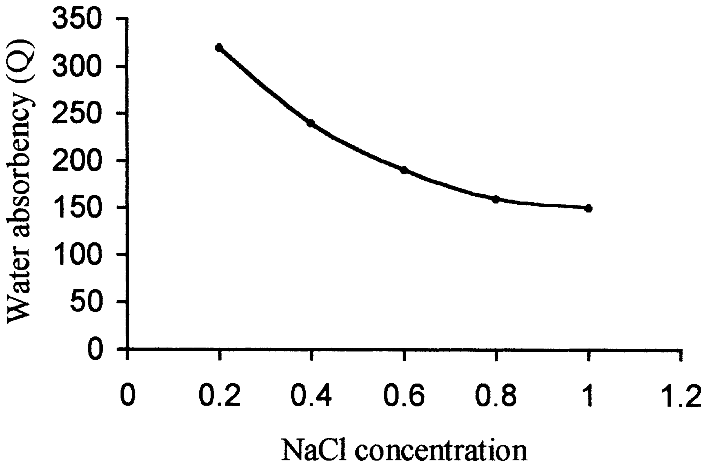

FIGURE 7 Influence of NaCl concentration on water absorbency (Q) in deionized water of Poly(AM-CA-SMA)(S_{10}).

The time required to reach the maximum swelling capacity of the copolymers was studied and the results are presented in Figure 8. The results indicate that the SAPs absorb maximum water within 50 minutes. All the gels have good absorbency.

The water retention capacity of these SAPs was also studied at higher temperatures ranging from 60°C and 100°C in an oven and the results are presented in Figure 9. The photographs of dry and swollen superabsorbent copolymers are presented in Figure 10.

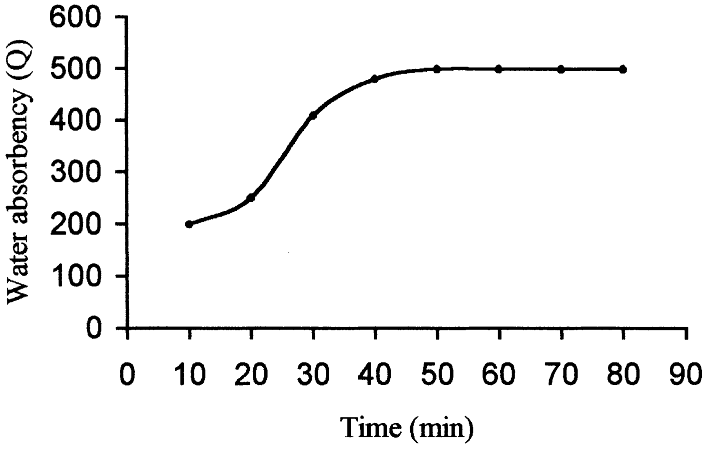

FIGURE 8 Water absorbency (Q) Vs time of Poly(AM-CA-SMA)(S_{10}).

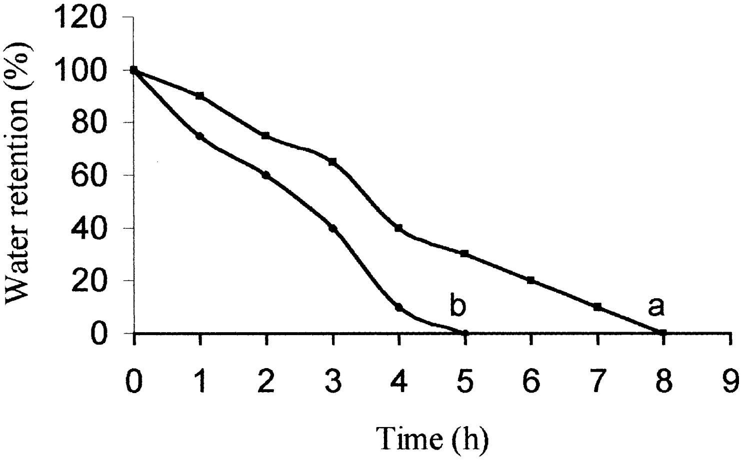

FIGURE 9 Effect of higher temperatures on water retention capacity of Poly(AM-CA-SMA)(S_{10}) (a) 60°C, (b) 100°C.

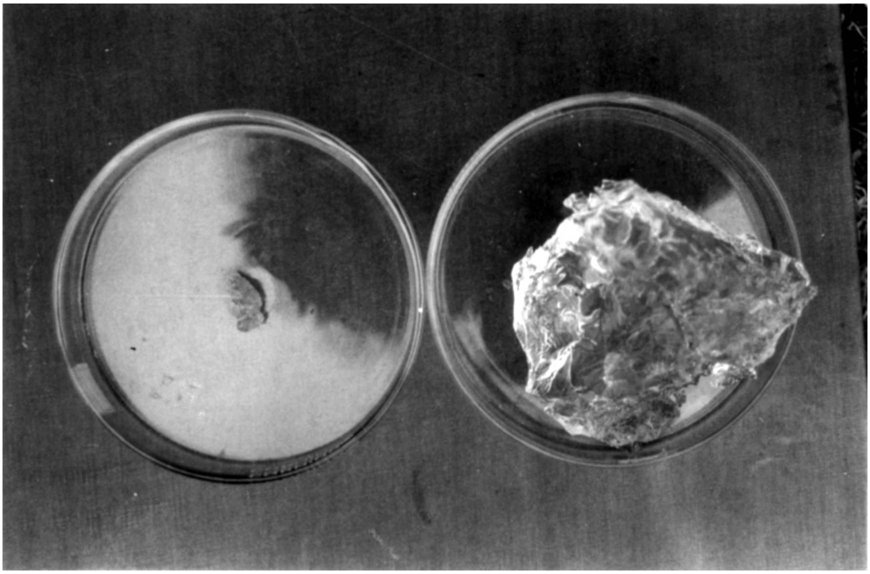

FIGURE 10 Dry and swollen superabsorbent copolymers (S_{10}).

CONCLUSION

A number of novel superabsorbent copolymers were synthesized in an aqueous solution by copolymerization of acrylamide, calcium acrylate, and sodium methacrylate with N, N-methylene-bis-acrylamide, ethylene glycol dimethacrylate and diallyl phthalate as crosslinking agents and ammonium persulfate as initiator. The water absorbency of the copolymers is maximum when MBA is used as crosslinking agent. The synthetic variables monomer feed ratios, crosslinker concentration and initiator concentration were also studied. The copolymers were characterized by IR spectroscopy. The absorbency of the SAPs was measured in water and in NaCl solutions. The superabsorbent coded S_{10} has the highest water absorbency ($Q_{max} = 500$ g/g H_2O) (g/l). These SAPs have fast swelling capacity. The results of the present work indicate that the SAPs have good water retention capacity and will find application in agriculture especially in drought−prone areas where the availability of water is insufficient.

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