# Minimization of Residual Monomer Content of Superabsorbent Hydrogels via Alteration of Initiating System

**K. Kabiri,[1] S. Hesarian,[2] A. Jamshidi,[3] M. J. Zohuriaan-Mehr,[1] H. Boohendi,[1] M. R. Poorheravi,[2] S. A. Hashemi,[3] F. Ahmad-Khanbeigi[3]**

[1]*Department of Color, Resin, and Surface Coatings, Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14965-115, Tehran, Iran*
[2]*Department of Chemistry, Payam Nour University, P.O. Box 97, Abhar, Iran*
[3]*Department of Novel Drug Delivery Systems, Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14965-115, Tehran, Iran*

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**ABSTRACT:** Production of superabsorbent polymer hydrogels with minimized residual monomer content is an essential prerequisite particularly in their related hygienic, pharmaceutical, and food packaging products. Effect of two thermodissociating initiators and an innovative two-step initiation approach on the residual monomer content of acrylic acid-based SAP was preliminarily investigated. Ammonium persulfate (APS) and 4,4′-azobis(4-cyanopentanoic acid) (ACPA) were used as water-soluble initiators for the aqueous solution polymerization. FTIR spectroscopy was used for the structural characterization. It was found that APS was more effective than ACPA, and residual monomer was determined in the range of 2200–3000 and 8900–16,600 ppm for APS- and ACPA-initiated polymerization products, respectively. Residual monomer resulted from APS/tetramethyl ethylenediamine (TMEDA) initiation system was measured to be about 4500 ± 117 ppm for one step initiation. However, a two-step initiation strategy using the APS-TMEDA was exposed to be a very effective method to decrease residual monomer to 212 ± 6 ppm. The variation of the hydrogel properties (i.e., gel content, swelling capacity, and the residual monomer content) versus the initiator system and concentration was discussed based on the basic literature and supported by some rheological evidences obtained from rheoanalysis of water-swollen samples. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2716–2723, 2011

**Key words:** superabsorbent hydrogel; residual monomer; initiation; acrylic acid; polymerization; swelling

## INTRODUCTION

Lightly crosslinked networks with ability to absorb and retain large amounts of water and physiological solutions are known as superabsorbent polymer (SAP) hydrogels.[1] They are mainly used in hygienic products such as baby diapers and feminine napkins[1,2] so that the worldwide SAP production is exceeded than 1.5 million tones per year.[2,3] They are also employed in a wide range of various nonhygienic applications reviewed most recently by the author.[3]

Numerous papers have been published in field of basic research on SAP hydrogels in last two decades.[2–7] There are nearly 1200 nonpatent articles on superabsorbents published during years 1976–2009. However, except for a recent paper,[8] none of them investigated effect of fundamental parameters on the SAP residual monomer content as a key characteristic especially for those used in hygienic, medical, pharmaceutical, and food packaging applications.

The theme of residual monomer has merely been reported as several patents. For instance, Bailey and Marek[9] could achieve reduced residual monomer of acrylic acid (AA) from 2000 to 200 ppm by employing at least 0.5 mol % of either amino acid cyctein or lysine per mole of AA for at least 15 min at $> 80^{\circ}C$. The gel heating by microwaves or radiofrequency radiation in the absence of circulation air has been reported to be useful to achieve samples with 200–400 ppm of acrylic acid residual monomer.[10] Rebre et al.[11] invented a stepwise strategy via a suspension polymerization process for preparing SAP products with nonuniform morphology and less than 50 ppm of residual monomer. In another extensive work, effects of potassium bromate and potassium chlorate on reducing residual monomer content in the acrylic hydrogels were claimed without talking about the involved mechanisms.[12]

In a previous paper, we introduced a method for measurement of residual monomer in acrylic SAPs.[13] Initiation, as one of the basic influencing factors on residual monomer (RM), has also been focused.

*Correspondence to:* K. Kabiri (k.kabiri@ippi.ac.ir) or (kouroshkabiri@yahoo.com).

**TABLE I**
**Gelation Time Versus the Initiator Concentration, [I], for the Single-Step Crosslinking Polymerization of Partially Neutralized Acrylic Acid Initiated by APS and ACPA**

| | Gelation time recorded (s) | |
|---|---|---|
| [I] × 1000 (mol $L^{-1}$) | APS | ACPA |
| 5.4 | 135 | 180 |
| 8.2 | 115 | 150 |
| 10.9 | 90 | 100 |
| 16.4 | 80 | 87 |
| 21.9 | 70 | 75 |
| 27.4 | 60 | 60 |

Persulfate initiators are the most conventional initiators for synthesizing SAPs to initiate thermal or redox polymerization.[4,5,7,14] Redox pair initiating systems practically favor industrial polymerization processes because they often have no need of heating.[2,4,14] Pairs of ammonium persulfate (APS)/sodium metabisulfite (SMBS)[4,8,14] and APS/tetramethyl ethylenediamine (TMEDA)[1,8,15–17] are the most conventional initiating systems for the superabsorbent hydrogel synthesis. Thermally-induced single initiators such as APS,[18] potassium persulfate (KPS)[19] and 4,4′-azobis(4-cyanopentanoic acid) (ACPA)[20,21] have also been reported for the SAP synthesis.

We have started to investigate the effect of different parameters on the residual monomer content in recent years. In a previous article, the effect of redox initiating system type and initiator concentration on the residual monomer content was studied.[8] Thermodecompositing initiators are even more conventional than redox initiators for SAP synthesis.[22] Among them, persulfate and azo initiators are the most common initiators. APS is extensively used for thermal initiation of SAPs, superabsorbent composites, and superabsorbent nanocomposites.[22] Azo initiators such as azobis isobutyronitrile are mostly insoluble in aqueous systems. In contrary, ACPA is a kind of azo initiator with higher solubility in water-based polymerization systems often employed for the hydrogel synthesis. The present article deals with the effect of thermodecomposing initiator type and concentration on the gel content, swelling capacity, and residual monomer content of SAP hydrogels obtained from solution polymerization. A new approach (two-step initiation strategy) was also introduced preliminarily.

## EXPERIMENTAL

### Materials

Acrylic acid (AA, Fluka), sodium hydroxide (NaOH, Merck) ammonium persulfate (APS, Merck), polyethyleneglycol diacrylate (PEGDA MW 400, Rahn), 4,4′-azobis(4-cyanopentanoic acid) (ACPA, Merck) tetramethyl ethylenediamine (TMEDA, Merck) were of analytical grade.

### Synthesis of SAP hydrogels using single step initiation

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 PEGDA (0.04 g) was employed in all syntheses, while the initiator concentration was varied. Desired initiator dissolved in 2.0 mL distilled water was added to the reactor placed in a water bath at 60°C to start the exothermic reaction. Gelation was observed in less than 3 min for both initiating systems (Table I). The elastic gel product was removed from the reactor to cut into small pieces. It was dried in an air-drafted oven at 100°C for 6 h. The dried gel pieces were pulverized by a hammer-type minigrinder to sugar-like particles, and then screened (mesh size 35–100) and stored in a dry place.

### Synthesis of SAP hydrogels using two-step initiation

A similar mixture with the same amounts of the monomer and crosslinker was prepared according to the above foresaid procedure. Here, initiator was added at room temperature in two steps. At the first step, a fixed amount of initiator components (0.20 g APS and 0.10 g TMEDA dissolved in 2.0 mL $H_2O$) was added. The second step (i.e., the time of addition of the second part of initiator components) was practically of significant importance; so that it had not to be later than the gelation time. As the gelation point in our system occurred around 30 min, the second part of the initiator pair (0–0.50 g APS and 0–0.25 g TMEDA; dissolved in 2.0 mL $H_2O$) was added to the reactor at 25th min after the polymerization started by the first part addition of the same initiator pair. The rest of treatments on the elastic gel product were similar to the single step procedure.

### FTIR

FTIR spectrum of dried sample of poly(sodium acrylate-acrylic acid) SAP as KBr tablets were conducted by using EQUINOX 55 FT-IR spectrophotometer (Bruker, Germany).

### 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 a polyester gauze to remove the excess water. Then,

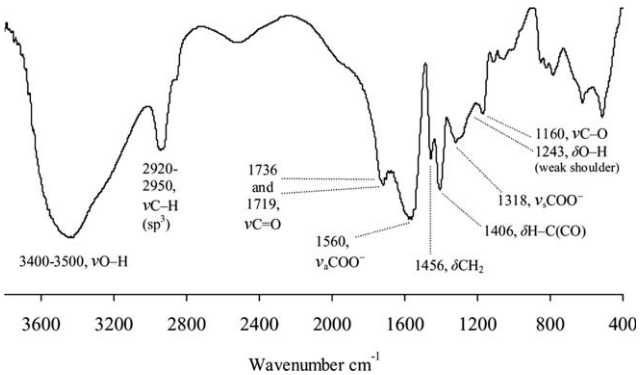



**Figure 1** Representative FTIR spectrum of a typical purified synthetic SAP sample.

the swollen gels were weighed. Swelling capacity (g $g^{-1}$) was calculated via dividing the weight of the swollen gel by the initial weight of dried sample.[2] The standard deviation for this method has been reported to be ±3.

### Residual monomer measurement

High performance liquid chromatography technique was used for quantifying residual monomer acrylic acid (AA) in the synthesized samples. Detailed procedure has been reported elsewhere.[13] As the extracting liquid and mobile phase was an aqueous orthophosphoric acid, the residual sodium acrylate salt was converted to the acid AA in this acidic medium. The standard deviation for this method has been reported to be ±2.6.[13]

### Rheological measurement

The rheological measurements of the water-swollen gels (0.50 g sample in 15.0 mL distilled water) were performed using a Paar-Physica oscillatory rheometer (MCR300, Germany) at 25°C with parallel plate geometry (plate diameter of 25 mm, gap of 3 mm). The detailed procedure was previously reported.[23]

### Gel content measurement

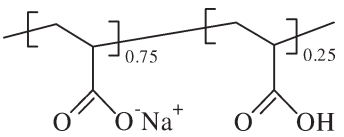
A 1.00 g SAP was poured in 600 mL distilled water and kept for 48 h to be fully swollen and extracted. The gel was filtered and placed in 100°C oven for 6 h to be dried. The gel content was calculated by eq. (1)[2].

$$\text{Gel content} = 100\ (\text{weight of sample after extraction}/\text{initial weight of sample}) \quad (1)$$

## RESULTS AND DISCUSSION

### Preparation and characterization

Two different water-soluble thermodissociating initiators (i.e., APS and ACPA) as well as the APS-TMEDA pair were employed in one- or two-step process for the hydrogel synthesis via aqueous solution polymerization. The general structure of the hygienic SAP is shown below. As the crosslinking degree is very lightly, the crosslinks are not exhibited in the structural formula.




It should be pointed out that the most conventional crosslinker *N,N′*-methylenebisacrylamide (MBA) was not preferred to be used for the crosslinking polymerization; instead, another water-soluble crosslinker, i.e., PEGDA, was used. MBA crosslinkages are recently established to be thermo hydrolytically cleaved upon heating in the oven-drying stage,[24] while PEGDA is a macromolecular bifunctional compound with more favorable characteristics including hydrolytic stability as well as rather nontoxicity and biocompatibility.

FTIR spectrum of a typical purified synthetic sample is representatively shown in Figure 1. The main peaks assigned in the figure are convincing evidences about the acrylic structure shown in the above formula. Because of very low concentration of the crosslinker, its infrared spectral bands cannot be observed in the spectrum.

The very wide intense band at 3400–3500 $cm^{-1}$ and an intense peak at 1710–1740 $cm^{-1}$, which corresponds respectively, to the O—H and C=O bond stretching vibrations proves preliminarily the presence of the carboxyl group. Because of the negative charge resonance in $COO^-$, the carbonyl bond requires lower energy to be vibrated in comparison with that of COOH. That is why the wavenumber 1719 $cm^{-1}$ is attributed to stretching of the anion carbonyl, while the closest peak at 1736 $cm^{-1}$ (partially overlapped by the earlier peak) is attributed to the acid carbonyl.[25] The latter is appeared as a shoulder with lower intensity, because the COOH : $COO^-$ ratio is 1 : 3.

Other characteristic peaks appeared at 1560 and 1318 $cm^{-1}$ are attributed to the asymmetric and symmetric stretching vibrations of the carboxylic acid sodium salt, respectively.[25,26] The C—O stretching coupled with the O—H in-plane bending of carboxyl groups is appeared at 1160 and 1243 $cm^{-1}$ (a weak shoulder).[26,27] A medium intensity doublet at 1456 and 1406 $cm^{-1}$ is assigned to bending vibrations of $CH_2$ and H—C(CO) groups, respectively.[26,27]

### APS initiation

Figure 2 shows residual monomer versus initiator concentration, [I], for thermal initiation using APS.

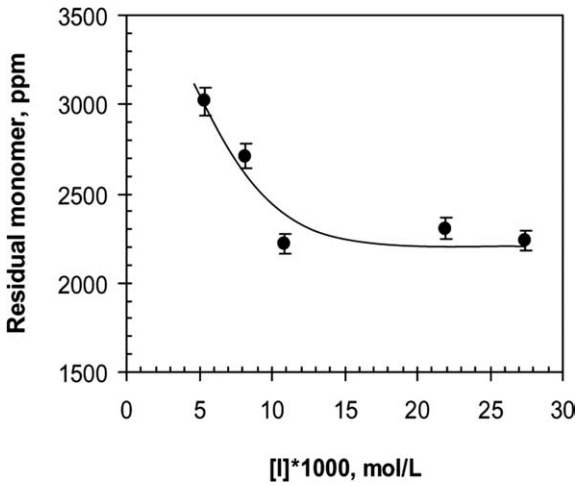



**Figure 2** Residual monomer dependency on the APS initiator concentration, [I].

Residual monomer was 3020 ± 78 ppm at [I] 5.4 × $10^{-3}$ mol $L^{-1}$. First, it had an abrupt descending trend with [I] enhancement up to 10.9 × $10^{-3}$ mol $L^{-1}$ in which the residual monomer was measured to be 2217 ± 57 ppm. It became nearly constant at higher amounts of [I]. Increase of [I] from 10.9 × $10^{-3}$ to 27.4 × $10^{-3}$ mol $L^{-1}$ had no considerable influence on the residual monomer content in this system, so that it was remained around 2200 ppm.

According to data obtained for thermal initiation using persulfates at neutralization degree 65%,[28] polymerization rate of poly(sodium acrylate) has shown direct relationship with a half power dependence on initiator concentration. Plateau region in Figure 2 can be attributed to gelation. Gelation time was observed in less than 3 min for this crosslinking polymerization initiated by APS (Table I). After the point of gelation, reaction mixture was converted from liquid phase to a rubber like semisolid state. At this point, polymerization had to be continued in the solid phase. As motion and diffusion of reactants is considerably restricted in the solid state rather than in liquid state, probability of collision of free radicals to nonreacted monomers is decreased. Higher [I] enhances free radicals leading to faster gelation (Table I); e.g., it was decreased from 135 to 60 s with increase of [I] from 5.4 × $10^{-3}$ to 21.9 × $10^{-3}$ mol $L^{-1}$. It is supposed these two factors (i.e., increased [I] and fast gelation) take action in opposition to each other to nearly level off the residual monomer content at high [I] as shown in Figure 2. If the gelation time was not varied with [I], the residual monomer would be decreased monotonically with [I] enhancement.

Figure 3 shows swelling capacity and gel content versus [I] for the APS initiating system. At the initiator concentration range used here (i.e., APS concentration of 0.005–0.027 mol $L^{-1}$), a decreasing trend in swelling capacity is observed. It may be attributed to chain transfer to polymer during the polymerization that favors some additional crosslink formation between the growing polymer chains. These additional crosslinks decrease swelling capacity at high [I].

The swelling capacity and gel content can be anticipated as a result of two initiator-related factors acting contradictorily. Increase of [I] can simultaneously result in (a) increase of short polymer chains and (b) chain transfer to polymer.[29,30] As more initiator molecules involve more monomers, we will encounter reduced residual monomer as we can see in Figure 2. However, the just initiated chains are not necessarily well-grown to produce long chains involved in the network as anticipated; therefore, lots of short chains have to be formed. Since a fixed amount of crosslinker has been used, based on the Flory hypothesis,[29] these limited crosslinker molecules cannot crosslink these numerous short chains; as a result, an imperfect network is formed. Imperfect network means a network with higher soluble fraction, i.e., lower gel content (Fig. 3). Such a network is expected to exhibit higher swelling capacity, because the imperfection favors the crosslink density reduction. However, a swelling reduction is obvious from the figure which is attributed to increased density of crosslinking as a result of the secondly mentioned factor (i.e., chain transfer to polymer). As far as related to crosslink density, since the factor (b) prevails over factor (a) at the initiator concentration range used in this work, a decreasing trend is observed for the swelling capacity versus [I]. A rheological evidence for increasing the crosslinking with enhancement of the APS initiator concentration is given later (see section Rheological study).

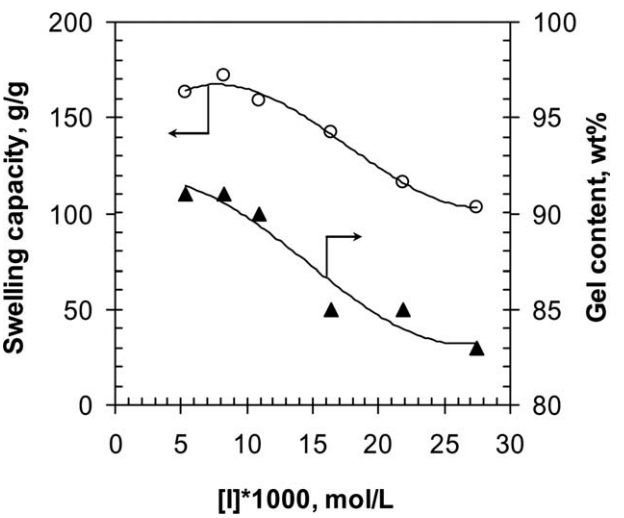



**Figure 3** Swelling capacity and gel content of acrylic SAP hydrogels obtained from the APS initiation system.

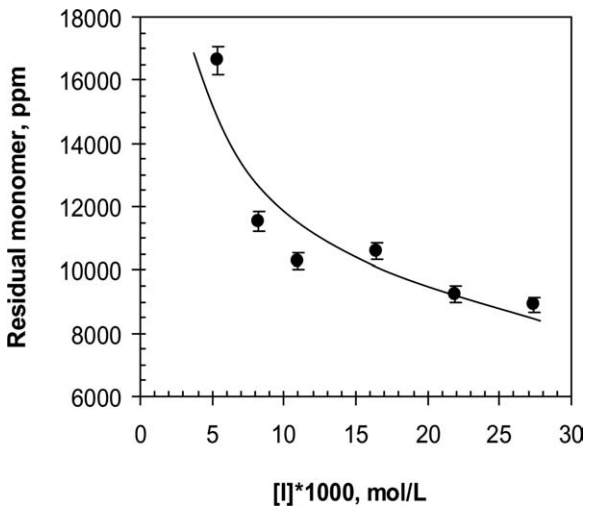
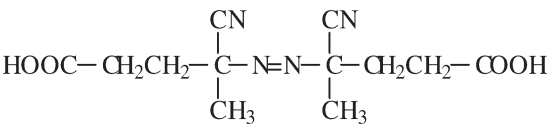


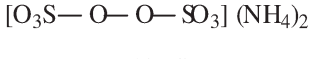

**Figure 4** Residual monomer dependency on the ACPA initiator concentration, [I].

### ACPA initiation

The compound **4**,4′-azobis(4-cyanopentanoic acid), ACPA, was employed to be compared with the persulfate initiator APS. It is soluble in the buffer-like moderately acidic polymerization medium, even though it structurally differs from APS.



(ACPA)



(APS)

Figure 4 shows residual monomer versus ACPA initiator concentration, [I]. High amounts of monomer were remained unreacted when initiator ACPA was employed (e.g., 16618 ± 432 ppm at [I] 5.4 × $10^{-3}$ mol $L^{-1}$). Although residual monomer was decreased with [I] enhancement; but its quantity was still very high (i.e., 8912 ± 231 ppm at 27.4 × $10^{-3}$ mol $L^{-1}$). These amounts were considerably higher than those of APS-initiated polymerization products (Fig. 2). Residual monomer the ACPA-initiated hydrogel products was ~ 4.4-fold greater than that of the APS-initiated counterparts. This definitely indicated that APS was a better thermal initiator for these SAP hydrogel production rather than ACPA. The difference of dissociation constant, $k_d$, of these initiators can be considered as a possible cause of the discrimination. The $k_d$ value for ACPA at 60°C in the aqueous solution has been reported to be about 0.9 × $10^{-5}$ $s^{-1}$ [30] which is lower than that of APS at similar conditions, i.e., ~ 1.2 × $10^{-5}$ $s^{-1}$.[31] In addition, value of the initiator efficiency factor ($f$) can be effective on the initiator action. In most solution polymerizations, $f$ is assumed to be constant throughout the process. However, it is known that, as the reaction medium becomes increasingly viscous, $f$ approaches a value of near zero.[32] As crosslinking is simultaneously occurred during polymerization, the free radical diffusivity might be exceedingly restricted particularly near and after gelation point. No $f$ value was found in the literature for the initiators used here. However, ACPA may be expected to produce large radicals with lower diffusivity, $C(CH_3)(CN)(CH_2CH_2COOH)$, partially due to their bulkier structure in comparison with the APS-originated radicals (i.e., $SO_4^-$, HO).

Figure 5 shows swelling capacity and gel content versus [I] for ACPA-initiated product. Swelling capacity had an ascending trend with [I] except at [I] of 27.4 × $10^{-3}$ mol $L^{-1}$. Swelling enhancement with increase [I] ranged ~ 4–20 × $10^{-3}$ mol $L^{-1}$ can be ascribed to loss crosslink density resulted from imperfect network formation discussed earlier in the previous section (see APS initiation). This reasoning was supported by rheological evidences (see Rheological study).

Gelation point was decreased with increase of [I] (Table I), i.e., it was decreased from 135 to 60 s with increase of [I] from 5.4 × $10^{-3}$ to 27.4 × $10^{-3}$ mol $L^{-1}$. According to Cutie et al.,[28] polymerization rate of acrylic acid was reported to be proportionally depended on $[monomer]^{3/2}$ and $[I]^{1/2}$. Therefore, at a fixed monomer concentration, higher [I] results in faster polymerization led to shorter time of gelation. Quicker gelation has negative effect respecting to the residual monomer content. According to our previous study, the higher the gelation time, the lower the residual monomer will be.[8] A phase conversion from liquid to solid is occurred at gelation point which

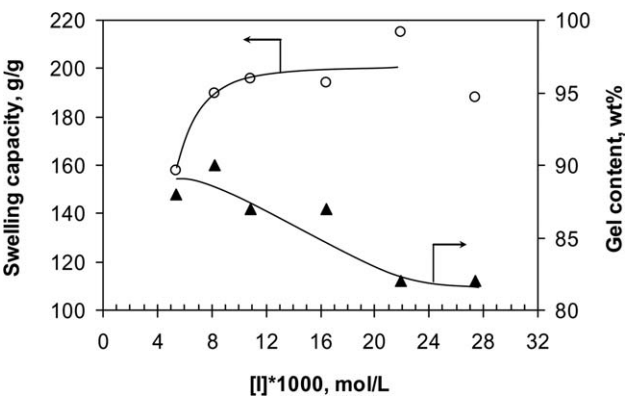



**Figure 5** Swelling capacity and gel content of acrylic SAP hydrogels obtained from the ACPA initiation system.

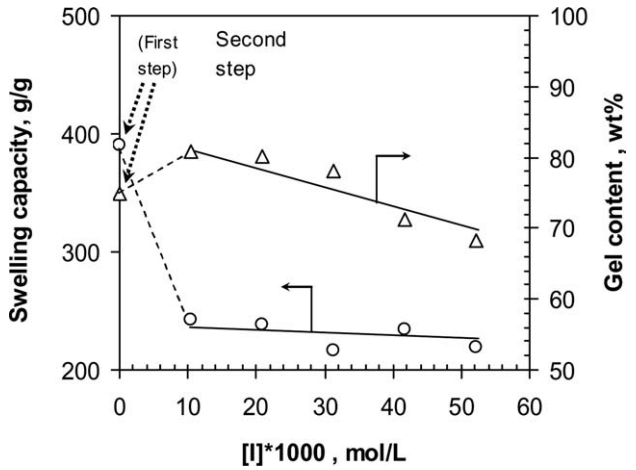



**Figure 6** Variation of the swelling capacity and gel content of acrylic SAP hydrogels versus [I] of the second step addition of the initiator (APS-TMEDA).

causes to decrease probability of collision of free radials to unreacted monomers due to lower diffusion in the semisolid (gelled) medium.[8]

### Two-step initiation by APS-TMEDA redox initiation system

Two-step initiation could not be conducted for APS or ACPA initiators because the corresponding gelation times were very small (Table I). The rapid gelation did not permit us to have sufficient time for the addition and efficient mixing of the second part of the initiator. Therefore, we had to choose a slower system with a longer time of gelation. That was why one of the conventional initiating pair systems, i.e., APS-TMEDA, was used for evaluating a new approach of decreasing residual monomer of SAP hydrogels. The gelation time at room temperature for this system was around 1800 s at $10.9 \times 10^{-3}$ mol $L^{-1}$.

Figure 6 shows swelling capacity and gel content versus [I] for the products prepared from the two-step initiated polymerizations. The initiator added in the second step was ranged 0–$52.2 \times 10^{-3}$ mol $L^{-1}$. Swelling capacity of the hydrogel form the single-step initiation is $\sim$ 400 g $g^{-1}$. It is decreased to $\sim$ 240 g $g^{-1}$ with addition of more initiator at the second step. The reason can be attributed to contribution of unreated crosslinker which is involved in polymerization after addition of further initiator. As a result, increase of crosslink density causes an enormous loss of swelling. However, more increase of [I] (>0.01 mol $L^{-1}$) of the second stage has not particular influence on the swelling capacity. This can be attributed to the formation of many short chains lead to imperfect network formation[29] (see section APS initiation). This increasing effect compensates the aforementioned decreasing effect of the addition of the further initiator at the second step. As an overall result, no significant change was observed in the swelling capacity versus secondly added [I] at higher than 0.01 mol $L^{-1}$.

Gel content is 75% for one step initiation which is increased to $\sim$ 82% with increase of [I] in the second stage up to around $30 \times 10^{-3}$ mol $L^{-1}$. It can be attributed to slightly increased crosslink density through attaching linear chains to the network. Inversely, gel content was decreased after [I] of 30 m*M*. The reason is similar to what discussed previously for the APS initiation (Fig. 3). This interpretation will also be evidenced by some rheological proofs (see Rheological study).

Figure 7 shows residual monomer versus [I] of the second stage. Residual monomer was 4481 $\pm$ 116 ppm for the one-step initiation by APS-TMEDA ([I] $31.26 \times 10^{-3}$ mol $L^{-1}$). Addition of additional initiator at the second step has significant influence on the residual monomer reduction. Residual monomer was diminished to 1755 $\pm$ 46 ppm using $20 \times 10^{-3}$ mol $L^{-1}$ initiator at the second step. Increase of [I], from the single-step to the two-step method of initiation, causes an abrupt loss of residual monomer, but it shows a low-slope decreasing trend with [I] enhancement in the second step [Fig. 7(a)]. It finally reached to 937 $\pm$ 24 ppm at $52 \times 10^{-3}$ mol $L^{-1}$.

Figure 7(b) proves that by the one-step initiation with higher initiator concentration, e.g., $41.77 \times 10^{-3}$ mol $L^{-1}$, the residual monomer is even additionally decreased to around 600 ppm. At the second step, it is diminished to 212 $\pm$ 6 ppm using the initiator concentration of $52.1 \times 10^{-3}$ mol $L^{-1}$. The comparison of the Figure 7(a,b) verifies that the higher the

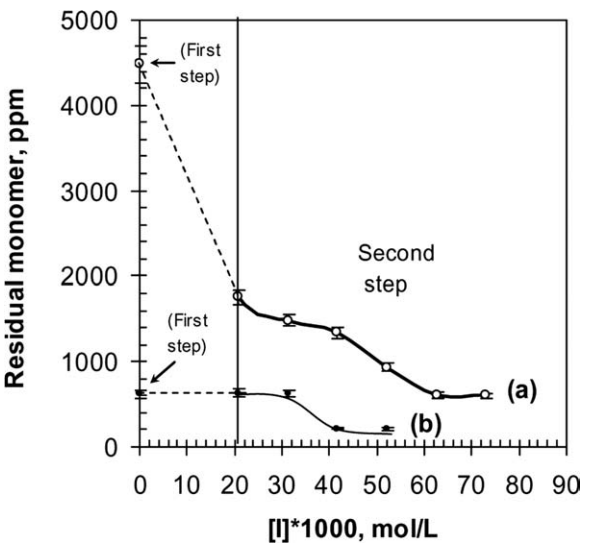



**Figure 7** Residual monomer dependency on [I] of the second step addition of the initiator pair APS-TMEDA. (a) The [I] of the first step is $31.2 \times 10^{-3}$ mol $L^{-1}$. (b) The [I] of the first step is $41.7 \times 10^{-3}$ mol $L^{-1}$.

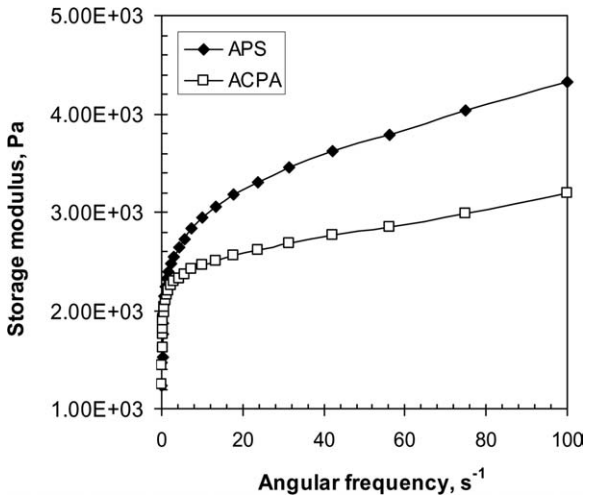



**Figure 8** Swollen gel modulus versus angular frequency for samples prepared from APS- and ACPA initiated polymerizations. The initiator concentration for both sample preparation was $27.4 \times 10^{-3}$ mol $L^{-1}$.

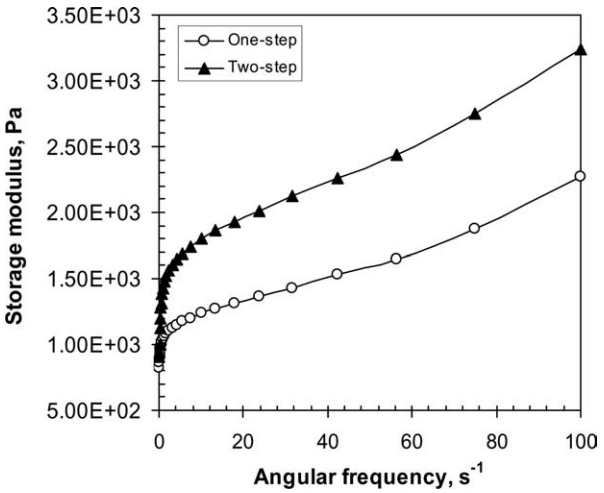



**Figure 9** Swollen gel modulus versus angular frequency for samples from one-step and two-step initiated polymerizations. The latter was prepared by the initiator pair APS-TMEDA with concentration of $5.2 \times 10^{-3}$ mol $L^{-1}$ used in the second step.

[I] at the first step, the lower the residual monomer at the second step will be.

These results show that the idea of adding initiator in two steps is considerably successful. As mentioned before, this procedure can be only carried out for the systems having extended gelation time (longer than 20 min). If gelation time occurs too rapidly, then the second part of initiators cannot be completely dispersed in the reaction mixture. Here, the thermal initiator systems of ACPA and APS with gelation time of <3 min are not suitable for being used in this two-step strategy.

## Rheological study

We have shown that the swollen gel strength, one of three main practical features of SAPs with irregular shaped sugar-like particles, can be measured rheometrically[23] and correlated with the absorbency under load.[33] In addition, the gel strength may also be taken as a SAP characteristic parameter being affected strongly by the basic structural parameters.[18,24,33]

Rheological studies were carried out to follow gel strength of typical hydrogels swollen previously in water.[23] The storage modulus may be taken as a measure of the mechanical strength of the hydrogel. Figure 8 shows storage modulus versus angular frequency for APS- and ACPA-initiated polymerization products.

Storage modulus is obviously higher for APS-initiated sample. It should be remembered that APS-initiated sample has lower residual monomer in comparison with ACPA-initiated sample. In other word, increased residual monomer is somehow related to decreased storage modulus. As the modulus is proportionally affected by crosslink density,[32] most probably, some unreacted crosslinker is increased together with increase of the residual monomer. This causes a decreased crosslink density (ρ) which has direct relationship with storage modulus, $G$ [eq. (2)].[33]

$$G = \rho RT \tag{2}$$

As mentioned in previous sections, according to Flory,[29] it can be concluded that higher residual monomer for the ACPA-initiated samples in comparison with their APS-counterparts (as can be seen from Figs. 2 and 4) is followed by creation of imperfect network possessing lower mechanical stability. It proves that the initiator type has a definite influence on the mechanical properties of the SAP hydrogel products.

Table II shows storage modulus for the hydrogel samples prepared from polymerizations using APS initiator systems with two different concentrations. Storage modulus is increased with increase of [I], i.e., it is 3510 and 3620 Pa at [I] $5.4 \times 10^{-3}$ and $21.9 \times 10^{-3}$ mol $L^{-1}$, respectively. The results indicate that crosslink density is increased with [I] enhancement. These results prove increase of crosslinking with [I] enhancement for the APS initiator system.

**TABLE II**
**Storage Modulus for the SAP Hydrogel Samples Prepared from Polymerization Reactions s Using APS Initiator with Two Different Concentrations**

| | Storage modulus (Pa) of sample from polymerizations using [I] of | |
|---|---|---|
| Angular frequency ($s^{-1}$) | 5.4 mmol $L^{-1}$ | 21.9 mmol $L^{-1}$ |
| 17.8 | 3060 | 3180 |
| 23.7 | 3170 | 3310 |
| 31.6 | 3310 | 3460 |
| 42.2 | 3510 | 3620 |

Figure 9 comparatively shows storage modulus versus angular frequency for samples obtained from the single- and two-step initiation systems. The two-step initiation approach has inevitably great increasing influence on the swollen gel modulus. This is actually a rheological evidence for the reasoning previously offered for the positive effect of the two-step strategy on decreasing the residual monomer content (Fig. 7) and the swelling capacity (Fig. 6). In fact, unreacted crosslinkers participates in the polymer network just after addition of further initiator in the second step. As a result, a crosslink density enhancement led to increased storage modulus [eq. (2)]. This observation is in agreement with the swelling capacity changes when the two-step initiation polymerization is conducted (Fig. 6).

## CONCLUSIONS

In this work, effect of initiation systems on the swelling capacity, gel content as well as the residual monomer content of acrylic SAP hydrogel products was preliminarily investigated. The main conclusions may be summarized as follows.

APS-initiated polymerization products had considerably lower residual monomer content and higher storage modulus in comparison with the ACPA-initiated counterparts. Therefore, initiation with APS was recognized to be more efficient than that of ACPA.

A two-step initiation approach was introduced for lowering the residual monomer in acrylic SAP hydrogels. It was exhibited to be considerably efficient in comparison with the conventional single-step initiating process. In a practical viewpoint, this procedure can only be employed in relatively slow systems in which the polymerization takes sufficient time to arrive gelation (e.g., $>$30 min).

APS/TEMDA initiating system has an advantage in comparison with the APS-initiated polymerization. Because of its longer gelation time, the two-step strategy can practically be applied using APS/TEMDA initiator pair. Therefore, SAPs with lower residual monomer content (about 210 ppm) can be achieved by this initiation system, whereas the minimum residual monomer from the APS-initiated polymerization was found to be around 2200 ppm.

Concerning the minimization of residual monomer, the aforementioned beneficial of the two-step initiation is expected to be even more developed by employing a multi-step initiation, and preferably, a continuous incorporation of the initiator into the polymerization system. However, it should be pointed out that the soluble fraction will simultaneously be increased in lieu of increased initiator concentration (decreased gel content). Therefore, it would be necessary to balance all the essential parameters affecting the swelling capacity, gel content and residual monomer. For example, the upper crosslinker dose will compensate the loss of gel content, at the expense of a swelling capacity decrease. Consequently, the polymerization variables such as the type and the system of initiation, the initiator concentration, the crosslinker type and concentration, the monomer concentration, etc. will be significant factors for optimization of the SAP production processes.

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