

Preparation of Superabsorbent Polymers by Crosslinking Acrylic Acid and Acrylamide Copolymers

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ABSTRACT: High water-absorbent copolymers comprising acrylic acid (AA) and acrylamide (AM) were prepared in the presence of a crosslinking agent, monofunctional aldehyde, by a solution polymerization technique using a redox initiation system. Such copolymers have very high water absorbency and absorbing kinetics to the distilled water. The copolymer formed which absorbed about 900 g water/g dry copolymer was used to study the influence of sodium chloride on the absorption capacity at 24°C. The swelling of this copolymer was studied in alcohol/water mixtures of increasing alcohol content at 294, 304, and 314 K. The main transition for ethanol/water and methanol/water mixtures is a rapid decrease of the retention capacity of the copolymer at 50–60 vol % ethanol and 55–65 vol % methanol, respectively. Swelling in distilled water at different temperatures (T) and the effect of solvent composition were also studied. Among the variables examined were initiator concentration, polymerization temperature, and amount of AM in the copolymer. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1345–1353, 1997

INTRODUCTION

In our daily life, cotton, paper, and sponge are commonly used to absorb water. These materials absorb only a few times their weight of water and have rather poor properties with respect to water retention. However, some types of polymers and copolymers do function as high water absorbents and also have very good properties for water retention. With water as a swelling agent, products with a high affinity for water are termed hydrogels.^{1,2} Hydrogels have received significant attention, especially in the last 30 years, because of their considerable applications in many areas. They can be used as absorbents in baby diapers,³ ion-exchange resins,⁴ biomedical materials, such as soft contact lenses⁵ or carriers for the controlled release of drugs,⁶ and supports for catalysts.⁷

The synthetic polyacrylate derived from acrylic acid (AA) has emerged as an important absorbent, because AA is cheap and easy to polymerize to products of high molecular weight. Several methods have been described in the literature for the preparation of superabsorbent polyacrylates. Parks⁸ prepared polyacrylate absorbents by copolymerizing AA with a divinyl crosslinker such as tetraethylene glycol diacrylate at a concentration of about 10% in aqueous solution, with sodium persulfate as the initiator at 60°C. The polymer was neutralized with sodium hydroxide and then mixed with a solution of divalent ion salt, such as zinc acetate dihydrate. Yoshida et al.⁹ reported absorbent polyacrylates obtained by polymerizing sodium acrylate at a concentration of 16% in aqueous solution, in the presence of poly(ethylene glycol diglycidyl ether) as the crosslinker. A persulfate–triethanolamine redox initiator was used to generate free radicals. Yamasaki and Harada¹⁰ prepared polyacrylate absorbents by suspension polymerization. Stanley et al.¹¹ studied a suspension polymerization process for polyacrylate ab-

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sorbents, which employed a combination of hydrophobic silica and a copolymer of AA and lauryl methacrylate as the suspension agents. Fanta et al.¹² graft-polymerized AA onto starch using either the Ce^{4+} ion or an Fe^{2+}/H_2O_2 initiation system. Gugliemelli et al.¹³ prepared starch-acrylonitrile graft copolymers without a crosslinker, followed by saponification to polyacrylate absorbents.

Finding new methods of synthesizing superabsorbents and developing their applications still represent interesting research areas. Caraness et al.¹⁴ reported the copolymerization of AA and acrylamide (AM) and found that pH affected the reactivity ratios r_1 and r_2 (the subscripts 1 and 2 refer to AA and AM, respectively). It is noted that at pH values between 3.77 and 4.73 the reactivity ratios of r_1 and r_2 both are less than 1. At this condition, it is supposed that statistical copolymers can be obtained. Due to the existence of the reactive groups of NH_2 , the copolymers can be crosslinked by chemical modification reactions to form high water absorbents. In this article, we report the preparation of superabsorbents by crosslinking AA and AM copolymers. Aspects investigated included the optimum synthesizing conditions.

EXPERIMENTAL

Materials

Acrylic acid (AA) (Aldrich, USA, 99%) was distilled under a vacuum. After distillation, it was stored at 10°C until required. All reagents, acrylamide (AM) (Aldrich, USA, 97%), formaldehyde solution (B.D.H., Canada, analytical reagent), potassium persulfate (B.D.H., England, analytical reagent), potassium metabisulfite (J. T. Baker, USA, Baker analytical reagent), and sodium hydroxide (B.D.H., Canada, analytical reagent) were used as received. Distilled water was used for the swelling. DSS [3-(trimethylsilyl)propane-sulfonic acid, sodium salt; Aldrich, USA] was used as an internal NMR standard for use with D_2O .

Preparation of Superabsorbent

Typically, in a flask fitted with a mechanical stirrer, condenser, thermometer, and dropping funnel, a solution of 90 mL distilled water, 0.048 g (18 mmol) of potassium persulfate, and 0.02 g (0.09 mmol) of potassium metabisulfite were added. At

65°C, 11.82 g (0.16 mol) of AA and 0.18 g (0.0025 mol) of AM in 15 mL distilled water were added dropwise in 10 min, followed by adjusting the pH to about 4.5 with the sodium hydroxide solution. The mixture was heated to 75°C. The polymerization began in about 10 min. The system was maintained for 2 h at 70°C. The formaldehyde solution, 1.1 mL, was then added at 45°C and maintained for 1 h. The system was heated to 70°C and maintained for 3 h. The product was dewatered with ethanol and dried to a solid product at 80°C overnight. The product was referred to as CCPAA (1.5% AM; Crosslinked Co-Polymer of Acrylic acid and Acrylamide). The linear product was referred to as LCPAA (Linear Co-Polymer of Acrylic acid and Acrylamide).

Swelling Measurement

The particle size of CCPAA was milled to be less than 250 μm . To determine the water-absorption capacity of CCPAA, an accurately weighed 0.200 g sample was allowed to soak for 30 min in 500 mL distilled water at 24°C. The swollen polymer was then separated from unabsorbed water by screening through a tared 60 mesh sieve. The polymer on the sieve was allowed to drain for 10 min and the sieve was then weighed to determine the weight of the water-swollen gel. The swelling characteristic is expressed as

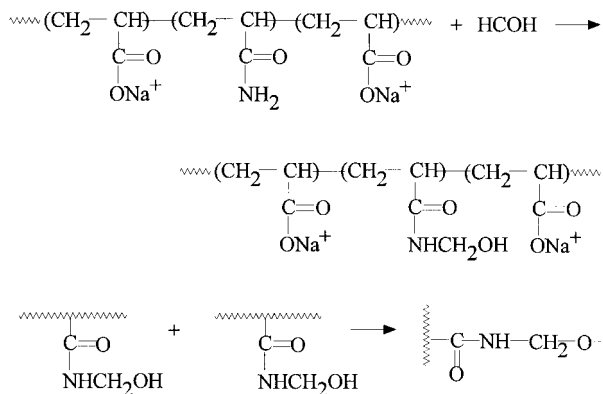
$$\text{Absorption capacity} = A = \frac{(W_1 - W_2)}{W_2} \quad (1)$$

where W_1 and W_2 are the weights of the water-swollen gel and the dry absorbent, respectively. The absorption capacity was calculated as grams of water per gram of CCPAA. The error in absorption capacity was found to be about $\pm 2\%$.

RESULTS AND DISCUSSION

Copolymer Characterization

The possible mechanism of the crosslinking reaction of the copolymer and formaldehyde is shown in Scheme 1. The reaction of formaldehyde with the amine group commences with the formation of a *N*-methylol polymer. Most polymers of this nature are highly reactive, with a tendency to condense with another similar molecule, with loss of



Scheme 1

water. Therefore, the copolymers were cross-linked.

IR Spectra Analysis

Spectra of CCPAA (5% AM) and LCPAA (5% AM) were obtained using a Nicolet 520 FTIR spectrophotometer equipped with an IBM PC and Omnic software and using nujol mulls. The infrared spectrum of CCPAA is shown in Figure 1(b). This can be compared to the spectrum of LCPAA shown in Figure 1(a). The characteristic peak at 1040 cm⁻¹ arises from the ether group —O— of CCPAA, providing evidence of a crosslinking reaction between two *N*-methylol polymers.

Elemental Analysis

The nitrogen contents of copolymer products (CCPAA) were analyzed. The results are summa-

Table I Elemental Analysis of Copolymer Products

| Sample CCPAA % AM | Elemental Analysis N % |
|-------------------|------------------------|
| 1.0% AM | 0.33% |
| 1.25% AM | 0.35% |
| 1.5% AM | 0.55% |
| 3% AM | 0.64% |
| 5% AM | 1.04 |

riized in Table I. It can be seen that the increase of AM content in the copolymers results in increase of the nitrogen content in the copolymers. In Table I, it is noted that there is a factor of 5 increase in AM content, but only a factor of 3 increase in %N. This can be explained by the fact that a lower conversion of the polymer was obtained at higher AM concentration. For instance, 99% conversion can be obtained for the 1.0% AM system; however, only 96 and 94% conversion can be obtained for the 3 and 5% AM systems, respectively. This could account for some of the %N deviation.

¹³C-NMR Analysis

¹³C-NMR spectroscopy is a very powerful tool for polymer structure characterization. The ¹³C-NMR analyses for LCPAA (5% AM) and CCPAA (5% AM) were carried out in a D₂O swelling agent using a Bruker AM 250 MHz instrument.

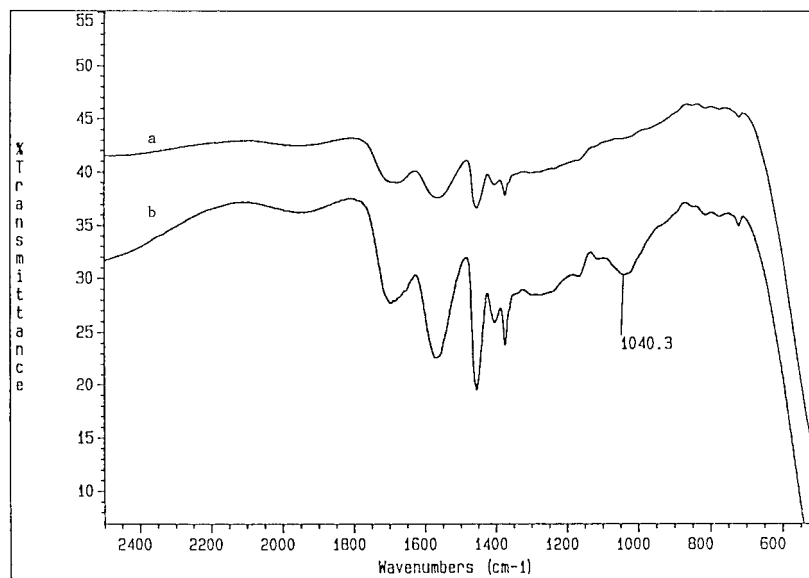


Figure 1 IR spectrum of (a) linear (5% AM) and (b) crosslinked (5% AM) copolymers.

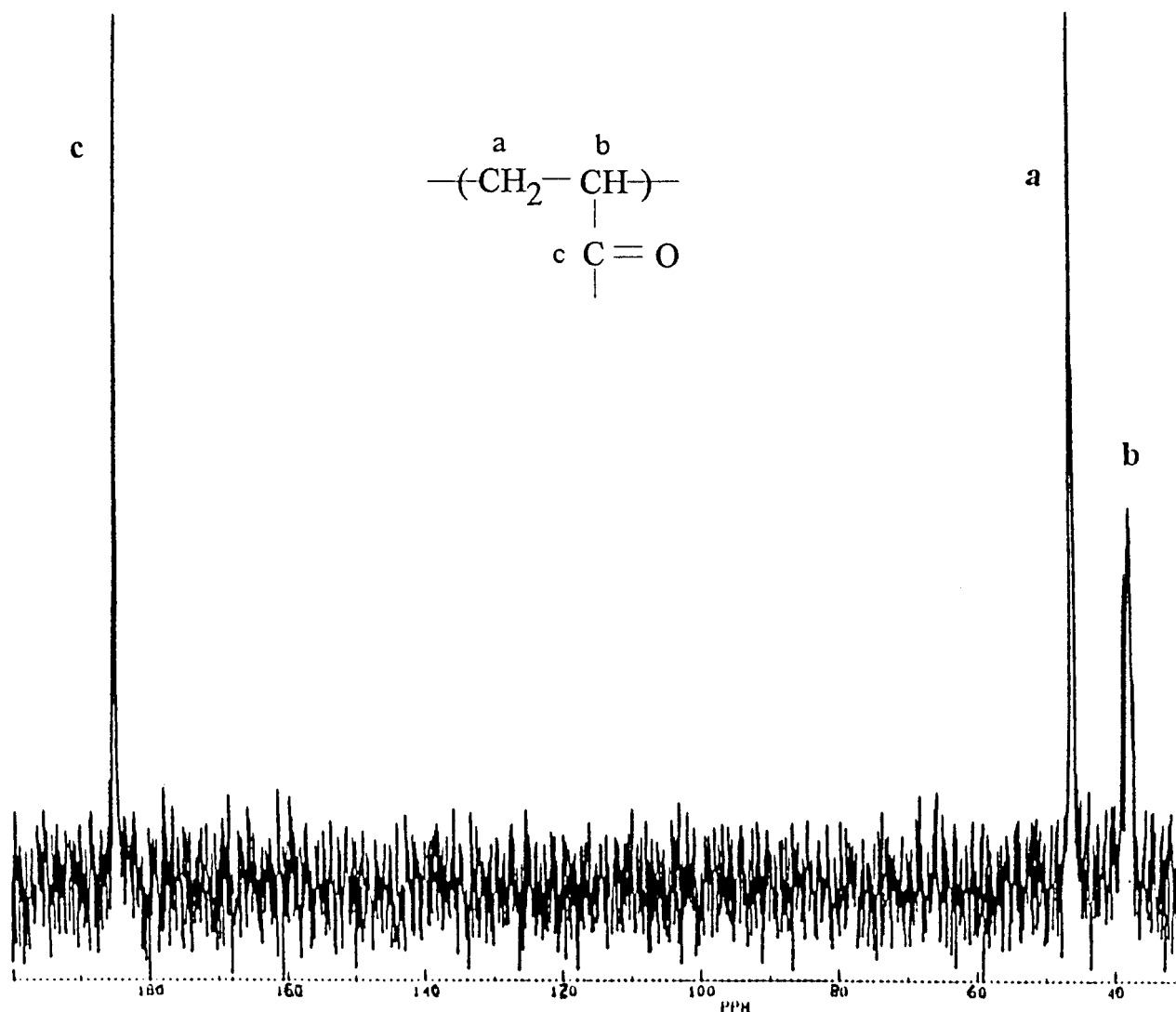


Figure 2 ^{13}C -NMR spectrum of LCPAA (5% AM).

The spectra of LCPAA (5% AM) is shown in Figure 2. The spectra of CCPAA (5% AM) is shown in Figure 3. When the CCPAA spectrum in Figure 3 is compared to the LCPAA spectrum in Figure 2, it is obvious that a new resonance peak at 84 ppm for CCPAA appeared. It was assigned to C from the $-\text{CH}_2\text{O}-$ group of CCPAA. This could indicate that crosslinking reactions between two *N*-methylol polymers occurred. This result supports the observations resulting from the IR spectra.

DSC Analysis

Crosslinking influences the glass transition temperature (T_g). As the crosslinking density

increases, the free volume of a material decreases and T_g increases correspondingly. Crosslinking is accomplished by the reaction between two *N*-methylol polymers. The DSC thermograms of copolymers were obtained using a Perkin-Elmer DSC-4 differential scanning calorimeter with a Perkin-Elmer thermal analysis data station Model TADS-101. The temperature at the inflection point was taken as the glass transition temperature (T_g). The results are summarized in Table II. It is noted that T_g increased with increase of the AM contents of the copolymers, which reacted with formaldehyde, e.g., with crosslinking density. The linear copolymers have lower glass transition temperatures. Based on the analyses of IR, NMR, and

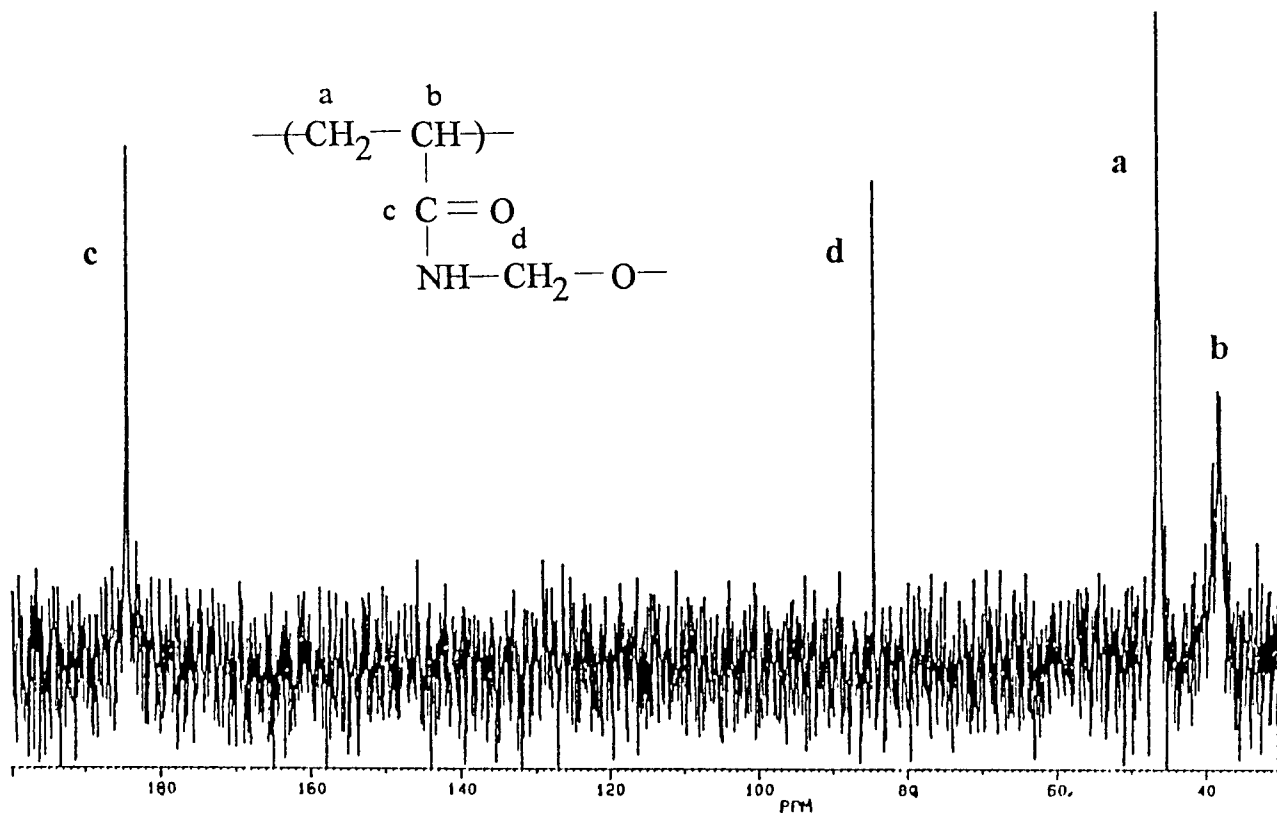


Figure 3 ¹³C-NMR spectrum of CCPAA (5% AM).

DSC, the conclusion can be drawn that cross-linked copolymers were formed.

Effect of Polymerization Temperature

It is well known that in radical polymerization started by thermal decomposition of an initiator where transfer reactions are negligible, as temperature is increased, the rate of polymerization is strongly enhanced and the molecular weight of the polymer is reduced because of increase of the rate termination and transfer reactions.¹⁵ The effect of polymerization temperature on the absorp-

tion capacity of the copolymer (CCPAA 1.5% AM) was investigated. Figure 4 shows that the absorption capacity of the copolymer is decreased when polymerization temperature is increased. This is

Table II Glass Transition Temperatures of CCPAA

| Crosslinked CPAA % AM | T _g (°C) | Linear CPAA % AM | T _g (°C) |
|-----------------------|---------------------|------------------|---------------------|
| 1.5% | 105.5 | 1.5% | 99.8 |
| 2% | 107.9 | 2% | 98.2 |
| 2.5% | 110.3 | | |
| 3% | 113.1 | | |
| 5% | 113.5 | 5% | 96.6 |

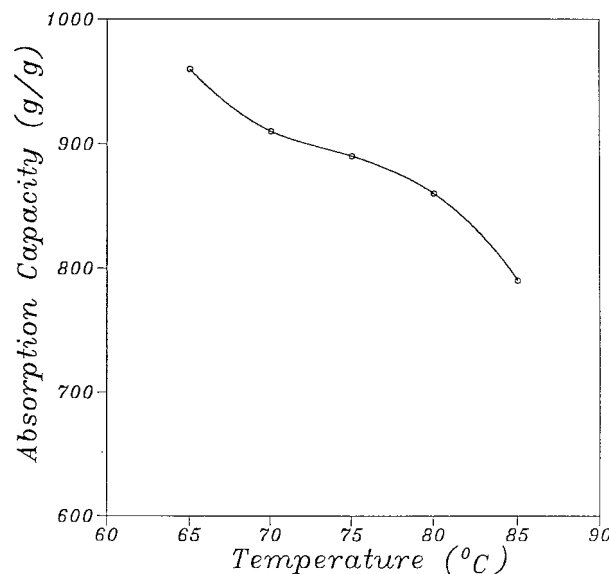


Figure 4 Effect of polymerization temperature.

because an increase of temperature decreases the molecular weight, with increase of the relative amount of the polymer chain end. Polymer chain ends do not contribute to the absorption capacity. Therefore, increasing the polymerization temperature results in decrease in the absorption capacity of CCPAA. Another reason for the effect of polymerization temperature on the absorption capacity probably is the change in copolymer composition with temperature due to a change in the reactivity ratio. It is found that there are small differences of %N in the polymers obtained at different temperatures.

Effect of AM Content of the Copolymers

Figure 5 shows that the swelling properties of CCPAA are affected drastically by changing the AM contents in the copolymers, indicating that the absorption capacity is reduced as the AM contents of the copolymers are increased and that an increase of the AM content of the copolymer formed a denser network of the copolymer and affected the \bar{M}_c (average molecular weight between two crosslinks).¹⁶ It is well known that a decrease of \bar{M}_c is accompanied by a decrease of the swelling ratio.¹⁷ This can be seen from Figure 5, but as AM content is less than 1.25%, the absorption capacity of the copolymer is reduced drastically. This is because the copolymer has a lower crosslinking degree and some of the copolymer is dissolved in water. This can be supported by weighing 1.5% AM and 1% AM dried polymers,

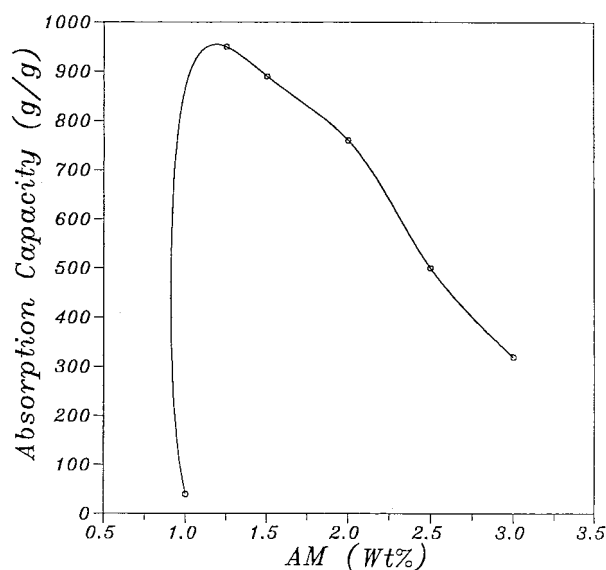


Figure 5 Effect of AM content.

Table III Effect of Initiator Concentrations on the Absorption Capacity

| Potassium Persulfite (g) | Potassium Metabisulfite (g) | Absorption Capacity (g/g) |
|--------------------------|-----------------------------|---------------------------|
| 0.036 | 0.015 | 910 |
| 0.042 | 0.018 | 900 |
| 0.048 | 0.020 | 890 |
| 0.054 | 0.023 | 760 |
| 0.060 | 0.025 | 750 |
| 0.066 | 0.028 | 750 |

after the absorbing experiments. The loss of weight for 1.5% AM was around 4%, whereas for 1% AM, it was around 45%.

Effect of Initiator Concentration

It is clear that in free-radical chain polymerization using a chemical initiator, the number-average degree of polymerization (\bar{X}_n) is inversely proportional to the square root of the concentration of the initiator. It can be expressed by the Seymour and Carraher eq. (2)¹⁸:

$$\bar{X}_n = \frac{[M]}{[I]^{1/2}k'} \quad (2)$$

where k' is a combination of constants, $k' = k_p / (2k_d k_t f)^{1/2}$. It is suggested that at a given monomer concentration, polymerization temperature, and crosslinking agent concentration the higher the initiator concentration the smaller the molecular weight of the polymer obtained. With decrease of the molecular weight, the relative amount of polymer chain ends increase. As mentioned before, the polymer chain ends do not contribute to the absorption capacity. Therefore, increasing initiator concentration results in decrease in the absorption capacity of CCPAA. The results of this study are shown in Table III.

Effect of Sodium Chloride

For many applications, it is more important to know the behavior of the absorbent in a physiological solution, usually simulated by 1% aqueous

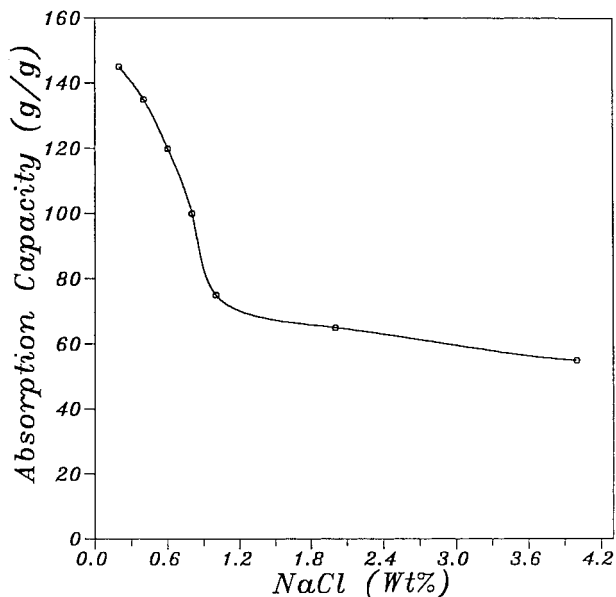


Figure 6 Effect of NaCl concentration.

NaCl. Figure 6 shows the effect of NaCl on the absorption capacity of CCPAA (1.5% AM). The absorption capacity decreased with increase of NaCl in the distilled water. A possible explanation of this behavior could be associated with the formation of carboxylic anions in the copolymer networks, a fact which leads to the development of strong electrostatic forces contributing to the network expansion.¹⁹ Because of the attraction of the strong electrostatic forces, the concentration of the ions, e.g., Na⁺, is higher inside the copolymer than outside the copolymer, resulting in an osmotic pressure. Figure 7 shows this possible process of osmotic pressure. The water-absorption properties are thought to result from osmotic pressure and interaction through hydrogen bonding of the carboxylic groups of the copolymer with water molecules. When distilled water or deionized water are used as swelling agents, the absorption capacity is higher. When a certain amount of NaCl in distilled water is used as a

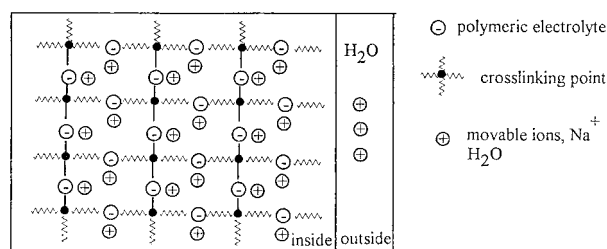


Figure 7 Ionic network of superabsorbent.

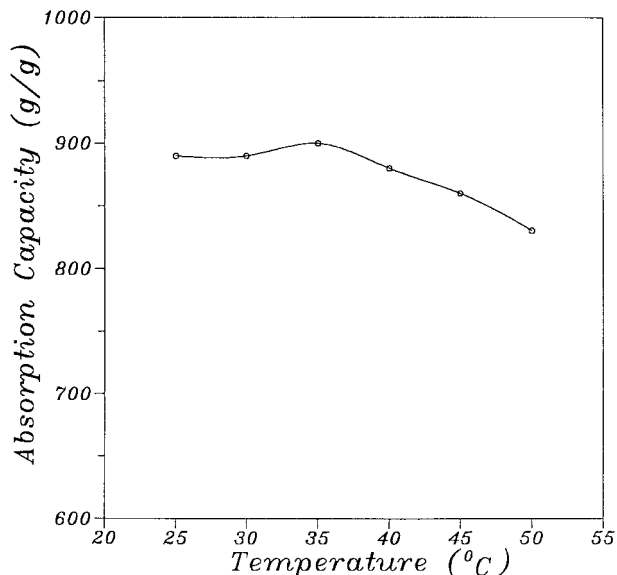


Figure 8 Effect of water temperature.

swelling agent, the osmotic pressure outside the copolymer decreased drastically. So, the absorption capacity is lower. This phenomenon can also be explained by the effect of the ionic strength in the absorbent. In pure water, the polymer containing charged groups along its backbone will tend to expand its dimensions in order to minimize the repulsion between them. If a simple electrolyte, such as common salt (NaCl), is dissolved in the water, the ions of opposite charge to those carried by the polymer can neutralize its charge. Thus, as the ionic strength is increased, the polymer returns to its coiled shape. This effect is known as the polyelectrolyte effect.²⁰

Effect of Water Temperature

CCPAA (1.5% AM) was used to study the effect of water temperature on the absorption capacity. Figure 8 shows that at temperatures between 24 and 35°C little increase of absorption capacity can be seen along with increase of temperature because of the easy movement of the copolymer chains. When temperature is greater than 35°C, there is little decrease of absorption capacity. This indicates a release of water-soluble materials, i.e., a lower crosslinking degree copolymer. Huglin²¹ studied the swelling at different times and found that water retention decreases after 7 hours because of the release of water-soluble materials. Osada and Ross-Murphy²⁰ described the phase transition causing a thermosensitive polymer gel to collapse as its temperature increases. When the

gel is cold, the swollen state is thermodynamically stable, but as the gel warms, interaction among the molecular chains stabilizes the shrunken state instead. The gel formed by the CCPAA polymer seems to be a thermosensitive polymer gel.

Swelling Kinetics

In practical applications, not only is a higher absorption capacity required of the absorbent, but also a higher absorbing rate. CCPAA (1.5% AM) is also characterized by its high swelling kinetics. The results are presented in Figure 9, which shows that 1 g of dry CCPAA can absorb up to 825 g of water in 10 min.

Effect of Solvent Composition

Since Tanaka^{22,23} reported the collapse of saponified polyacrylamide gels caused by changing temperature and acetone concentration in the acetone-water gel fluid mixture, gel transitions have interested many researchers. Phase transitions of polymer gels were widely studied.²⁴⁻²⁶ Rodehed and Rånby²⁷ studied a saponified starch-*g*-polyacrylonitrile polymer gel/water-alcohol system and found gel collapse at 50–60 vol % ethanol and 60–70 vol % methanol, respectively. For the CCPAA absorbent, the liquid retention of the gels as a function of solvent composition was studied for water/alcohol mixtures (methanol or ethanol) at different temperatures. A weighed sample of

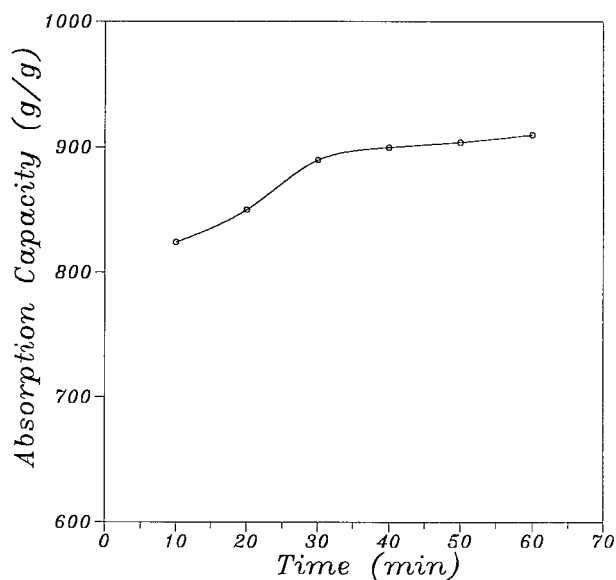


Figure 9 Absorbing rate for CCPAA (1.5% AM).

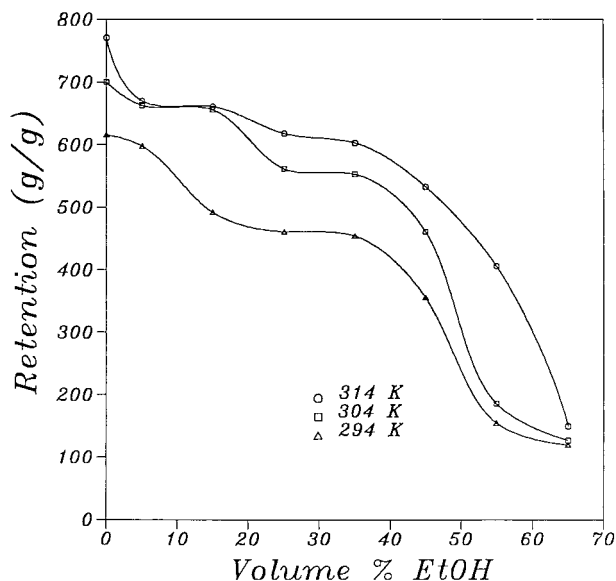


Figure 10 Effect of vol % ethanol at 294, 304, and 314 K.

dry polymer (0.010 g) (CCPAA 1.5% AM) was immersed in a known amount (in g) of a water/alcohol mixture in a test tube. After 30 min at constant temperatures (294, 304, and 314 K, respectively), the slurry was filtered using filter paper (Whatman #114) and the amount of the retained liquid (difference in weight between initial liquid added and final filtrated) calculated. Figure 10 shows the liquid retention (in grams of solvent

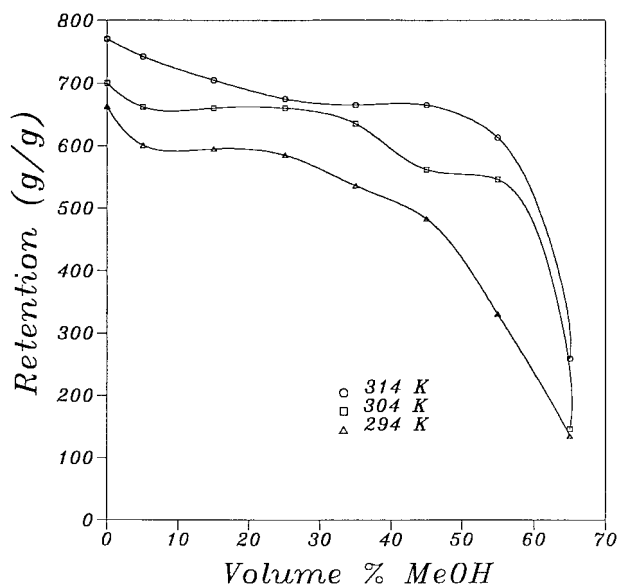


Figure 11 Effect of vol % methanol at 294, 304, and 314 K.

per gram of dry sample) as a function of solvent composition for water/ethanol mixtures. Raising the temperature caused the retention of water/ethanol mixtures to increase, especially at higher ethanol concentration. This is also found for the water-methanol system shown in Figure 11. Presentation of retention data in Figures 10 and 11 leads to the impression of continuous transitions in these systems. The same phenomenon also was reported by Rodehed and Råndy.²⁷

CONCLUSIONS

In this work, superabsorbents comprising acrylic acid (AA) and acrylamide (AM) were prepared in the presence of formaldehyde by a solution polymerization technique using a potassium persulfite-potassium metabisulfite redox initiation system. The absorption behavior of superabsorbents is related to their chemical composition and the nature of the solvent. A superabsorbent (1.5% AM) has a high water-absorption capacity and a fast rate of absorption. As expected, the absorption capacity decreases with increasing crosslink density.

The addition of NaCl results in a continuous absorption capacity decrease for the superabsorbent (1.5% AM). The decrease of absorption capacity is due to the decrease of the osmotic pressure difference between the gel and the external solution. The effects of initiator concentration, polymerization temperature, and amount of AM in the copolymers were investigated. It is noted that absorption capacities decrease with increasing initiator concentration, polymerization temperature, and amount of AM in the copolymers.

The swelling of the copolymer formed, which retains a 900 g water/g dry copolymer, was studied in alcohol/water mixtures of increasing alcohol content at 294, 304, and 314 K. The main transition for ethanol/water and methanol/water mixtures is a large decrease of retention capacity of the copolymer at 50–60 vol % ethanol and 55–65 vol % methanol, respectively.

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