Residual Monomer in Superabsorbent Polymers: Effects of the Initiating System

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ABSTRACT: Minimized residual monomer is an essential requirement particularly in hygienic, pharmaceutical, and food packaging polymer products such as superabsorbent polymers (SAPs). The present article is the first non-patent report on the study of a highly effective polymerization variable (e.g. initiator) on the residual monomer of SAPs based on partially neutralized acrylic acid. Two persulfate systems, i.e. ammonium persulfate (APS)/sodium metabisulfite (SMBS) and APS/tetramethyl ethylenediamine (TMEDA), were examined to initiate the free-radical polymerization at room temperature. It was shown that chromatographically measured residual monomer and swelling capacity was strongly dependent on the type and concentration of the initiator. A kinetic model was also derived to describe the experimental results. Dissociation rate of initiation system was recognized to be a key factor to obtain a SAP with low residual monomer. It was found that, in aqueous solution polymerization, the effect of a slowly dissociating system such as APS/TMEDA on decreasing the residual monomer was much higher than that of a rapidly dissociating system like APS/SMBS. Under selected conditions, residual monomer could be reduced up to 5327 $\pm$ 138 and 1715 $\pm$ 44 ppm for APS/SMBS and APS/TMEDA initiating systems, respectively. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2533–2540, 2009

Key words: superabsorbent; residual monomer; hydrogel; initiator; acrylic acid

INTRODUCTION

Superabsorbent polymer (SAP) hydrogels are lightly crosslinked networks which can absorb and retain large amounts of water and other physiological solutions.[1] They are used in hygienic,[1,2] and agricultural[1] applications, controlled drug delivery,[1] water swelling rubber,[3] coal dewatering,[4] and so on.

Numerous papers have been published in field of SAP hydrogels in last two decades. Different aims were considered in these papers such as enhancing absorption rate through using porogens,[5,6] improving gel strength mostly by preparing superabsorbent composites or nanocomposites,[7–9] preparing hybrid superabsorebnts by simultaneous use of natural polymers and acrylic monomers,[10,11] or investigation of reaction parameters such as initiator concentration, monomer concentration, reaction temperature or comonomer content on swelling properties.[12,13] There are nearly 1150 papers on superabsorbents published during years 1976–2008.

The subject of residual monomer is a very important aspect of superabsorbents which has been nearly forgotten in the academic papers for the time being. Residual monomer is a key feature especially for SAPs used in hygienic, pharmaceutical, and food packaging applications. Surprisingly, there is no non-patent published report about relation of the reaction parameters such as initiator concentration [I], reaction temperature, and neutralization degree on the residual monomer content of SAPs. This theme has merely been studied in a few patents.[14] For instance, effects of potassium bromate and potassium chlorate on reducing residual monomer content in the acrylic hydrogels were claimed without mentioning the involved mechanism.[14] In a previous paper, we introduced a method for measuring residual monomer in acrylic SAPs.[15] Persulfate initiators are the most conventional initiator for synthesis of SAPs to initiate thermal or redox polymerization.[5,6,9] Redox initiating system is industrially favor due to economical aspects.[5,6] The conventional redox initiating system for SAP synthesis is APS/SMBS[5,6] and APS/TMEDA.[16,17] Thermal initiators such as APS,[9] potassium persulfate(KPS),[18] and 4,4_-Azobis(4-cyanovaleric acid) (ACVA)[19,20] are also used for SAP synthesis. Relationship between residual monomer and initiator concentration were not investigated in all these papers.

This article deals with the effect of initiator type and concentration on the residual monomer content of the SAPs obtained from solution polymerization of partially neutralized acrylic acid using two

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commonly used redox persulfate initiating systems. A kinetic model was also derived to describe the results of the experiments.

EXPERIMENTAL

Materials

Acrylic acid (AA, Fluka), tetramethyl ethylenediamine (TMEDA, Fluka), sodium hydroxide (NaOH, Merck) ammonium persulfate (APS, Merck) sodium metabisulfite (SMBS, Merck), polyethyleneglycol dimethacrylate (PEGDMA, MW 330, Aldrich) were used as received.

Synthesis of SAP hydrogels

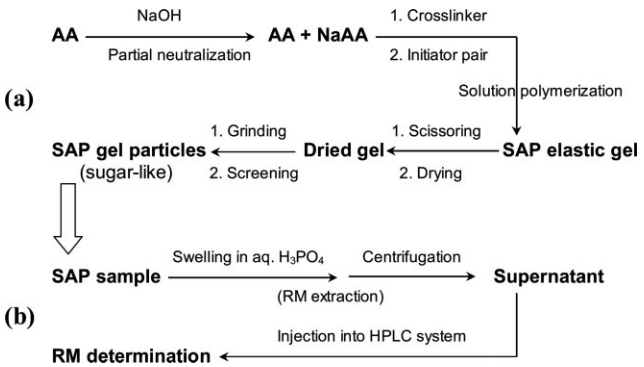
Acrylic acid (15.0 g) was neutralized partially (75 mol %) with sodium hydroxide solution (6.25 g NaOH in 20.0 mL H_2O). A fixed amount of crosslinker PEGDMA (0.04 g) was employed in all syntheses, while the initiator concentration was varied. Desired initiator pair was added to the reactor and stirred at room temperature to start the exothermic reaction. Monomer and crosslinker concentration were 8.3 mol/L and 0.005 mol/L, respectively. The initiator ranges were $2.5–6.2 \times 10^{-3}$ and $5.9–20.7 \times 10^{-3}$ mol/L for APS/SMBS and APS/TEMED initiating systems, respectively. Gelation was observed within 5 min (with rapid increase of temperature) and 1–3 h for the APS/SMBS and APS/TMEDA initiating systems, respectively. The elastic gel product was removed from the reactor to cut into small pieces. It was dried in an air-drafted oven at 80°C for 8 h. The dried gel pieces were pulverized by a hammer-type minigrinder, screened and stored in a dry place.

Swelling measurements

A 0.20 g sample of dried polymer (mesh 35–100) was dispersed in an excess volume (100 mL) of distilled water and allowed to swell for 1 h to reach equilibrium swelling. The dispersion was filtered through polyester gauze to remove the excess water. Then, the swollen gels were weighted. Swelling capacity (g/g) was calculated via dividing the weight of the swollen gel by the initial dry sample. The standard deviation for this method was ± 3 ($n = 10$).

Residual monomer measurement

The chromatographic system was composed of a Model 510 computer-controlled HPLC pump, a Model U6K injection valve equipped with a 20-mL sample loop, a Model 486 UV/vis detector all from Waters (Milford, MA). Waters Maxima Software Model 820 was used for the system and data management. The separation was performed in isocratic mode at a 1.8 mL/min flow rate and ambient temperature on a analytical column (250 × 4.6 mm, 5 μm) containing the Tracer EXEL 120 ODSA stationary phase. The mobile phase was an aqueous 0.01% orthophosphoric acid (sodium acrylate is converted to acrylic acid in this acidic medium). The UV–vis absorbance over the 190–400 nm range was recorded and the wavelength used for quantification of the monomer acrylic acid was 200 nm.[15]



Scheme 1 Typical steps for (a) SAP gel preparation and (b) residual monomer analysis. Abbreviations: AA, NaAA, and RM stand for acrylic acid, sodium acrylate, and residual monomer, respectively.

A stock solution containing 10.0 mg/mL acrylic acid was prepared in the 0.01% orthophosphoric acid and calibration standards were prepared by appropriate quantitative dilution from the stock solution with the mobile phase. Quantities of 100 mg of the hydrogel beads were extracted with the same orthophosphoric acid (20 mL) through overnight stirring. The completely swollen samples were centrifuged at 2000 rpm for 15 min and the supernatant was injected into the chromatographic system.[15] The standard deviation for this method is $\pm 2.6\%$.

Oligomers can be estimated from subtraction of residual monomer from sol content.

RESULTS AND DISCUSSION

Scheme 1 represents concisely the practical steps for the SAP gel preparation and determination of its residual monomer. Aqueous solution polymerization of partially neutralized acrylic acid was conducted at room temperature in the presence of fixed and small amount of the water soluble crosslinker, PEGDMA (0.06 mol % in relation to the initial monomer concentration).

Two different persulfate-based initiating systems, i.e. APS/SMBS and APS/TMEDA were used to initiate the polymerization reactions. The main cause of employing the redox pair initiators instead of thermally induced initiating systems (such as APS alone), was prevention of undesirable thermal effects of the heating conditions on the swelling properties

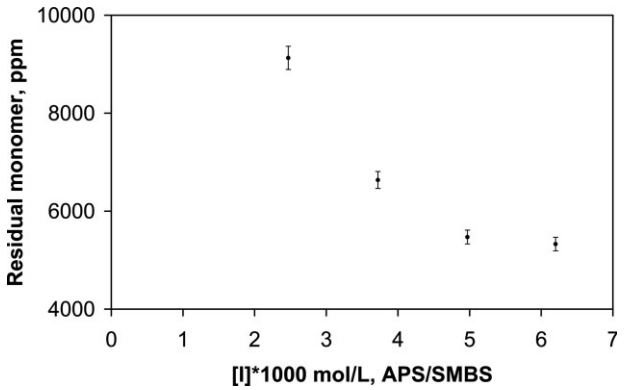


Figure 1 Residual monomer dependency on the APS/SMBS initiator concentration, [I].

of the final SAP product.[21] By using desired initiator pairs, polymerizations were started at room temperature, ~ 22°C. With APS/SMBS initiating system, the reaction temperature reached to around 39°C after ~ 6 min. The temperature enhancement for APS/TMEDA system was as small as ~ 6°C during a longer period (0.5–2 h) depending on the initiator concentration.

The conventional crosslinker *N,N′*-methylenebisacrylamide (MBA) was not preferably employed, because of some certain unfavorable thermo-hydrolytic cleavage of MBA crosslinks occurred in the oven-drying stage.[21]

APS/SMBS initiation

In this series of reactions, APS/SMBS redox-pair initiating system was used to prepare the SAP samples. Figure 1 shows residual monomer versus the initiator concentration. The residual monomer content was 9128 ± 237 ppm at the lowest initiator concentration, 2.47 mmol/L. It was decreased to 5327 ± 138 ppm when the initiator was enhanced to 6.2 mmol/l.

Figure 2 shows the influence of APS/SMBS initiator concentration, [I], on swelling capacity and gel content of the SAP products. An overall ascending trend is observed for the swelling capacity versus [I]. At high [I], a lot of short chains were formed which could not join the polymer network with low crosslinker content. As a result, crosslink density was reduced and led to swelling enhancing. The gel content measurement fairly supported this assumption. With enhancing [I] from 2.47 to 6.2 mmol/L, the gel fraction were decreased slightly from 76 to 72% (Fig. 2); in other word, the soluble (sol) fractions composing the detached chains, oligomers, and nonreacted monomers were somewhat increased at higher [I]. This suggests that at higher [I], the fixed concentration of crosslinker was not adequate to join lots of short chains to the gel network. As a result, the sol content was increased (i.e., a slight loss of gel content). Estimated oligomer content was between 22 and 28% for APS/SMBS redox-pair initiating system which was increased with [I] enhancement. It was observed that the main part in sol content was belong to oligomers and residual monomer had lower contribution (about 4%) in sol content.

APS/TMEDA initiation

In APS/TMEDA series, a fully alkyl-substituted diamine (TMEDA) was used as an accelerator of the persulfate initiation.[22] Figure 3 shows the residual monomer content of the SAP samples prepared by employing various concentrations of the APS/TMEDA initiation system. Residual monomer was measured to be 3951 ± 102 ppm at the initiator 5.95 × 10^{-3} mol/L. It was considerably decreased with enhancement of the initiator concentration. For example, at 2.07 × 10^{-2} mol/L, it decreased to 1715 ± 44 ppm. On the other hand, a substantial difference between residual monomer content in two initiation systems was observed. By using APS/TMEDA initiation system, the residual monomer

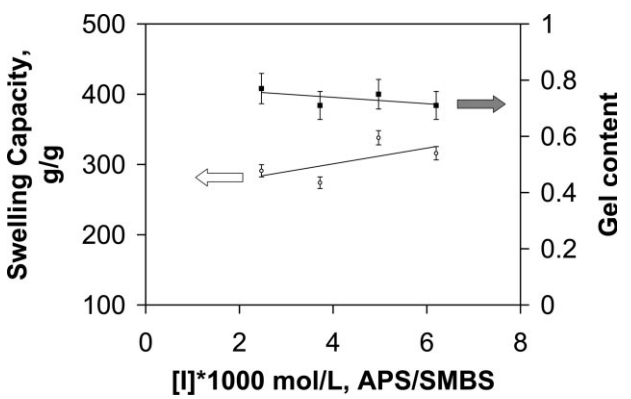


Figure 2 Swelling capacity and gel content of acrylic SAP product obtained from the APS/SMBS initiation system.

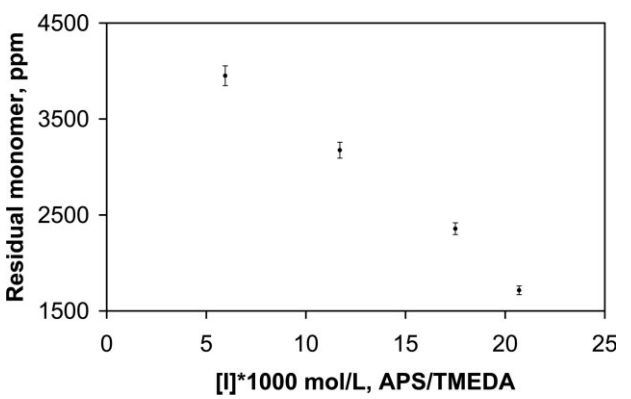


Figure 3 Residual monomer dependency on the APS/TMEDA initiator concentration, [I].

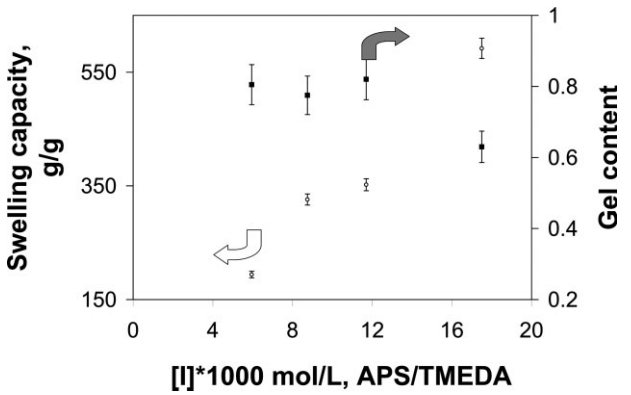


Figure 4 Swelling capacity and gel content of acrylic SAP product obtained from the APS/TMEDA initiation system.

was significantly diminished at all concentrations of the initiator.

The difference could be related to kinetic parameters particularly rate of initiator dissociation, rate of initiator consuming, monomer concentration, and initiator concentration. A kinetic model was derived in next section to describe the residual monomer changes theoretically with the mentioned parameters.

Figure 4 shows the swelling capacity and gel content versus the concentration, [I], of APS/TMEDA. At the lowest concentration used (2.07 mmol/L), swelling capacity was measured to be 194 g/g. It exhibited an ascending trend with increase of [I], so that it finally reached to 592 g/g when [I] was 5.95 mmol/L. Gel content was moderately decreased (from 80 to 63%) with increase of [I] from 0.002 to 0.006 mol/L. Oligomers were varied between 17 and 36% with increase of [I]. Residual monomer only varies between 0.18 and 0.37% with [I] increasing. It is clearly seen that oligomer content is much higher than residual monomer content. It should be considered that low quantity of residual monomer content is more important than high sol content. The main problem was attributed to toxicity of acrylic acid monomer which can be removed in form hydrated gel in hygienic applications. Although minimizing oligomer content in SAP is desirable but poly(acrylic acid) has not toxicity like monomer.

The results can be explained by the use of the meaning of defects (chain ends) formed in the hydrogel network. According to the theory of Flory,[23] the chain ends are considered as defects of the polymer network, so that an increase of [I] leads to more chain ends. Therefore, the higher the [I], the higher network defects will be. As a result, increasing of [I] results in more imperfect network leading to less gel content (Fig. 4). It means that fewer junctions are formed between the chains and consequently the crosslink densities are diminished. Decreased crosslink densities lead to enhanced swelling capacities.[13] According to Figures 2 and 4, the slope of the swelling capacity increase for the SAP prepared by the pair APS/TMEDA is much more than that of the APS/SMBS pair. It suggests that APS/TMEDA system causes comparatively more imperfect networks with higher swelling capacities at high levels of initiator concentration.

It should be pointed out that there are some reasons for using different concentration scale of the initiator pairs. First, owing to the some undesirable thermal effects partially mentioned before, we used initiating systems with no need to external heating. So, APS/TMEDA and APS/SMBS, with ability to initiate polymerization at room temperature, were employed. However, the latter had a high dissociation rate, so that at high concentration ($> \sim 0.007$ mol/L), the reaction temperature enhancement was very much (the temperature was increased even up to 100°C), where the unfavorable thermal destructions[21] were highly possible.

Second, to have a rough assumption of an isothermal condition (for being comparable with the model-derived results; next section), we did not intend to have a maximum temperature difference more than $\sim$ 10°C. Therefore, we avoided the APS/SMBS concentration to be increased more than 0.007 mol/L.

The APS/TMEDA system, however, did not have such problem. Therefore, it could be examined at higher concentration levels (up to 0.02 mol/L) without increasing temperature more than 6°C. Indeed, since no significant changes in residual monomer were obtained at very low concentration (i.e. $< \sim$ 0.007 mol/L), we had to necessarily rise its concentration range up to around 0.02 mol/L.

The kinetic model

A general kinetic model for free radical polymerization was used to investigate the experimental founding including level of the residual monomer.[23] This simple model should be able to calculate monomer conversion, the quantity of the residual monomer and non-reacted initiator. Since the crosslinker concentration in SAP preparation reactions is extremely small, it can be assumed to be negligible. The model was derived for AA polymerization at neutral pH, therefore, the monomer (with pH $\sim$ 4) has to be partially neutralized to reach pH 7, where the monomer composition is nearly the same composition of the majority of hygienic SAPs (having 70–80 mol % sodium acrylate (NaAA) and 20–30 mol % AA). Here, in spite of performing a NaAA-AA *co*polymerization, such system is frequently taken as a *homo*polymerization of AA at a constant neutral pH resulting in a copolymeric product. The initiation rate constants for AA polymerization have been reported to be pH-independent.[24,25]

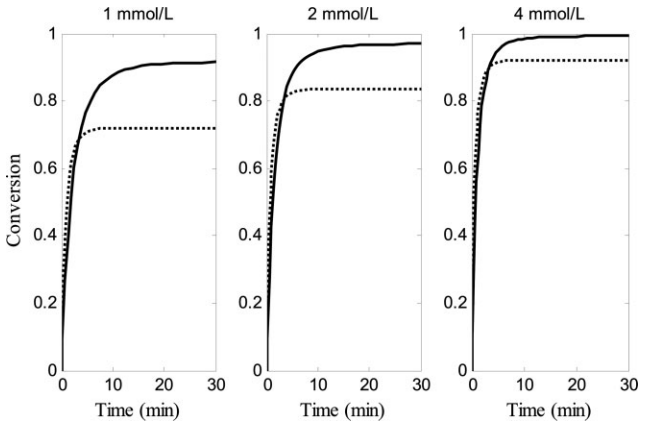


Figure 5 Conversion versus time for APS/SMBS (.....) and APS/TMEDA (—) initiation systems of three different concentrations (Modeling results obtained from computing by Matlab software).

The overall equation of polymerization rate (R_P) was used to drive monomer conversion equation[18];

$$R_p = -k_p[M][M^*] \tag{1}$$

where $[M^*]$ is the macroradicals concentration. It was calculated by using Quasi Steady State Assumption (QSSA) approach. According to this assumption, the rate of primary radical generation (R_i) is equal to the rate of macroradicals termination (R_t).

The rate of redox initiation[26–28] and the macromolecular termination are written as follows;

$$R_i = k_i[I_1]^{\alpha}[I_2]^{\beta} \qquad \text{Initiation} \tag{2}$$

$$R_t = k_t[M^*]^2 \qquad \text{Termination} \tag{3}$$

where I_1 and I_2 stand for oxidation (APS) and reduction (SMBS or TMEDA) agents, respectively. k_t is the overall termination rate constant and is the sum of combination and disproportionation rate constants ($k_t = k_{tc} + k_{td}$).

By using QSSA theory, the macroradical concentration can be calculated by eq. (4);

$$[M^*] = \left(\frac{k_i[I_1]^{\alpha}[I_2]^{\beta}}{k_t}\right)^{\frac{1}{2}} \tag{4}$$

Then eq. (1) can be rewritten as the following differential equation;

$$R_p = \frac{-d[M]}{dt} = -k_p[M]\left(\frac{k_i}{k_t}\right)^{\frac{1}{2}}\left([I_1]^{\alpha}[I_2]^{\beta}\right)^{\frac{1}{2}} \tag{5}$$

The residual (non-reacted) monomer concentration can be calculated by solving differential eq. (5) and then the monomer conversion P can be calculated as follows;

$$P = \frac{[M]_0 - [M]}{[M]_0} \tag{6}$$

The concentration of oxidation and reduction agents was decreased in the eq. (5) because of their consumption during the polymerization period. Equations (7) and (8) give the rate of oxidation and reduction agents' consumption in the course of the polymerization.

$$\frac{d[I_1]}{dt} = -k_i[I_1]^{\alpha}[I_2]^{\beta} \tag{7}$$

$$\frac{d[I_2]}{dt} = -k_i[I_1]^{\alpha}[I_2]^{\beta} \tag{8}$$

The concentrations of non-reacted monomer, oxidation, and reduction agents were calculated by solving the differential eqs. (5), (7), and (8), respectively.

To solve the differential equations, software MATLAB, Version 7.04, was used (see Appendix). Figures 5–8 were also plotted by this software. The required kinetic constants and other parameters[27–30] of aqueous solution polymerization of acrylic acid sodium salt are listed in Table I.

The model results

The kinetic model can be used to perceive polymerization behaviors that have been observed in the experimental section. This simplified kinetic model is able to investigate the behavior of free radical solution polymerization of a water soluble monomer such acrylic acid or acrylamide and predicts the effect of redox-pair type on the polymerization feature.

Figure 5 shows conversion vs. time for both redox-pair initiators at three concentrations 1, 2, and

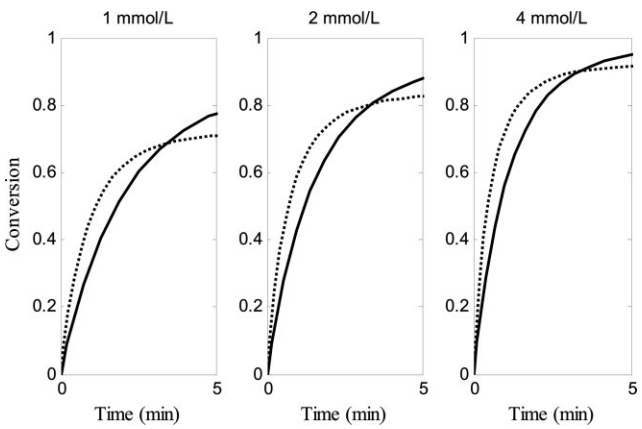


Figure 6 Conversion versus time for APS/SMBS (.....) and APS/TMEDA (—) initiation systems (of three different initiator concentrations) plotted for early minutes of the polymerization reaction (Modeling results obtained from computing by Matlab software).

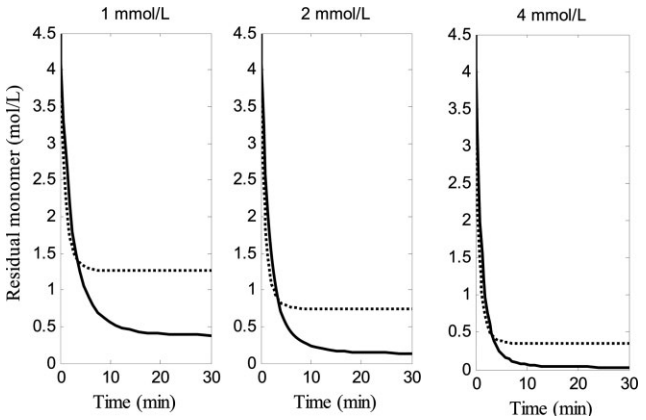


Figure 7 Residual monomer versus time for APS/SMBS (...) and APS/TMEDA (—) initiation systems of three different concentrations (Modeling results obtained from computing by Matlab software).

4 mmol/L under a fixed monomer concentration (4.29 mol/L). The slope of conversion curve was steeper for APS/SMBS comparing with that of APS/TMEDA system. This indicated that conversion was increased faster for this system in comparison with APS/TMEDA system. This result is evidenced obviously when diagram of conversion versus time of early minutes of the reaction is plotted (Fig. 6).

Conversion reached to a nearly constant value after a short time (less than 10 min) for APS/SMBS system. Rapid increase of temperature (see experimental part) observed after 5 min for this system is related to this part of the conversion plot. After this short time, conversion levels off at 70–90% depending upon the initiator concentration.

Conversion curve for APS/TMEDA comprises distinctive difference with APS/SMBS system so that the conversion increase for APS/TMEDA is slower than that for APS/SMBS system. In practice, it was observed in experimental section that the rapid temperature enhancement was not seen for APS/TMEDA initiation system. In contrast of APS/SMBS system, a mild and very slow temperature enhancement up to 5°C was observed for APS/TMEDA system. Here, a remarkable difference was observed in plateau region for these two systems. At an initiator concentration of 2 mmol/L, for example, theoretical conversion reaches to more than 97% which is significantly higher than 83% of APS/SMBS system. It was observed experimentally that APS/TMEDA was a superior initiating system rather than APS/SMBS (compare Fig. 1 and 3). This empirical observation, i.e. lesser content of the monomer remained after the polymerization using APS/TMEDA, is theoretically re-confirmed by the kinetics model, as illustrated in Figure 5 where the ultimate conversion is greater for APS/TMEDA system.

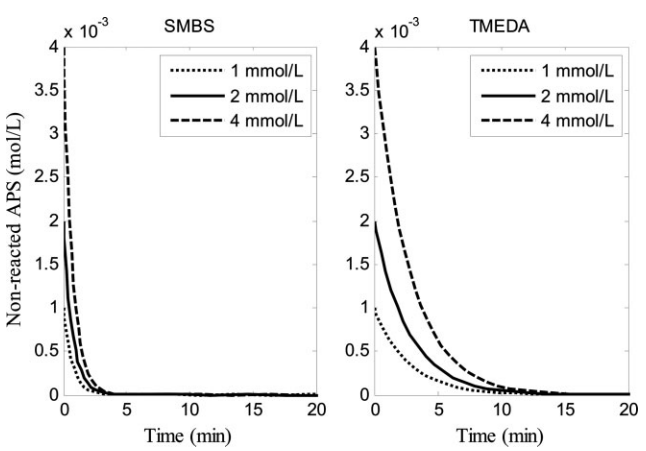


Figure 8 Non-reacted persulfate initiator (APS) versus time variations for APS/SMBS and APS/TMEDA initiation systems of three different concentrations (Modeling results obtained from computing by Matlab software).

TABLE I
Kinetic Constants for Aqueous Solution Polymerization of Acrylic Acid Sodium Salt, used for Computing by Matlab Software

Constant	Value	Reference
k_p	$7.9 \times 10^4 \frac{L}{\text{mol s}}$	23, 24
k_t	$6.6 \times 10^8 \frac{L}{\text{mol s}}$	23, 24
k_i for APS/SMBS pair	$1.4 \frac{L}{\text{mol min}}$	21
k_i for APS/TMEDA pair	$0.37 \frac{L}{\text{mol min}}$	21, 22
α	0.5	21, 22
β	0.5	21, 22

Figure 7 shows residual monomer versus time for the initiation systems. According to the model, the residual monomer level is lower for APS/TMEDA, particularly when higher concentration of initiator is employed. In conclusion, both the experimental (Figs. 1 and 3) and theoretical data (Figs. 6 and 7) verify that APS/TMEDA is a significantly superior initiation system rather than APS/SMBS for the SAP synthesis.

Figure 5 reveals that increase of initiator concentration caused increase of conversion. Equation (5) shows that propagation rate is directly proportional to quadratic root of concentration of the initiator components oxidizing and reducing agent. As a result, conversion was improved with concentration of the initiator enhancement in both systems. For thermal initiation of acrylic acid with sodium persulfate, a half power dependence of polymerization rate with initiator concentration has been reported.[30] It has been mentioned that the final conversion and polymerization rate were significantly improved by initiator concentration enhancement.[30]

In spite of the desirable influence of high-concentration initiator on the residual monomer decrease, the high initiator concentration possessed some distinctive disadvantages for SAP production. It results in increase of soluble content (i.e., slightly decreasing gel

content) which was shown in Figures 2 and 4. Another drawback is reduction of the swollen gel strength which is directly correlated with the value of the absorption under load, AUL.[31,32] We recently studied the effects of reaction variables such as redox-pair initiator, crosslinker, and porosity on the rheological characteristics such as storage modulus. It was found that increase of the initiator concentration led to loss of storage modulus or loss of AUL[32] which is taken as a serious deficiency for a SAP product.

Figure 6 shows conversion versus the initiator concentration at the in the early minutes of the polymerization. Monomer conversion was improved faster in the APS/SMBS system at first. Then, conversion of the APS/TMEDA system becomes higher with the time progression. The model-based curves suggest that APS/TMEDA is a preferred initiation system rather than APS/SMBS for the superabsorbent synthesis. As discussed earlier, these results logically explain the experimental data (Figs. 1 and 3).

Figure 7 shows the effect of initiator concentration on residual monomer content. It is obviously observed that the higher the initiator concentration the lower the residual monomer content will be. Higher initiator concentration decreases the residual monomer as it is experimentally observed in Figures 1 and 3. Free radicals are significantly increased at high concentration of the initiator; therefore the probability of free radical-monomer collision is increased. As a result, residual monomer is decreased with enhancing concentration of the initiating system.

According to Figure 7, APS/TMEDA initiation system had considerable advantage in comparison with APS/SMBS redox pair due to its lower residual monomer at every one of the concentration of the initiator systems. Therefore, APS/TMEDA initiation system was more efficient and proper for using in the superabsorbent production. Meanwhile, residual monomer difference was lower at higher concentrations.

To recognize behavior difference cause in the free radical polymerization by TMEDA and SMBS components, the rate of APS consumption by TMEDA and SMBS agents are illustrated in Figure 8. According to this figure, the rate of APS/SMBS consumption is excessively high; so that no APS initiator is remained after less than 5 min. It means that new free radicals cannot be generated for producing free radicals after 5 min. Therefore, non-reacted monomers can only be attached to the growing polymer chains. Furthermore, termination via recombination reaction causes diminished concentration of polymer radicals with the time progression. Consequently, in the case of APS/SMBS, chance of participation of non-reacted monomers in polymerization is exceedingly declined, i.e., the residual monomer is increased, which was previously shown experimentally in Figures 1, 3, and 7.

On the contrary, rate of APS consumption in the APS/TMEDA initiation system is significantly lower than that of APS/SMBS system (Fig. 8). This is related to a lower dissociation rate constant (k_i) of APS/TMEDA (Table I). As a result, relatively considerable non-reacted APS initiator is remained in the polymerization medium within the times longer than 5 min (whilst the APS/SMBS is dissociated very rapidly and its concentration enormously diminished after less than 5 min). In conclusion, decreasing initiator consumption rate is taken very important in the superabsorbent synthesis. New free radicals can be generated if the dissociation rate of initiation system is low. This causes an increased possibility of monomer consumption leading to the residual monomer reduction. In addition, residual initiator concentration was increased with the increasing the initial concentration of the initiator from 1 to 4 mmol/L (Fig. 8). As a result, more opportunity of generation of new free radicals during the longer times leads to a loss of residual monomer comparing to the APS/SMBS system (Figs. 1 and 3).

Finally, it should be pointed out that the polymerization reactions were conducted under practical and non-isothermal conditions. The kinetic model, however, was simply derived for an isothermal polymerization. Therefore, the experimental data were not logically possible to be fitted with the kinetic model. Nevertheless, as discussed above, the simple model provided an excellent means to account for the empirical observations via a theoretical approach.

CONCLUSIONS

Effect of two initiation systems on the swelling capacity, gel content and specially the residual monomer was investigated experimentally and theoretically. The main conclusions are summarized as follows.

Residual monomer is strongly related to dissociation rate of initiators. The slower the dissociation rate of initiator, the lower the residual monomer content will be. Therefore, APS/TMEDA was recognized to be a better initiating system rather than APS/SMBS systems for synthesis of SAP hydrogels. Thus, residual monomer could be reduced up to 5327 ± 138 and 1715 ± 44 ppm for APS/SMBS and APS/TMEDA initiating systems, respectively.

Increase of initiator concentration, [I], causes the residual monomer decrease. However, enhancement of [I] possesses some drawbacks in the SAP synthesis; i.e., the gel content and the swollen gel strength are decreased.

A simplified model was derived for explanation of the experimental data. The model revealed that conversion was increased faster for APS/SMBS system, but the final conversion of APS/TMEDA was higher

than that of APS/SMBS. On the other hand, lower rate of APS consumption (lower dissociation rate constant of the initiator) was recognized to be a key factor to increase monomer consumption leading to the residual monomer reduction.

APPENDIX: THE MAIN MATLAB PROGRAM FOR THE MODELING

```
clc
clear
disp('***main program1 for solution polymerization***');
disp('***Moment modeling- molecular weight measurement***');
% c,denotes concentration in continuous phase; d,denotes concentration in
% dispersed phase
%************************************
%Constants
global kp kt ki a b
Mm=72;  %molecular weight of monomer;
I1=1*10^-3;   % initial concentration of oxidizing agent;
I2=1*10^-3;   % initial concentration of reduction agent;
M0=4.5;   % initial concentration of monomer;
ki=0.37;    %initiation rate constant
kt=6.6*10^8 *60;  %/60;   % termination rate constant;
kp=7.9*10^4 *60;%/60;    % propagation rate constant;
a=0.5 ;
b=0.5;
tf= 30;%*60;   % final time;
xi= [M0,I1,I2];
[t,x]= ode23s ('deq', [0,tf],xi);
%**********************************
Mr=x(:,1)' ; %Monomer residue
I1r= x(:,2)'; %oxidizing agent
I2r=x(:,3)'; %reduction agent
P= ((M0-x(:,1))/M0)'; %monomer conversion
tt=t';
Xn1=  (kt*ki.*(x(:,2)).^a.*(x(:,3)).^b).^0.5./(kp.*x(:,1)) ;
Xn= 1/Xn1; %number average degree of polymerization

%*********************************
M- file for solving Differential equations
function dx= deq (t,x);
global kp kt ki a b
% x(1) monomer concentration;
% x(2) Oxidizing agent concentration;
% x(3) reducing agent concentration;

dx(1)= -kp.* x(1)*(ki/kt)^0.5* (x(2)^a *x(3)^b)^0.5;
dx(2)= -ki .* x(2)^a *x(3)^b;
dx(3)= -ki .* x(2)^a *x(3)^b;
dx=dx';
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