Superabsorbent Hydrogels from Concentrated Solution Terpolymerization*

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ABSTRACT

A new outlook on a preparative process of superabsorbing hydrogels is presented in this paper. The hydrogels based on acrylic acid (AA), acrylamide (AM) and potassium acrylate (KA) were prepared through polymerization of concentrated solution of the acrylic monomers. Ammonium persulphate/sodium metabisulphite redox pair initiating system was used for the free radical terpolymerization and methylenebisacrylamide was used as a cross-linker. Some certain process variables (cross-linker and initiator concentration) affecting either swelling capacity or swelling rate were thoroughly investigated. Temperature variations of the polymerization mixture were also studied. The synthetic method was found to be an efficient and facile approach for making superabsorbents with quantitative yield under atmospheric conditions. Meanwhile, by swelling measurements in both water and saline media, power law relationships between cross-linker content and swelling capacity were found.

INTRODUCTION

Superabsorbent hydrogels are hydrophilic networks with a high capacity of water uptake. Superabsorbents have received prominent attention in the last decade due to their numerous applications in many areas. They are used in hygienic products [1,2], agriculture [1,2], drug delivery systems [1,3-5], sealing [6,7], coal dewatering [8], and artificial snow [1]. Early agricultural water absorbents were based on biopolymers through grafting of hydrophilic monomers onto starch.

and other polysaccharides [9-11]. Natural superabsorbents were gradually replaced by synthetic superabsorbent which have long service life, high capacity of water absorption and high gel strength during last two decades. Hygienic superabsorbents are mainly based on acrylic acid and its salts. Acrylamide is a main component of agricultural superabsorbents [1,12-14]. Synthesis of superabsorbent based on acrylamide, acrylic acid and its salts by inverse suspension polymerization [15,16] and diluted solution polymerization [12-14] have been investigated in many papers. Fewer studies have been done on high concentrated solution polymerization of acrylic monomers, which are mostly patented [17]. Chen [18,19] synthesized acrylic acid-sodium acrylate superabsorbent through concentrated (43.6 wt%) solution polymerization using potassium persulphate as a thermal initiator. This work was conducted following our previous studies on porous potassium-based superabsorbing hydrogels [20-22].

This paper deals with the synthesis of acrylamide (AM), acrylic acid (AA) and potassium acrylate (KA) by solution polymerization at high monomer concentration (60 wt%). This is the first international paper that emphasizes the synthesis of terpolymeric potassium-based superabsorbent polymers via very "high concentrated" solution polymerization. Ammonium persulphate (APS) and sodium metabisulphite (SMBS) were used as a redox pair initiator. Influence of reaction parameters such as concentration of cross-linker and initiator on swelling properties of the AM-AA-KA superabsorbents were investigated in detail.

Materials
Acrylic acid (AA) and acrylamide (AM) monomers and N,N'-methylenebisacrylamide (MBA) cross-linker supplied by Fluka were used as received. Ammonium persulphate (APS), sodium metabisulphite (SMBS), and potassium hydroxide (KOH) were supplied by Merck and used without further purification.

Synthesis
The monomer AA (0.33 mol) was partially (75%) neutralized with potassium hydroxide (0.27 mol) solution under ice cooling. Then AM and MBA solutions were added to the above solution. The exact amounts of the reactants are given in Table 1.

As a representative example (preparation of sample S2), a detailed synthetic procedure is as follows: AM (0.08 mol) and MBA (0.12 mmol) were dissolved in 6 and 4 mL distilled water, respectively. They were then added to the solution contained in a 600-mL beaker equipped with a magnetic stirrer and thermometer for

| Table 1. Amount of reactants used in polymerization reactions and the gelation times recorded. |
|---|---|---|---|---|---|---|---|
| Exp. series | Sample | AA+KA, (mol/L) | AM, (mol/L) | AM (mol%) | [MBA] × 1000 | APS (mol/L) | SMBS (mol/L) | Gelation time (s) |
| AM monomer | S1 | 5.94 | 0 | 0 | 1.85 | 4.69 | 4.69 | 85 |
| | S2 | 4.75 | 1.19 | 20 | 1.85 | 4.69 | 4.69 | 90 |
| | S3 | 3.56 | 2.37 | 40 | 1.85 | 4.69 | 4.69 | 290 |
| | S4 | 2.37 | 3.56 | 60 | 1.85 | 4.69 | 4.69 | 450 |
| | S5 | 1.19 | 4.75 | 80 | 1.85 | 4.69 | 4.69 | 600 |
| | S6 | 0 | 5.94 | 100 | 1.85 | 4.69 | 4.69 | 40 |
| MBA cross-linker | S7 | 2.36 | 3.56 | 60 | 0.925 | 4.69 | 4.69 | 470 |
| | S8 | 2.36 | 3.56 | 60 | 2.77 | 4.69 | 4.69 | 445 |
| | S9 | 2.36 | 3.56 | 60 | 3.7 | 4.69 | 4.69 | 430 |
| | S10 | 2.36 | 3.56 | 60 | 4.625 | 4.69 | 4.69 | 425 |
| Initiator | S11 | 2.36 | 3.56 | 60 | 2.77 | 3.12 | 3.12 | - |
| | S12 | 2.36 | 3.56 | 60 | 2.77 | 9.38 | 9.38 | 80 |
| | S13 | 2.36 | 3.56 | 60 | 2.77 | 14.07 | 14.07 | 65 |
monitoring temperature changes during exothermic reaction. The persulphate (APS 0.39 mmol dissolved in 2 mL water) and metabisulphite (SMBS 0.39 mmol dissolved in 2 mL water) were added to the AA-KA-AM-MBA mixture. The mixture temperature and viscosity was increased in 90 s to reach the gelation point where the stirrer rotation is stopped due to gelation. The time elapsed to reach the gelation point is referred to as gelation time. After this point, the temperature was rapidly increased which led to the solvent evaporation. The product (as an elastic transparent gel) was scissored to small pieces and dried in an airforced-draft oven for 18 h at 70 °C to reach a constant weight. Quantitative yields were generally obtained. Dry products were ground with a hammer-type minigrinder and screened.

Swelling Measurements
Equilibrium swelling capacity was measured in distilled water according to a previously reported method [23]. Swelling rate (SR, g/g.s) was defined as follows:

\[ SR = S_t/t_{mr} \]  

(1)

where, \( S_t \) stands for swelling at the time related to minimum rate parameter \( t_{mr} \) (s) obtained from superabsorbents of a set of similar experiments. The rate parameter is the time required reaching 0.63 of the equilibrium swelling. It is based on a Voigt-like model for the swelling of SAPs [24].

RESULTS AND DISCUSSION
Polymerization Process and Monomer Composition
Temperature variations versus the polymerization reaction time are shown in Figure 1. Each curve can be divided into two stages, according to temperature changing. The temperature was mildly increased with time at the first stage and then it was raised vigorously in the second stage. In this article, the reaction time is defined as the time at the maximum temperature. These concepts are shown typically on the time-temperature profile of the reactions in Figure 1. Acrylamide percent (AM%) is defined as the mole percent of acrylamide to total mole of monomers used. The reaction time was 150 s in the case of acrylamide-free sample (S1). The reaction time was enhanced to 450 and 645 s, at 40 and 80 AM%, respectively. The higher the AM percent, the longer would be the reaction time.

The gelation time versus the AM percent is illustrated in Figure 2. The gelation time is 85 s for the acrylamide-free sample (S1). It is slowly enhanced to 95 at 20 % AM. Then increasing the AM % rapidly enhances the gelation time. It is reached 290 and 600 s at 40 and 80 AM %, respectively.

Two parameters, i.e. ART1 and ART2, may be defined as the average rate of temperature elevation at the first and second stages of the temperature profiles, respectively (eqns (1 and 2)). These parameters were calculated to help us to better understand the polymerization process.

![Figure 1. Time-temperature profiles at different acrylamide mole percentages in the reaction mixture.](image)

![Figure 2. Gelation time vs. acrylamide mole percent in the polymerization mixture.](image)
ART1 = \( \Delta T_1/\Delta t_1 \)  
ART2 = \( \Delta T_2/\Delta t_2 \)

Where, \( \Delta T \) and \( \Delta t \) denote temperature increase (°C) and the corresponding time (min), respectively. The numbers 1 and 2 indicate the first and second stages of temperature increase, respectively.

Figure 3 exhibits the parameters ART1 and ART2 versus the acrylamide percentage. The ART1 is found to be 18.0 C/min for acrylamide-free sample, it is reduced to 11.2 C/min at 20.0 AM percent. Increasing the AM percent continuously diminishes the ART1. Eventually it is reduced to 3.5 C/min at 80 AM %.

Variations of the gelation time and the reaction time at the first stage are indirectly proportional to polymerization rate. In these experiments, only the AM % was changed while other influencing factors (e.g., initiator concentration, monomer concentration, and reaction bath temperature) were kept constant. Regarding the reactivity ratios of the monomer AA (1.36) and AM (0.598) [25], it may be concluded that propagating chain with either AA- or AM- end group comprises more tendency to react with acrylic acid rather than acrylamide. Consequently, the higher the AM percent, the lower would be the polymerization rate.

The average rate of temperature elevation at second stage (ART2) has a reducing trend by increasing the AM percent. Their values were much higher than the ART1 especially in the reactions with higher AM % (Figure 3). As a stereotype, the ART2 value was 80 C/min for the AM-free sample. It was decreased to 71 and 53 C/min at AM % of 20 and 80, respectively. The second stage period is very shorter than the first stage period (Figure 1). The second stage is nearly lengthened changed just 0.5-1.0 min that is very shorter than the first stage (2-10 min).

The reaction mixture is converted from viscose liquid to elastic solid at gelation point, where the second stage is nearly started. Translation diffusion of the radical ended chains toward each other, and in turn, termination reaction possibility, is decreased due to high viscosity of the reaction medium. As a result, the diminished termination reactions as well as the radical population enhancement cause a great increasing the polymerization rate as recorded at the second stage (Figure 1).

**Swelling Behaviour Versus AM% Variation**

Water absorbency vs. the AM % are shown in Figure 4. It is observed that superabsorbency was considerably enhanced by the AM % rising. Swelling is increased from 237 to 824 g/g with the AM % enhancement from 0 to 80.

Several reasons may be presented for the swelling increase versus AM%. Since higher AM% causes lengthening the first stage of the polymerization (Figure 1), the average chain length between cross-linking points will be enhanced. Therefore, the swelling capacity is increased because it is proportionally dependent.
on the average molecular weight between cross-links at a certain degree of ionization [15]. Another reason may be related to lower tendency of the cross-linker to react with AM rather than with AA and KA. Methylenebisacrylamide (MBA) cross-linker is structurally very similar to the monomer MA rather than to comonomers AA and KA. So, as it is stated above on the monomer reactivity ratios of AA and AM, at a fixed amount of the cross-linker in all the experiments, it would react less with AM than with the comonomers. As a result, fewer joints between chains are formed and would lead to enhancement of swelling.

An additional reason for the swelling increase versus AM% may be due to easier auto-crosslinking through hydrogen abstraction from the polymer backbone when AA content is higher. Here, according to Figure 1, the heat of polymerization is evolved during a shorter time, so this hot system favours the heating induced cross-linking followed by radical combination [15]. These crosslinker-free crosslinking (i.e., auto-crosslinking) results in decreased swelling capacity of the samples with lower AA and KA contents.

Cross-linker Effect

Cross-linker content has been changed at fixed AM % in this series (Table 1, samples 4 and S7-S10). Swelling capacity in distilled water vs. cross-linker concentration, [MBA], is illustrated in Figure 5.

Swelling capacity is decreased from 940 to 171 g/g as cross-linker content is increased from 0.00092 to 0.0046 mol/L and hydrated gel was changed from sticky-loose substance to elastic-stiff material by crosslinker content rising.

Four main forces have influence on swelling capacity of ionized superabsorbents [26]. They are: polymer-solvent interaction which depends on solubility tendency of a polymer in solvent, elastic interaction which is proportional to average molecular weight between two consecutive junctions, osmotic pressure due to mobile-ion-concentration difference between gel and solution phase, and the electrostatic repulsion between ionic groups located on macromolecular chains. The latter is usually negligible comparing to three other forces. As cross-linker concentration was increased, the free energy of mixing, the electrostatic repulsion and the ionic content remained constant. Only the elastic interaction of network is increased due to further junction formation. This force counter acted against swelling that caused an absorption reduction.

A power law relationship was found between the swelling capacity and the cross-linker concentration eqn (4):

\[ S_q = 0.480 \times [\text{MBA}]^{-1.076} \]  

where, \( S_q \) is equilibrium swelling (g/g) and [MBA] is the molar concentration of the cross-linker.

According to the known behaviour shown in Figure 5, the swelling is influenced to cross-linker concentration at lower [MBA]. In other word, a small change in [MBA] has a large influence on the swelling capacity at lower range of the cross-linker concentration.

It was found that the rate of swelling of the superabsorbent is decreased at higher cross-linker concentration. This fact is also demonstrated in Figure 5. Again, a reductive trend is obvious from the curve. As [MBA] is increased, the rate of water absorption is decreased based on a power law relationship (eqn (5)).

\[ \text{SR} = 0.183 \times [\text{MBA}]^{-0.523} \]  

Swelling in 0.15 M salt solutions is shown in Figure 6. In NaCl solution, swelling was measured to be 63.7 g/g at the least amount of [MBA] (0.00092 mol/L). Following a known power law behaviour, the swelling is
reduced remarkably as the cross-linker concentration is increased.

Swelling capacity measured in saline (Figure 6) is much lower than its value determined in distilled water (Figure 5) that is related to osmotic pressure. The osmotic pressure difference between gel phase and swelling media, which is a motive force for swelling, is reduced by presence of cations in swelling media that caused large reduction of swelling capacity. Comparing the values of the power law index (in distilled water -1.076, in saline -0.48), it may be concluded that the cross-linker concentration influences the swelling in water much greater than that in saline.

Swelling in two- and three-valent salt solutions vs. [MBA] is also shown in Figure 6. In calcium chloride solution, swelling is decreased by [MBA] increasing in a similar manner but with a lower extent. In AlCl₃ solution, although more reduced osmotic pressure difference results in noticeable swelling loss in comparison with the swelling in CaCl₂ and NaCl, the cross-linker concentration shows no certain influence on the swelling capacity. In the case of the multivalent ions Ca²⁺ and Al³⁺, additional cross-linking between carboxylic groups of the hydrogel chains and the metal cations are formed to lead to more reduction of swelling capacity.

**Initiator Effect**

The polymerization did not take place when the initiator concentration, [I], was lower than 0.004 mol/L. Since the syntheses took place without inert gas purging, soluble oxygen might have reacted with free radicals to form peroxo and hydroperoxy radicals with lower reactivity [21]. As a result, the polymerization could not start properly.

The time-temperature profiles of samples S4, S12 and S13 are plotted in Figure 7. The reaction time was greatly decreased from 575 to 80 s by enhancement of [I].

The polymerization rate is directly proportional to square root of [I], therefore, the higher [I], the higher polymerization rate would be [26]. The ART1, ART2, gelation time, gelation temperature and reaction time are listed in Table 2. By increasing the initiator concentration from 0.00469 to 0.01407, ART1 (from 6.5 to 34 C/min) and ART2 (from 48 to 73 C/min) are intensely enhanced. These data indicated that polymerization rate is highly increased in both stages by the initiator concentration enhancement. Again the ART2 values were much higher than ART1 due to an accelerated polymerization reaction after gelation (Figure 7).

Swelling capacity was 404 g/g in distilled water when [I] was at the lowest value, i.e. 0.00469 mol/L. It was enhanced to 606 g/g when [I] was doubled. The sample S13, which was prepared using highest [I] (0.01407 mol/L), was completely soluble in water (infinite swelling). Chain ends are known as imperfections in a polymer networks [27,28]. Imperfections become
more by chain ends enhancement. Here, higher imperfections mean that fewer junctions are formed between chains that, in turn, cause increased swelling.

## CONCLUSION

Synthesis of acrylic-based superabsorbent hydrogels through cross-linking terpolymerization of acrylic monomers (AM, AA, KA) in concentrated solution is of importance due to practical viewpoints. The influences of AM/AA-KA mole percent, cross-linker and initiator concentration on the process and on the swelling properties were studied to achieve hydrogels with higher capacity and rate of water absorption. Main conclusions are summarized as follows:

- Solution polymerization of concentrated acrylic monomers with redox pair APS/SMBS comprises of two stages. Polymerization proceeds slowly at the first stage and it is progressed very fast at the second stage. Decreasing of acrylamide percent as well as increasing the initiator concentration caused a polymerization rate rising.

- Acrylamide percent enhancement in the monomer mixture causes an increase of reaction time, gelation time as well as the swelling capacity.

- Increasing the cross-linker content leads to a decreased swelling capacity and absorption rate. A power law behaviour as $S_q = 0.48 \cdot [\text{MBA}]^{-1.076}$ was found for the swelling and the cross-linker content relationship.

- Rate of swelling was shown a power law relationship with the cross-linker concentration as $SR = 0.18 \cdot [\text{MBA}]^{-0.523}$ with the cross-linker concentration.

- Power law relationships were found between the cross-linker concentration and the capacity of swelling in 0.15 M of NaCl and CaCl$_2$ solutions.

- The reaction and gelation times were decreased and water absorption was enhanced by increasing the initiator concentration.

## REFERENCES


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