

Studies of Crosslinked Poly(AM-MSAS-AA) Gels. I. Synthesis and Characterization

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ABSTRACT: Novel superabsorbent copolymers were prepared from acrylamide (AM), sodium methallylsulfonate (MSAS), sodium acrylate (AA), and *N,N'*-methylenebisacrylamide (BisA) in aqueous solution using potassium persulfate (KPS)/*N,N,N',N'*-tetramethylethylenediamine (TMEDA) as the redox initiator. The copolymers were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The experimental results show that absorbency increases with an increase in crosslinker concentration but decreases with excessive crosslinking. The ionic groups in the polymer network significantly increase the equilibrium swelling. Water retention at pressures of 1–10 kg/cm² and temperatures of 60 and 100°C are also reported. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1001–1007, 1997

Key words: water absorbent; hydrogel; swelling; crosslinking; copolymer

INTRODUCTION

Since the first superabsorbent polymer was reported by the U.S. Department of Agriculture,¹ there has been considerable interest in water-swallowable polymers capable of absorbing and holding large amounts of water. These materials are used in a wide range of health applications and are especially important as materials for absorption of large amounts of fluids in diapers or incontinence products.^{2,3} Recently, they were also found to be valuable in a variety of more specialized applications, including matrices for controlled drug-delivery systems^{4–8} and materials for agriculture mulches.⁹

In the application of superabsorbents in agriculture and horticulture, Shimomura and Namba¹⁰ described that the poly(acrylic acid)-type superabsorbent

can increase vegetable yield about 10% compared to control, and the improvements were even greater when sulfonate type superabsorbents were used under water-saving conditions. These observations reflect the fact that the sulfonate absorbent is less sensitive to polyvalent cations from soil, water, and fertilizers and thus can maintain its performance for a longer period of time.¹⁰ Our previous studies on the water-retention of sulfonate type absorbents also showed that absorbent treated soil retained more moisture for a longer time and that bean plants live longer after germination.^{11,12} Here, we report a copolymer superabsorbent prepared from acrylamide, sodium methallylsulfonate, sodium acrylate, and *N,N'*-methylenebisacrylamide in aqueous solution using potassium persulfate/*N,N,N',N'*-tetramethylethylenediamine as the redox initiator. The relationship between swelling and both crosslinking and ionic content is studied as well as the water retention of the copolymer under different temperature and pressure conditions.

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EXPERIMENTAL

Materials

Acrylamide (AM) was purified by recrystallization from benzene (mp 84–85°C). Sodium methallylsulfonate (MSAS) was purified by recrystallization from 95% alcohol and vacuum-dried to constant weight.¹³ Potassium persulfate (KPS) was recrystallized from water. Sodium acrylate (AA), *N,N,N',N'*-tetramethylethylenediamine (TMEDA), and *N,N'*-methylenebisacrylamide (BisA) were used as purchased. All solutions were prepared in distilled water.

Gel Preparation

A series of the copolymer superabsorbents were prepared 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 deoxygenated with nitrogen while stirring for 20 min. TMEDA was then added and, after 4 h at 35°C, the resulting product was cut into small pieces. The gel was then immersed in and washed with ethanol, vacuum-dried at 50°C to a constant weight and milled through a 40-mesh screen.

Characterization

1. Polymer infrared (FTIR) spectra were recorded with a NICOLET FT-20 SX spectrometer (KBr disk).
2. Copolymer composition analysis was determined by nitrogen and sulfur content using Kjeldahl and oxygen flask methods.
3. Thermal stability studies of dry samples were performed using a Perkin-Elmer TGS-2 thermogravimetric analyzer. The temperature range in these experiments covered 30–600°C at a heating rate of 10°C/min using a dry nitrogen purge at a flow rate of 40 mL/min.
4. The morphology of the dried polymer was examined using a S-520 SEM instrument after coating the sample with gold film.

Water Absorbility and Retention Tests

A weighed quantity of the superabsorbent (1 g) was immersed in water at room temperature and allowed to stand to fully hydrate the polymer.

Swollen gels were then separated from unabsorbed water by screening, and the gel was allowed to drain on the sieve for 10 min. The sieve was then weighed to determine the weight of the water-swollen gel, and water absorbency was calculated using the following equation:

$$\text{Absorbency } Q \text{ (g H}_2\text{O/g sample)} = \frac{\text{water-swollen gel (g)} - \text{absorbent (g)}}{\text{absorbent (g)}}$$

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 under various pressures for 30 min (1–10 kg/cm²).

RESULTS AND DISCUSSION

Effect of Ionic Content and Crosslinking on Absorbency

Copolymer ionic content and crosslink density are extremely important swelling control elements. The swelling behavior of gels with different ionic content and crosslink densities was explored by varying the monomer feed ratio and determining the polymer composition. As shown in Table I, the absorbency of crosslinked poly(AM–MSAS–AA) is much higher than that of crosslinked poly(AM–MSAS). Indeed, even at low AA concentration, gel swelling of poly(AM–MSAS–AA) is significantly increased by the incorporation of carboxylate groups because the concomitant increase in ionic content results in strong electrostatic repulsion. However, with an increase of monomer concentration of MSAS or AA, the absorbency of poly(AM–MSAS) or poly(AM–MSAS–AA) decreases slightly. This slight decrease in absorbency may be the result of either short chain polymer network formation associated with MSAS chain transfer reactions¹⁴ or an increase in soluble materials related to the incorporation of —COONa groups at a fixed crosslinker concentration. Similar observations have been reported by others.^{12,15}

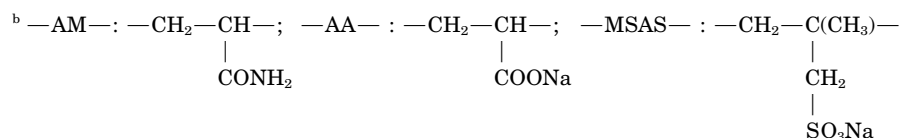
Relatively small changes in crosslinker density can play a major role in modifying the properties of superabsorbent polymers. Figure 1 illustrates the relationship between absorbency and crosslinker (BisA) concentration. It is clear that the gel absorbency is diminished at low BisA con-

Table I Influence of Ionic Unit Content on the Swelling of Crosslinked Poly(AM-MSAS-AA)

Entry	Monomer in the Feed (mol/L)			Composition of the Copolymer					
	AM	MSAS ^c	AA	Element Content ^a		Repeating Units (mol %) ^b			Absorbency (gH ₂ O/g) Q
				N	S	—AM—	—MSAS—	—AA—	
M1	0.97	0.03	0	16.97	1.24	93.21	6.79	0	72
M2	0.97	0.04	0	16.40	1.39	91.67	8.33	0	73
M3	0.97	0.05	0	16.30	1.50	91.35	8.65	0	51
A1	0.97	0.03	0.10	12.51	1.05	70.91	2.60	20.49	125
A2	0.97	0.03	0.20	11.66	0.84	66.64	2.10	31.26	118
A3	0.97	0.03	0.29	9.14	0.72	54.03	1.86	44.10	112

Reaction condition: [TMEDA] = 1.50×10^{-3} mol/L for M1, M2, M3; [TMEDA] = 3.00×10^{-3} mol/L for A1, A2, A3; [BisA] = 3.20×10^{-2} mol/L; [KPS] = 2.67×10^{-3} mol/L; at 35°C, 4 h.

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



^c When [MSAS] $\geq 0.04M$, the resulting gel is soft.

centration because of an increase of soluble material. A maximum absorbency of 125 is reached at BisA concentration of 3.20×10^{-2} mol/L. On the

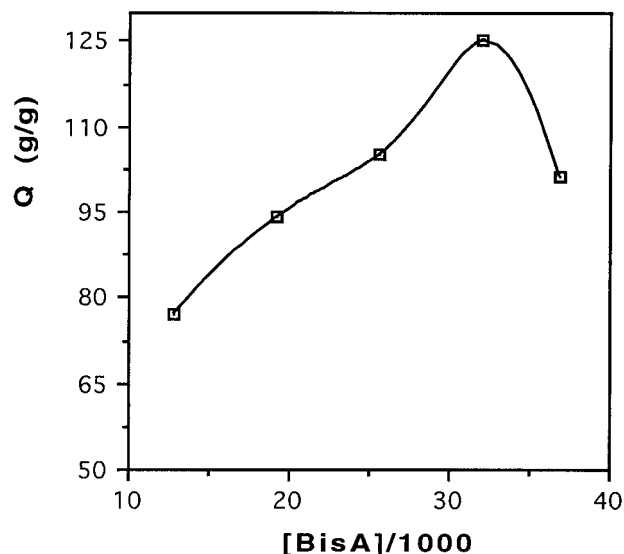


Figure 1 Absorbency of crosslinked poly(AM-MSAS-AA) as a function of the concentration of the crosslinking agent (BisA): [AM] = 0.97M, [MSAS] = 0.03M, [AA] = 0.10M, [KPS] = $2.67 \times 10^{-3}M$, [TMEDA] = $3.0 \times 10^{-3}M$; $t = 35^\circ\text{C}$, 4 h.

other hand, excess crosslinking also decreases gel absorbency.^{12,15}

Infrared Spectra and SEM Observations

The infrared (IR) spectra of crosslinked poly(AM-MSAS) (sample M1) and poly(AM-MSAS-AA) (sample A1) are shown in Figure 2. Stronger absorption peaks at 3400 and 3196 cm^{-1} in the spectra of both M1 and A1 are attributed to NH_2 groups. Absorptions at 1664 and 1617 cm^{-1} result from C=O stretching (—CONH_2), and the absorbencies at 1321, 1563, and 1044 cm^{-1} are characteristic peaks for AA and MASA units, respectively.

Since scanning electron microscopy (SEM) observations were difficult to make in the presence of water, these experiments were carried out on dried samples, which were prepared without destroying the gel microstructure. The micrograph of (1) uncrosslinked poly(AM-MSAS), (2) crosslinked poly(AM-MSAS) (sample M1), and (3) crosslinked poly(AM-MSAS-AA) (sample A1) are shown in Figure 3. SEMs of sample M1 and A1, which are crosslinked copolymers having good absorbency, show that the copolymers are microporous. In addition, A1 [poly(AM-MSAS-

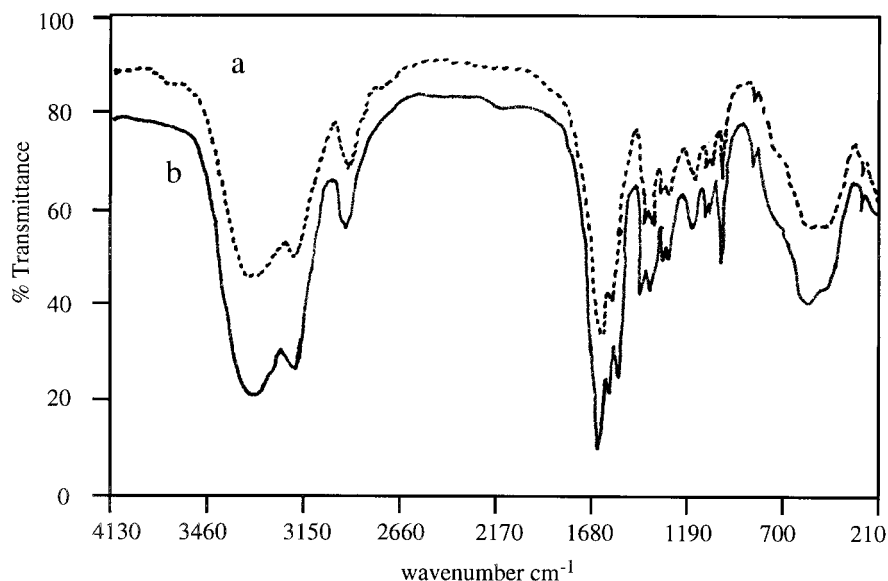


Figure 2 Infrared spectra of crosslinked poly(AM-MSAS) (sample M1) and crosslinked poly(AM-MSAS-AA) (sample A1): (a) M1 and (b) A1.

AA]) has a greater absorbency and shows a broad network structure [Fig. 3(c)], whereas M1 [poly(AM-MSAS)] has a fine network structure [Fig. 3(b)]. However, the SEM of uncrosslinked poly(AM-MSAS), which is water-soluble and has no absorbency, appears almost nonporous [Figure 3(a)]. These observations are in good agreement with our water absorbency observations.

Effect of pH on Absorbency

The influence of solution pH on the water absorbency of crosslinked poly(AM-MSAS) (sample M1) and crosslinked poly(AM-MSAS-AA) (sample A1) at room temperature are shown in Figure 4 (pH was adjusted with 0.1N HCl and 0.1N NaOH). It is clear that a sharp change in absorbency occurs between pH values of 3 and 7 and that the absorbency reaches a maximum at pH 6. The pK_a value of PAA is 4.28.^{16,17} Therefore, at $pH < 4$, the carboxylate groups of these hydrogels are not ionized. The swelling ratio of sample A1 (containing $-\text{CO}_2\text{Na}$ groups) varied greatly between pH 4 and 5, which is in agreement with previous reports that hydrogels containing anionic groups exhibit an abrupt phase transition at a particular pH.¹⁸ However, the swelling ratio of sample M1 (containing only $-\text{SO}_3\text{Na}$ ionic groups) is less affected between pH 4 and 5. These pH-sensitive gels may be very interesting from the point of view of biomedical applications.

Water Retention Test

Gel water retentions were determined at different temperatures (60 or 100°C; see Fig. 5) and pressures (1–10 kg/cm²; see Fig. 6). At 60°C, both samples M1 and A1 have similar water retention ability (M1 is slightly better than A1); and within 2.5 h, 50% of the water was lost. At 100°C, sample M1 has a better water retention capacity; however, within 1.5 h, both M1 and A1 suffer a 50% loss of water. Generally, the water in hydrogel can be classified into bound and free water (a more detailed classification is possible). Bound water is tightly held by the polymer and has a lower mobility. The difference of water retention ability between A1 and M1 under higher temperature may be due to the different percentage of free water content. That is, higher free water content in sample A1 (i.e., more ionic content) and thus more easily lost. These kind of gel dewatering properties under heating may prove useful in recyclable superabsorbent materials.

It is also important to know whether these gels have good absorbency or retention capacity under a load that influences pad performance. For this purpose, the retention capacity and leakage behavior of these gels were tested using a ZNS-2 Model fluid-loss meter under various pressures for 30 min (see Fig. 6 for swollen gel retentions under pressure). Water retention of swollen A1 reached about 95% under 10 kg/cm² for 30 min,

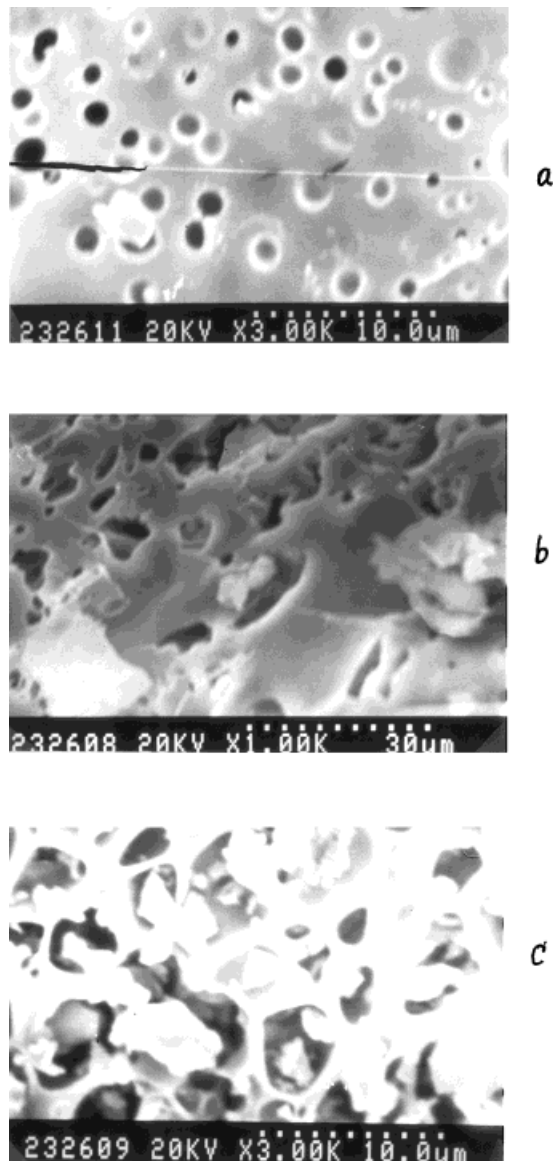


Figure 3 Scanning electron micrographs of (a) uncrosslinked poly(AM-MSAS), (b) crosslinked poly(AM-MSAS) (sample M1), and (c) crosslinked poly(AM-MSAS-AA) (sample A1).

showing that crosslinked poly(AM-MSAS-AA) gels have better water retention capacity under load than that of base-hydrolyzed starch-g-poly(AN-SAS) (90% under a pressure of 10 kg/cm² for 30 min) and H-SPAN (less than 50% under a pressure of 5 kg/cm² for 30 min).¹⁹ This characteristic water retention property of crosslinked poly(AM-MSAS-AA) gel under load will be extremely important in the performance of absorbent pads.²⁰ However, the same test with M1 shows water retention was lower than 90% under

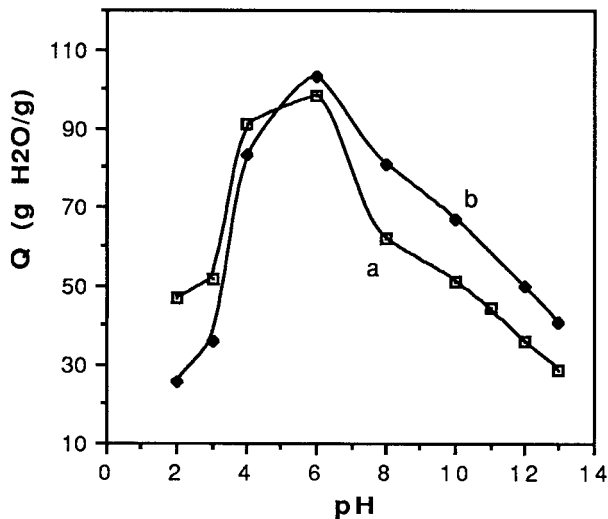


Figure 4 Influence of pH on the absorbency of crosslinked poly(AM-MSAS) (sample M1) and crosslinked poly(AM-MSAS-AA) (sample A1): (a) M1 and (b) A1.

a pressure of 10 kg/cm². Thus, A1 has better retention capacity than M1 under load.

Thermal Stability

The thermogravimetric analysis (TGA) of samples M1 and A1 are shown in Figure 7. Both samples show a very small weight loss below 100°C, implying a loss of moisture. It is clear that A1 has a significant weight loss at 192°C (10.2%),

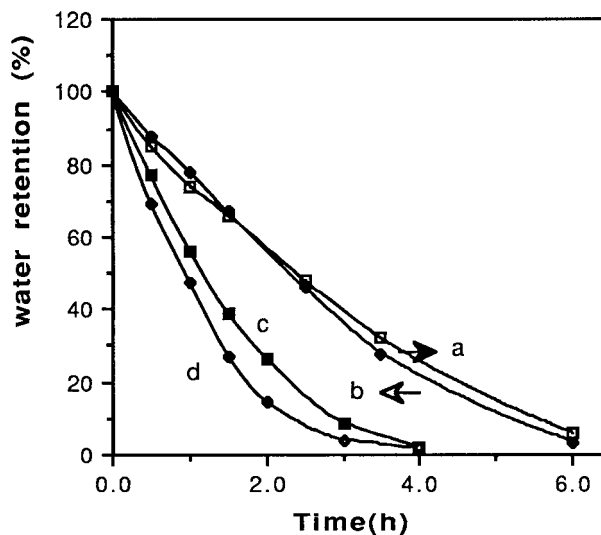


Figure 5 Water retention of the swollen gel at 60 and 100°C. At 60°C: (a) M1 and (b) A1. At 100°C: (c) M1 and (d) A1.

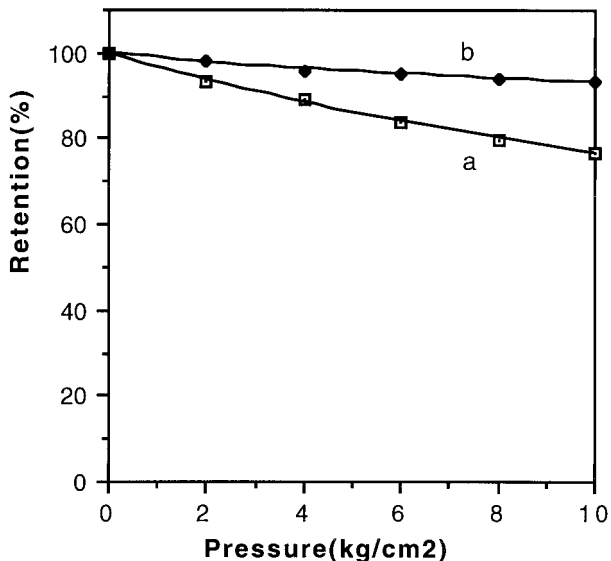


Figure 6 Water retention of the swollen gel at varying pressures (1–10 kg/cm² for 30 min): (a) M1 and (b) A1.

whereas M1 has a notable weight loss at 290°C. According to the equation of Wang et al.²¹ $\ln \ln(1/r) = K - 0.457(\ln 10)(E/R\theta)$, where r is the retained weight %, θ is the absolute temperature, E

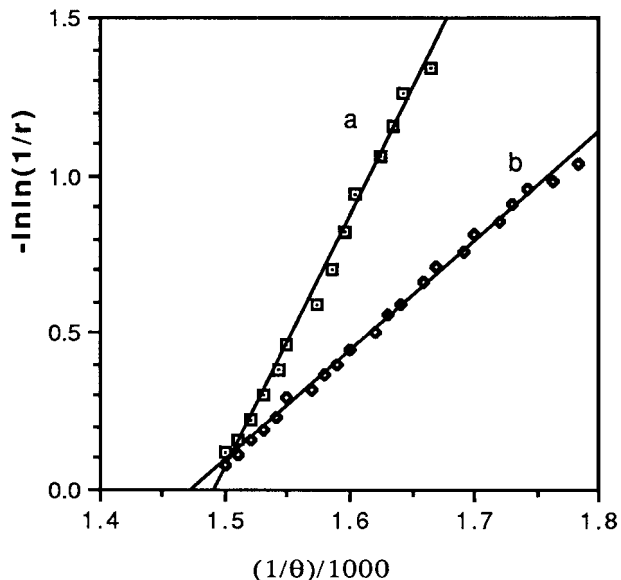


Figure 8 Pyrolysis activation energy of M1 and A1 samples: (a) M1 and (b) A1.

is the pyrolysis activation energy, and R is the gas constant.

Figure 8 is derived by plotting $-\ln \ln(1/r)$ versus $1/\theta$. From the slope obtained from Figure 8, the pyrolysis activation energies for M1 and A1

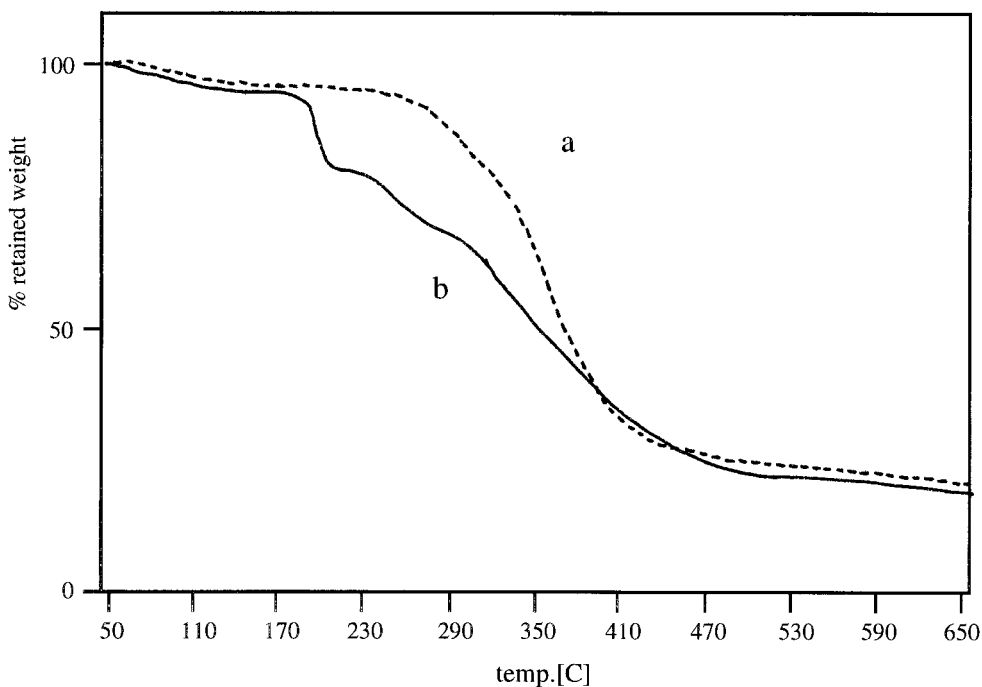


Figure 7 TGA curves of M1 and A1 under nitrogen at a heating rate of 10°C/min: (a) M1 and (b) A1.

are determined to be 58.7 and 28.7 kJ/mol, respectively. This difference in pyrolysis activation energy (E) illustrates that introducing carboxyl groups into the structural unit of the copolymer results in a decrease in thermal stability. However, sample A1 is still quite stable at 150°C (weight loss less than 5%).

CONCLUSION

Novel copolymer water absorbents of crosslinked poly(AM-MSAS) and poly(AM-MSAS-AA) were prepared in an aqueous solution by copolymerization of their respective monomers and N,N' -methylenebisacrylamide using KPS-TMEDA as the initiator. These synthetic copolymers were characterized by TGA, IR, SEM, and elemental analysis. The pyrolysis activation energies for M1 and A1 were determined to be 58.7 and 28.7 kJ/mol, respectively.

It was found that crosslinked poly(AM-MSAS-AA) has a higher water-absorbency and better water retention under load than poly(AM-MSAS). This excellent water retention under load may prove especially practical in personal hygiene applications.

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