

# Studies of Crosslinked Poly(AM-MSAS-AA) Gels. II. Effects of Polymerization Conditions on the Water Absorbency

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**ABSTRACT:** Hydrogels with varying crosslinking ratio and ionic content were prepared by copolymerization of 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 initiator. The influences of synthetic variables (reaction time, crosslinker concentration, monomer concentration, initiator concentration, temperature, and pH) on the polymerization conversion ( $\gamma$  %) and water absorbency ( $Q$ ) were studied in detail. These gels, which absorbed about 125 times their own weight in distilled water, have potential application as water superabsorbents. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1009–1014, 1997

**Key words:** water absorbent; hydrogel; swelling; crosslinking; redox initiator

## INTRODUCTION

Superabsorbent polymers are expanding into many product areas, especially personal hygiene products. Other applications are being explored based on the polymer's ability to absorb brine solutions, and superabsorbents have been used as sealing composites,<sup>1</sup> water-blocking tapes,<sup>2</sup> artificial snow,<sup>3</sup> and gel actuators.<sup>4</sup>

The physical properties of polymer gels depend on their network structure, and the latter is highly dependent upon the conditions under which the polymer gels are formed.<sup>5</sup> Of key importance in personal care applications are the swelling capacity and the elastic modulus of the gel. The monomer and crosslinker concentration, the initiator type and concentration, the relative reactivities and polymerization efficiencies of the monomers, and control of the reaction temperature are all important experimental control fea-

tures. Several studies have shown that the hydrogel structure, and thus the hydrogel properties, are strongly dependent upon the initial degree of dilution of the monomer.<sup>6–9</sup> As the amount of water present at polymerization increases, the network structure becomes increasingly loose. No continuous network is formed above a critical dilution factor.<sup>10</sup>

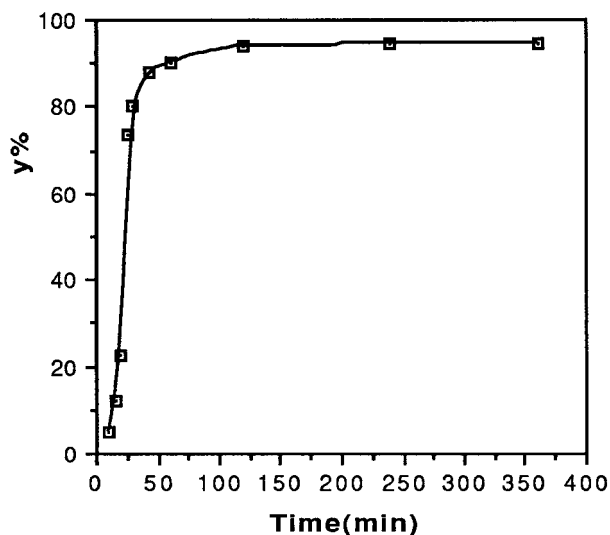
In the first part of this series,<sup>11</sup> attention was focused on the characterization, water retention, and relationship between absorbency and solution pH. In order to define the optimal conditions for syntheses of sulfonate-type poly(AM-MSAS) and poly(AM-MSAS-AA) [acrylamide (AM), methallylsulfonate (MSAS), and sodium acrylate (AA)] gels, we present here a detailed study of the effects of reaction conditions on conversion and absorbency.

## EXPERIMENTAL

The main procedure for polymerization and water absorbency measurements were similar

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**Figure 1** Effect of reaction time on polymerization conversion: AM = 0.97M; MSAS = 0.03M; BisA =  $3.2 \times 10^{-2}$ M; KPS =  $2.67 \times 10^{-3}$ M; TMEDA =  $3.0 \times 10^{-3}$ M;  $t = 35^\circ\text{C}$ .

to those previously described.<sup>11</sup> The effects of pH on conversion and absorbency was studied by adding *N,N,N',N'*-tetramethylethylenediamine (TMEDA) followed by potassium persulfate (KPS), and the pH of the reaction medium was adjusted by addition of 0.1N NaOH or 0.1N HCl solution. All hydrogels are transparent.

## RESULTS AND DISCUSSION

### Synthesis of Crosslinked Poly (AM-MSAS)

#### Effect of Reaction Time

The effect of reaction time on polymerization conversion ( $y\%$ ) is shown in Figure 1. The copolymerization was carried out in distilled water at  $35^\circ\text{C}$  varying the time of reaction from 10 min to 4 h while holding other parameters constant. Not surprisingly, an increase in reaction time results in a corresponding increase in monomer conversion. After 30 min, the conversion reaches 80%, and hard gel forms. Conversion continues to increase slowly to 94% as polymerization proceeds from 30 min to 2 h. The conversion reaches a plateau after 2 h; in order to insure polymerization completion, all gels were prepared with a 4 h reaction time. This figure also illustrates that conversion increases from 23 to 80% during the  $T + 20$  to  $T + 30$  min reaction window. This dramatic increase in reaction rate is due to a corresponding increase

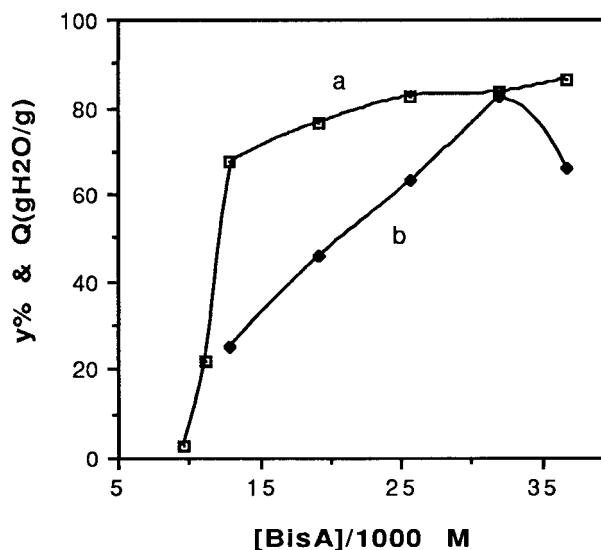
in radical concentration related to the gel effect. Subsequently, the radical concentration exhibits a small drop, followed by a gradual increase.<sup>12</sup> This is consistent with our data as shown in Figure 1.

#### Effect of Crosslinker Concentration

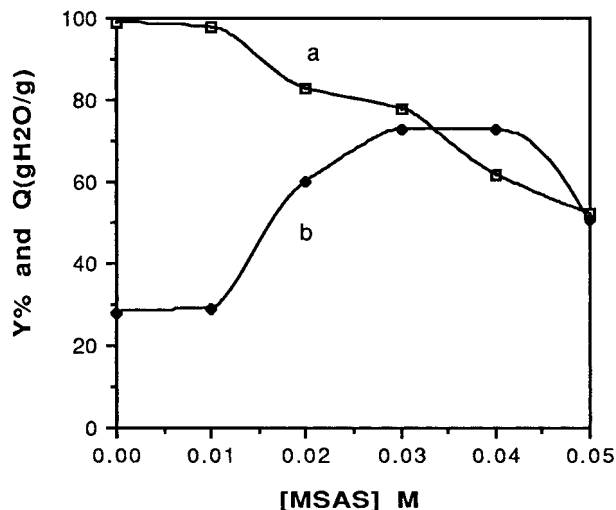
The influence of BisA concentration on conversion ( $y\%$ ) and absorbency ( $Q$ ) is shown in Figure 2. It is clear that both of these parameters increase rapidly with an increase in BisA concentration in the range of  $9.6 \times 10^{-3}$  to  $3.2 \times 10^{-2}$  mol/L. Beyond a BisA concentration of  $3.2 \times 10^{-2}$  mol/L, the absorbency decreases. Clearly, higher crosslinker concentration produces a larger number of growing polymeric chains, which are in turn involved in generating an additional network. Thereby, the absorbency increases with increased conversion, and the absorbency decreases when the crosslink density exceeds a certain degree because the space between crosslinks decreases. This tendency is similar to other superabsorbent hydrogels prepared by ourselves<sup>11,13,14</sup> and other groups.<sup>15,16</sup>

#### Effect of MSAS Concentration

The effect of monomer (MSAS) concentration on conversion and absorbency is depicted in Figure

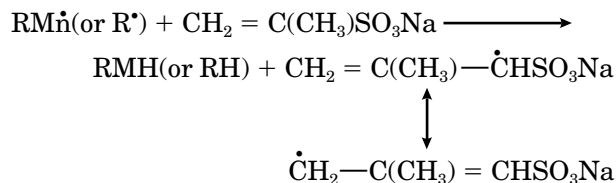


**Figure 2** Effect of BisA concentration on conversion ( $y\%$ ) and absorbency ( $Q$ ): AM = 0.97M; MSAS = 0.03M; KPS =  $2.67 \times 10^{-3}$ M; TMEDA =  $1.5 \times 10^{-3}$ M;  $t = 30^\circ\text{C}$ , 4 h; (a)  $y\%$ ; (b)  $Q$ .



**Figure 3** Effect of MSAS concentration on conversion ( $y$  %) and absorbency ( $Q$ ): AM = 0.97M; BisA =  $3.2 \times 10^{-2}$ M; KPS =  $2.67 \times 10^{-3}$ M; TMEDA =  $1.5 \times 10^{-3}$ M;  $t = 30^\circ\text{C}$ , 4 h; (a)  $y$  %; (b)  $Q$ .

3. It is apparent that an increase in MSAS concentration from 0.01 to 0.04 mol/L causes  $Q$  to increase significantly. Beyond [MSAS] = 0.04 mol/L, the absorbency decreases, and the conversion always decreases with an increase in MSAS concentration. These findings can be explained by the fact that MSAS functions as a chain transfer agents, as illustrated in the following mechanism:



Radical hydrogen atom abstraction from the  $\alpha$ -carbon of methallylsulfonate gives a stable radical; thereby, copolymerization is disfavored.<sup>17</sup> Consequently,  $y$  % decrease as the MSAS concentration increases. However, absorbency is increased when the MSAS concentration is between 0.01 and 0.04 mol/L because the ionic content in the network increases. When MSAS concentration is higher than 0.04 mol/L, absorbency decreases due to an increase in soluble material at a fixed crosslinker concentration. Similar results were reported in our previous work.<sup>13</sup>

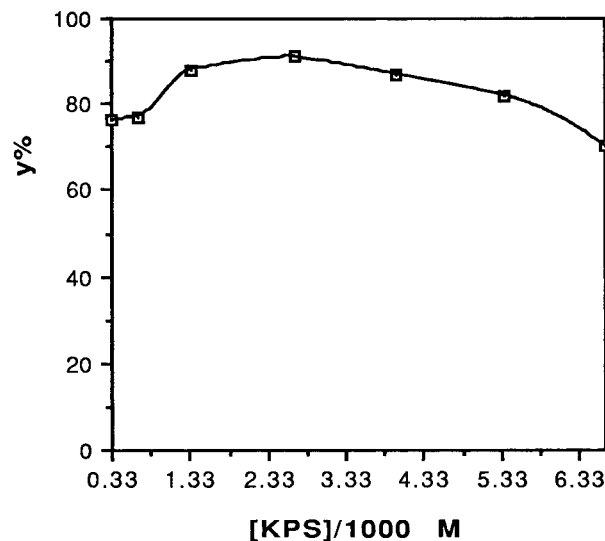
#### Effect of KPS Concentration

When KPS-TMEDA serves as a redox initiator, KPS is a source of free-radicals. Figure 4 shows

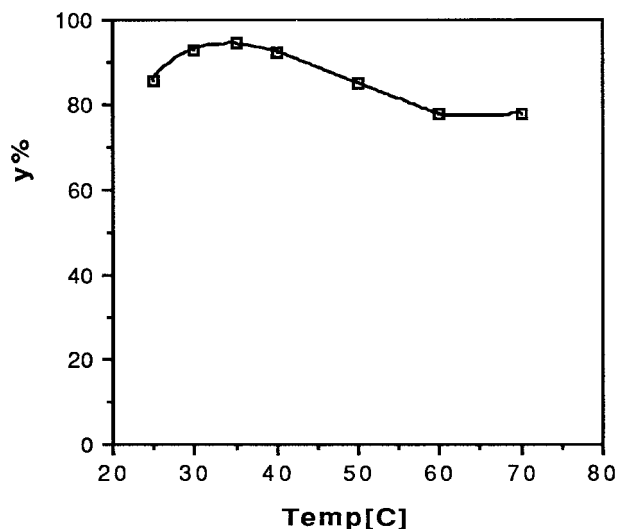
the dependence of conversion on KPS concentration. Conversion improves with an increasing KPS concentration but reaches a maximum value of 91% at  $2.67 \times 10^{-3}$  mol/L of KPS. Further increases in KPS concentration are accompanied by a decrease in yield. The initial increase in conversion is caused by an increase in concentration of radicals formed through the decomposition of initiator; the higher the concentration of radicals, the higher the initiation efficiency, and the higher the conversion. Furthermore, an increase in initiator concentration above a certain value ( $\geq 2.67 \times 10^{-3}$  mol/L) makes radical concentration excessive in the medium causing the rate of termination reactions to increase, the chain length between each crosslink to decrease, and conversion to decrease. The influence of KPS concentration on absorbency is both irregular and small.

#### Effect of Temperature

The effect of temperature on conversion is shown in Figure 5. The polymerization was carried out at 25, 30, 35, 40, 50, 60, and  $70^\circ\text{C}$  keeping all other variables constant. The optimum temperature ( $35^\circ\text{C}$ ) affords maximum conversion; beyond this reaction temperature, the conversion decreases. The increase in temperature increases the dissociation rate of KPS/TMEDA, initiation, propagation, and termination rates, as well as



**Figure 4** Effect of KPS concentration on conversion ( $y$  %): AM = 0.97M; MSAS = 0.03M; BisA =  $3.2 \times 10^{-2}$ M; TMEDA =  $1.5 \times 10^{-3}$ M;  $t = 30^\circ\text{C}$ , 4 h.



**Figure 5** Effect of reaction temperature on conversion ( $y$  %): AM =  $0.97M$ ; MSAS =  $0.03M$ ; BisA =  $3. \times 10^{-2}M$ ; KPS =  $2.67 \times 10^{-3}M$ ; TMEDA =  $1.5 \times 10^{-3}M$ ; 4 h.

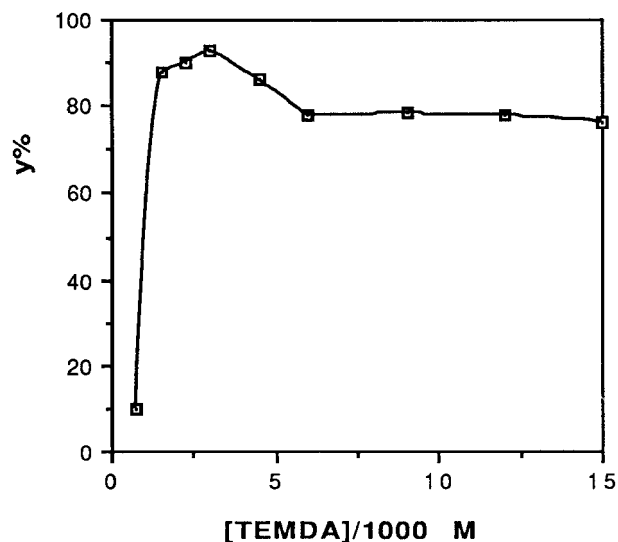
monomer mobility. All these factors, except increases in the rate of termination, increase conversion. Initially, the conversion increases with an increase in temperature. This is attributed to an increase in polymerization rate. With a further increase in temperature beyond  $35^{\circ}C$ ,  $y$  % decreases. This is due to the formation of small polymer chains because of the increase of the termination rate. Finally, test shows there are only small absorbency differences among the samples prepared at different reaction temperatures.

#### Effect of TMEDA Concentration

Figure 6 shows the effect of TMEDA concentration on conversion. The polymerization was carried out with various concentrations of TMEDA at  $35^{\circ}C$  for 4 h, holding all other reaction conditions the same as in Figure 5. Conversion increases with increasing TMEDA concentration and reaches a maximum at  $3.0 \times 10^{-3}$  mol/L of TMEDA. At higher TMEDA concentrations ( $3.0 \times 10^{-3}$  to  $6.0 \times 10^{-3}$  mol/L), conversion was found to decrease markedly. However, the decrease in conversion becomes minute when the concentration of TMEDA is higher than  $6.0 \times 10^{-3}$  mol/L. These results confirm that TMEDA is involved in copolymerization initiation.

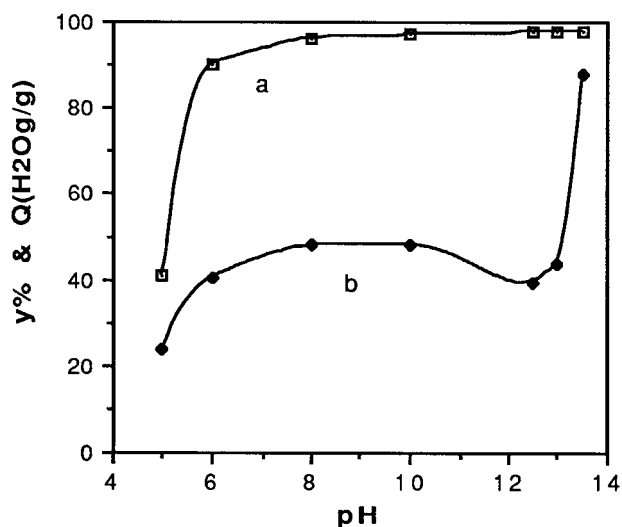
#### Effect of pH

Since TMEDA is a base in aqueous solution, studying pH effects on conversion and absorbency



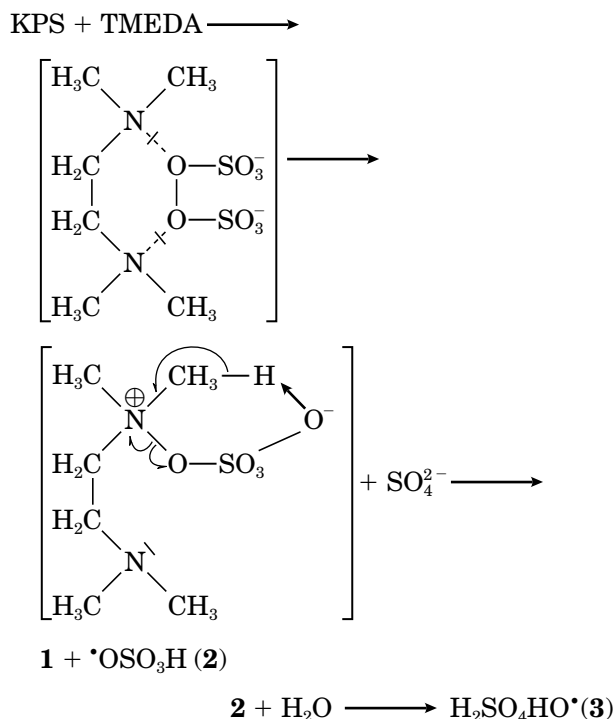
**Figure 6** Effect of TMEDA concentration on conversion ( $y$  %): AM =  $0.97M$ ; MSAS =  $0.03M$ ; BisA =  $3.2 \times 10^{-2}M$ ; KPS =  $2.67 \times 10^{-3}M$ ;  $t = 35^{\circ}C$ , 4 h.

require that TMEDA be added, the pH adjusted, and then KPS added. As seen in Figure 7, conversion increases with an increase in pH from 5 to 8 and reaches a plateau when the pH is greater than 8. Recently, Feng et al.<sup>18</sup> proposed that when using KPS-TMEDA as a redox initiator for the free radical polymerization of acrylamide,  $(CH_3)_2NCH_2(CH_3)NCH_2 \cdot$  (1),  $HOSO_3 \cdot$  (2), and  $OH \cdot$  (3) are responsible for initiation of vinyl polymerization. This redox initiation system has



**Figure 7** Effect of pH on conversion ( $y$  %) and absorbency ( $Q$ ): AM =  $0.97M$ ; MSAS =  $0.03M$ ; BisA =  $3.2 \times 10^{-2}M$ ; KPS =  $2.67 \times 10^{-3}M$ ; TMEDA =  $3.0 \times 10^{-3}M$ ;  $t = 35^{\circ}C$ , 4 h; (a)  $y$ %; (b)  $Q$ .

been applied to copolymerization of a number of monomers.<sup>14,19-23</sup> The following scheme illustrates the production of these radicals:



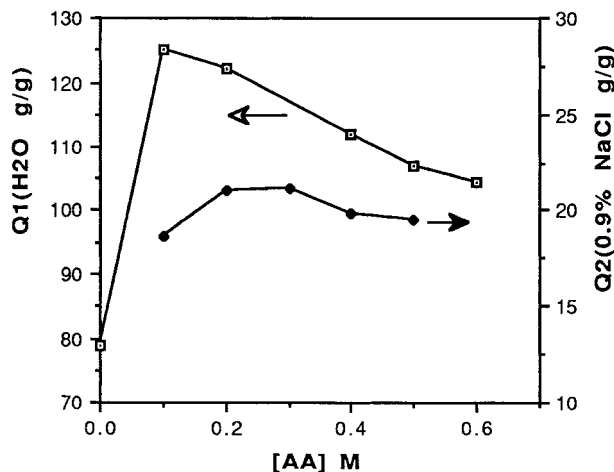
A lower pH should retard the production of radicals **1**, **2**, and **3**, which is in good agreement with the results of Figure 7.

As shown in Figure 7, the absorbency increases gradually with increasing pH values from 5 to 13 and drastically increases when the pH was higher than 13. This is due to an increase of ionic content in the network resulting from hydrolysis of amide groups. At a TMEDA concentration of  $3.0 \times 10^{-3}$  mol/L, the pH is  $\approx 9$ , and no auxiliary pH adjustment is needed to form polymers with high conversion and good absorbency.

### Synthesis of Crosslinked Poly(AM-MSAS-AA)

#### Effect of AA Concentration on Absorbency

In order to study the effect of AA concentration on conversion as well as absorbency, the polymerization was carried out with various concentrations of AA at  $35^\circ\text{C}$  for 4 h (all other reaction conditions were selected from the results obtained above). It is clear from Figure 8 that the absorbency is greatly increased by the incorporation of AA units from 79 to 125 times with AA concentration from 0 to 0.10 mol/L and reaches its maximum at a AA concentration of 0.10 mol/L. How-



**Figure 8** Effect of AA concentration on absorbency in distilled water ( $Q1$ ) and in 0.9% NaCl  $\text{H}_2\text{O}$  ( $Q2$ ): AM =  $0.97\text{M}$ ; MSAS =  $0.03\text{M}$ ; BisA =  $3.2 \times 10^{-2}\text{M}$ ; KPS =  $2.67 \times 10^{-3}\text{M}$ ; TMEDA =  $3.0 \times 10^{-3}\text{M}$ ;  $t = 35^\circ\text{C}$ , 4 h.

ever, a further increase of AA concentration leads to a decrease in absorbency, which is still as high as 105. This may be due to an increase of sol fraction caused by increasing the ionic content of the network. The 0.9% NaCl solution absorbency dependence on AA concentration shows that the absorbency reaches its maximum at 21 times the AA concentration from 0.2 to 0.4 mol/L. An increase in ionic strength decreases the swelling because the presence of ions in the solution surrounding the network counteracts the mutual repulsion of the fixed ions on the network itself. This observed effect of ionic strength swelling behavior is in agreement with the results of Gudeman and Pappas<sup>24</sup> and Choi et al.<sup>25</sup> All the conversions studied were higher than 95%.

### CONCLUSION

Hydrogel of crosslinked poly(AM-MSAS) and poly(AM-MSAS-AA) were synthesized with redox initiator by the aqueous solution polymerization technique. The dependence of material properties on the various reaction conditions was investigated. The important results are summarized as follows.

1. Conversion and absorbency increase with increasing BisA concentration, and absorbency reaches its maximum when the BisA concentration is  $3.2 \times 10^{-2}$  mol/L.

2. Conversion and absorbency increase with increasing MSAS concentration. Further increasing of MSAS concentration leads to a decrease in absorbency.
3. The optimal KPS concentration for the polymerization is from  $1.33 \times 10^{-3}$  to  $2.67 \times 10^{-3}$  mol/L.
4. The best concentration of TMEDA for this polymerization system was  $3.0 \times 10^{-3}$  mol/L in pH range from 9 to 12.
5. The conversion shows a maximum at 35°C and was more than 92% after 2 h.
6. The absorbency is greatly increased by incorporation of AA units. The best swelling ratio in distilled water is 125, and in 0.9% NaCl solution is 21.

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