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Degradation on polyacrylamides. Part II. Polyacrylamide gels

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Abstract

The stability of polyacrylamide (PAAm) gels, synthesized by free radical polymerization of acrylamide (AAm) and *N*,*N*′-methylenebisacrylamide (BIS), was investigated when subjected to thermal and irradiation conditions. The PAAm gels were stable and did not release AAm under fluorescent light. In aqueous solution at 95 °C, a small amount of AAm was observed and it is shown that this is found from the pendant unsaturation of BIS in the gel network. Under UV irradiation, approximately one molecule of AAm is released for every 20,000 repeat monomer units in the gel. Gels were also synthesized from methacrylamide with BIS, AAm with *N*,*N*′-methylenebismethacrylamide and AAm with bisacryloyl-piperazine. Their stability is compared to the AAm/BIS gels.

Keywords: Polyacrylamide gel; Thermal degradation; UV irradiation

1. Introduction

Polyacrylamide (PAAm) gel networks are formed in an aqueous medium and are widely used in electrophoresis [1] for protein separations or as membranes [2] for protein isolations or blood purifications. Because these hydrogels are used in some applications where human contact is involved, the products are required to be either non-toxic and/or biocompatible. Although acrylamide (AAm) monomer has been shown to be toxic, it is generally agreed that PAAm is not [3]. Consequently, purification of PAAm gels by removing residual monomers and then keeping the gels in a stable form becomes an important issue. In part I [4] of this series, we have described the purification of linear PAAms and their stability behaviour under hot aqueous and irradiation conditions. It was found that the carbon backbone of linear PAAm is stable when heated to 95 °C or exposed to fluorescent light although it dose liberate a small amount of AAm under UV irradiation.

In PAAm network formation, the polymer is covalently cross-linked by at least one vinyl type cross-linker with the AAm monomer. There have not been any previous studies on the degradation behaviour of these cross-linked gels. In this paper, the purification of PAAm gels is investigated and their behaviour under hot aqueous (thermal) and irradiation conditions is described.

2. Experimental and results

2.1. Materials

Electrophoresis-grade (>98%) AAm and methacrylamide (mAAm) were purchased from ICN Biomedicals Inc. and Aldrich Chemical Co. Cross-linkers, *N*,*N*′-methylenebisacrylamide (BIS) and *N*,*N*′-methylenebismethacrylamide (mBIS), were purchased from BDH Laboratory Supplies and Polyscience Inc., respectively. Bisacryloyl-piperazine (PIP) was obtained from Lancaster Synthesis. Ammonium persulfate (APS, >98.8) was obtained from Sigma Chemical Co., H_2O_2 (AR grade, 30% w/v) from AJAX Chemicals, and *N*,*N*,*N*′,*N*′-tetramethylethylene-diamine (TEMED, >99.5%) was from Aldrich. Bromine (AR grade) was obtained from FSE Pty. Ltd., and sodium thiosulphate (>99.5%) was purchased from AJAX Chemicals. Phenol red solution was from Merck Pty. Ltd.

Saturated bromine water was made by shaking Milli-Q water with bromine and then standing the mixture overnight at 4 °C. The aqueous phase was used.

Sodium thiosulphate was used as 1 M solution.

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2.2. Glassware

All glassware was washed with tap water, rinsed with distilled water, and then heated in an oven at 450 °C overnight to remove any organic residues.

2.3. Polymerization methods

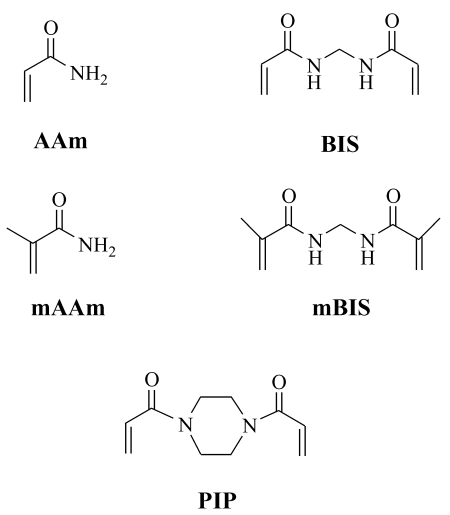
2.3.1. APS/TEMED redox initiated polymerization

AAm/BIS and AAm/PIP gels were obtained by redox initiated polymerization. Monomer solutions (20 %T/5 %C) were prepared in distilled water, where %T (w/w) refers to the concentration of total monomer in the solution and %C (w/w) refers to the concentration of cross-linking monomer in total monomers. The monomer solutions were purged with high purity argon until the content of oxygen was below 1%. The initiators, APS and TEMED in their 10% (w/w) solutions (2 and 1% (w/w) in total monomers, respectively), were then added into the monomer solution. Polymerization was allowed to proceed overnight at room temperature.

2.3.2. APS thermally-initiated polymerization

The compositions of monomers, initiators and cross-linkers for all the gels of AAm/BIS, mAAm/BIS, and AAm/mBIS (see Scheme 1) with thermally initiated polymerization using APS are shown in Table 1.

Monomers, cross-linkers and initiators were initially dissolved in distilled water in a 100 ml round bottom flask. The freeze-thaw degassing technique was used to remove oxygen in the solution. Then the flask containing the monomer mixture was immersed in an oil bath at 60 °C overnight to allow the polymerization to take place. The flask remained sealed throughout the entire process of polymerization.



Scheme 1. Molecular structure of monomers and cross-linkers.

2.4. Purification methods for polyacrylamide gels

It is important to ensure that all the gels have no detectable AAm in the gel suspension before degradation studies. Therefore, we initially investigated methods to purify the PAAm gels.

2.4.1. Washing

Once the polymerization was finished, the gel was collected and ground. The ground gel was then washed by rinsing with distilled water through a glass-sintered filter (size no. 3). Since AAm is highly soluble in water and gel is insoluble, rinsing with water allows selective removal of AAm from the gel. After physical washing with water (at least 10 times) the gel was then washed using methanol (twice) to replace the water in the gel network, and then dried in vacuo below 50 °C overnight.

2.4.2. Bromination

A further purification procedure was performed in order to remove trace amount of residual AAm in gels. In this method, bromine (Br_2) was used to react with the double bond of residual AAm. It also reacted with the pendant double bonds from the cross-linkers in the network.

The previously washed and dried gel (2 g) was soaked in Milli-Q water (100 ml) and stirred. The saturated bromine water was then added to the solution until it became brown indicating the presence of excess bromine. The solution was allowed to stand for a few minutes. The solution turned from brownish to colorless, indicating that all bromine had been reacted. More bromine water was then added. This step was repeated until there was no color change in the solution. Normally, a total reaction time of at least overnight was needed for this bromination. Excess bromine was then removed by a few drops of $Na_2S_2O_3$ solution (1 M). The gel was then washed again with distilled water for 15 times and finally rinsed with methanol twice.

With an AAm/BIS gel, repeated cold water washing could remove monomer residues to a level, where AAm was undetectable. However, it was found that if the gel was washed by hot water (85 °C), AAm kept leaching out. This will be discussed later.

2.5. Acrylamide detection (HPLC method)

Acrylamide was detected by HPLC with UV detector at $\lambda = 196$ nm. Sample solution (50 μl) was injected and delivered through a 3×4 mm reverse-phase 5 μm C18 guard column and a reverse-phase 5 μm Aqua column (C18125A, Phenomenex) with size of 250×4.6 mm. Filtered Milli-Q water was used as mobile phase and all HPLC samples were made up in water solution (1% (w/w)) using the same filtered Milli-Q water. The minimum sensitivity of detectable AAm level on an Aqua column was determined to be 1 part per billion (ppb).

Table 1
Compositions of monomers, cross-linkers and initiators

Gel	Total monomers (% (w/w) of total solution)	Cross-linkers (% (w/w) of total monomers)	Initiator (% (w/w) of total monomers)
AAm/BIS	20	5	2
AAm/BIS	20	10	2
mAAm/BIS	15[a]	5	2
AAm/mBIS	20	5	2

[a] 20 %T of mAAm/BIS was not soluble.

2.6. Degradation methods

2.6.1. Thermal degradation at 95 °C

Gel/water mixtures (10 ml, 1% (w/w)) were prepared using filtered Milli-Q water. Duplicates were made for each gel. No AAm was present in the solutions as measured by HPLC.

Thermal degradation of gel mixtures was carried out in an oven at 95 °C. Each 10 ml volumetric flask was covered with a glass vial to minimize water vapour escaping during heating at 95 °C. When necessary, water was added at regular intervals to prevent the gels from drying out.

Before taking samples, water was added to each volumetric flask to ensure a total solution volume of 10 ml, and then the mixture was mixed and allowed to stand for at least 4 h. This was intended to allow all the gel to settle to the bottom of the flask so that samples taken from the top did not contain any fine gel particles. The amount of sample taken was approximately 0.5 ml.

2.6.1.1. AAm/BIS gel. Thermal degradation was performed on AAm/BIS gels. These gels were either washed without treatment with bromine (non-brominated), or washed and treated with bromine for 1 h (1 h brominated) or overnight (overnight-brominated). The AAm/BIS gels were prepared using APS and APS/TEMED as initiators and the polymerization was carried out at 60 °C and room temperature, respectively. The number of AAm molecules released per 10^6 polymer repeat units in the gel from these samples was plotted against degradation time (Figs. 1 and 2).

2.6.1.2. AAm/mBIS gel and AAm/PIP gel. PAAm gels cross-linked with either mBIS or PIP were synthesized and were subject to similar thermal degradation.

For the AAm/mBIS gel, no AAm or mAAm was detected in the degradation solution after 7 days. A separate experiment on the degradation of a 10 ppm mBIS solution under the same conditions showed the release of mAAm. Similarly, the brominated AAm/mBis gels did not liberate AAm or mAAm.

For the AAm/PIP gel, no AAm or acrylic acid (an expected hydrolysis product) was observed from the degradation solution. A separate experiment on the degradation of 10 ppm PIP solution under the same conditions showed PIP was stable and did not release any acrylic acid. This may be because, the cyclic diamide ring is more stable and does not hydrolyze easily under the degradation conditions of this study. In this respect, the PIP amide can be regarded as a tertiary amide and these are known to be more stable hydrolytically than secondary or primary amides.

2.6.1.3. mAAm/BIS gel. The formation of AAm (in ppm of polymer repeat units) with degradation time for mAAm/BIS gel is shown in Fig. 3. Similar to AAm/BIS gel, the thermal degradation on mAAm/BIS gel resulted in the formation of AAm. Additionally, brominated mAAm/BIS gel gave less AAm compared to the non-brominated gel.

The amount of AAm formed during thermal degradation

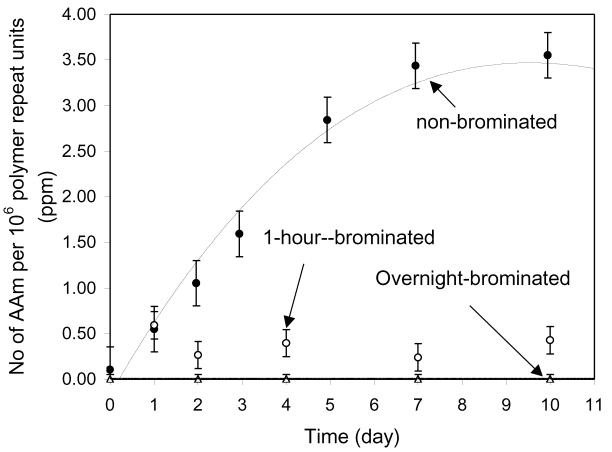


Fig. 1. AAm released from an AAm/BIS gel (redox initiation) under thermal degradation at 95 °C.

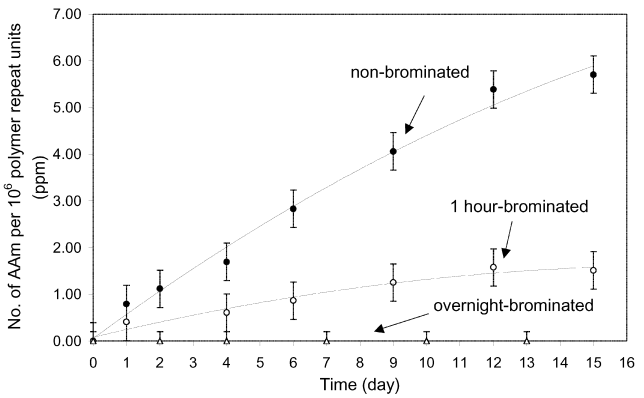


Fig. 2. AAm released from an AAm/BIS gel (APS initiation at 60 °C) under thermal degradation at 95 °C.

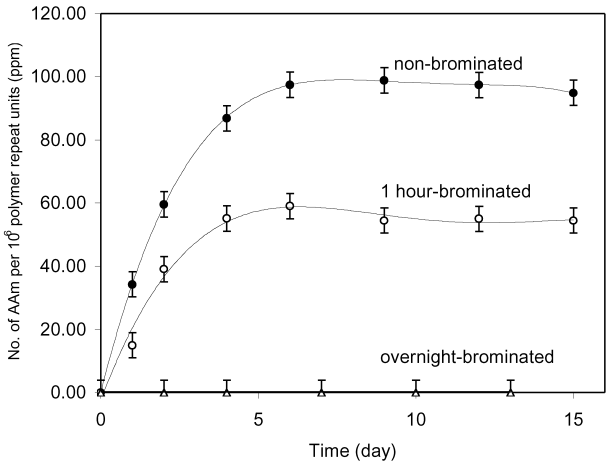


Fig. 3. AAm released from mAAm/BIS gel (APS initiation) under thermal degradation at 95 °C.

of a mAAm/BIS gel was approximately 10 times greater (Fig. 5) than the amount of AAm formed from an AAm/BIS gel. This indicates there are many more pendant double bonds in the mAAm/BIS gel.

2.6.1.4. Determination of hydrolysis content of gels after hot aqueous treatment at 95 °C. The hydrolysis content of PAAm gels from thermal degradation was determined by titration. First, the gel suspension was acidified by adding a small amount of HCl solution (2.5 M) and the pH value of the solution was adjusted to be around 2. The gel was then filtered, rinsed with distilled water (10 ×) and methanol (2 ×), and then dried in vacuo overnight before titration. Gel suspension (1% (w/w), 8–10 ml) was then made up in water and NaOH solution (0.0100 ± 0.0006 M) used to titrate the acid content of the gel. Phenol red indicator was used to show the end point (pH = 7.9). From the volume of NaOH solution at the end point, the amount of acid groups formed by hydrolysis of amide groups in the polymer chain was calculated. These results are shown in Table 2.

2.6.2. UV degradation when irradiated at 254 nm

Gel/water mixtures (10 ml, 1% (w/w)) were prepared in 28 ml sample vials (75 × 25 mm), covered with plastic film, which allows UV light to go through the gel solutions and minimize water loss. Filtered Milli-Q water was used to make up the solution. Similar to the thermal degradation experiments, samples were taken from each gel before degradation to ensure that no AAm was present in the solutions.

Sample vials containing gel mixtures were placed in a black box, where the UV irradiation (wavelength of 254 nm) was from the top of the box. Samples (about 0.5 ml) were taken, and 50 μl was injected directly into the HPLC column to determine the AAm level of the solution. The same amount of Milli-Q water was added back to the solution after sampling in order to keep the volume constant.

PAAm gels were made with different monomer and cross-linker compositions using different initiation methods. These gels were non-brominated, brominated for one hour or brominated overnight.

Using gels thermally initiated with APS at 60 °C a comparison of the gel degradation behavior with different monomer and cross-linker compositions was studied. The effect of initiation methods for polymerization was also investigated with the AAm/BIS gels.

2.6.2.1. Effect of monomer/cross-linker compositions. After an AAm/BIS gel was purified by washing, a 1% (w/w) gel suspension was subject to UV irradiation at $\lambda = 254$ nm. AAm monomer was released to the solution. The amount of AAm increased with the time of irradiation before leveling out at about 4 ppm polymer repeat units after 15 days (Fig. 4).

When partially brominated AAm/BIS gel was irradiated under the same conditions, an increased amount of the AAm monomer was observed. A completely brominated gel gave much more AAm in the solution. The maximum amount of AAm in the solution after 15 days was approximately 50 ppm polymer repeat units.

When an AAm/mBIS gel, thermally-initiated by APS, was used under the same irradiation condition, similar AAm release was observed. As shown in Fig. 5, we also observed the increase of AAm when the gel was brominated.

In contrast to the previous two cases, although the 1 h brominated mAAm/BIS gel showed an increase in AAm release, an overnight-brominated gel caused reduction of the AAm release from the polymer (Fig. 6).

In Fig. 7, it is shown that AAm/PIP gel initiated by TEMED/APS redox system also gives AAm under UV degradation. The non-brominated AAm/PIP gel gave much higher levels of AAm than the AAm/mBIS or AAm/BIS gels.

2.6.2.2. Effect of initiation methods. An AAm/BIS gel was also polymerized by using an APS/TEMED redox initiation

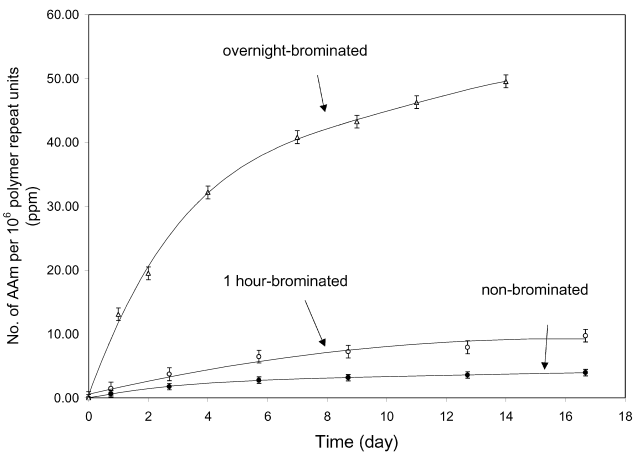


Fig. 4. AAm released from an AAm/BIS gel (initiated by a thermal method with APS at 60 °C) under UV irradiation at 254 nm.

Table 2
Hydrolysis content of various gels (acid%)

Gel	Initiators	Composition	Days of heating	Acid readings
AAm/BIS	APS	20T/5C	0	0.00
			2	1.69
			5	3.62
AAm/BIS	APS/TEMED	20T/5C	0	0.00
			2	1.45
			5	2.62
AAm/BIS	APS	20T/10C	0	0.00
			2	1.18
			5	2.14
			15	6.76
AAm/PIP	APS/TEMED	20T/5C	0	0.00
			2	1.21
			5	2.14
AAm/mBIS	APS	20T/5C	0	0.00
			2	2.87
			5	4.56
mAAm/BIS	APS	15T/5C	0	0.00
			2	0.59
			5	0.65
Linear PAAm [4]	APS	5T/0C	0	0.10
			2	2.25
			5	5.80

system at room temperature. The resultant gels, both non-brominated and overnight-brominated, were irradiated at 254 nm. The comparisons of these gels' degradation behavior to the one initiated by APS only are shown in Fig. 8.

The overnight-brominated gel released more AAm than the non-brominated gel, which is similar to the results for APS initiated gels observed previously. On the other hand, gel made by APS only gave much more AAm than the gel made by a redox method. This difference is particularly enhanced when these gels are brominated.

2.6.3. Stability under fluorescent light

Gel/water mixtures (10 ml, 1% (w/w)) in 28 ml sample vials (75 × 25 mm), covered with plastic film, were subject to continuous irradiation of fluorescent light at 30 cm. Samples (about 0.5 ml solution) were taken and 50 μl injected directly into the HPLC to determine the AAm level of the solution. No AAm was detected in a period of 15 days. Similar results were observed for a range of monomer/cross-linker compositions such as AAm/BIS, AAm/mBIS, AAm/PIP or mAAm/BIS gels.

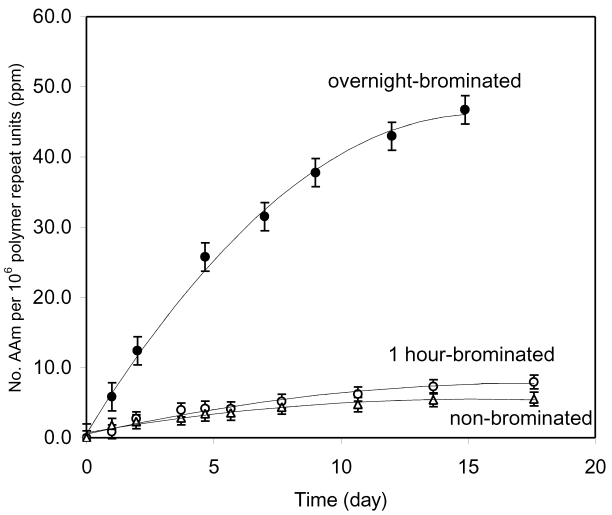


Fig. 5. AAm released from an AAm/mBIS gel (initiated by a thermal method with APS at 60 °C) under UV irradiation at 254 nm.

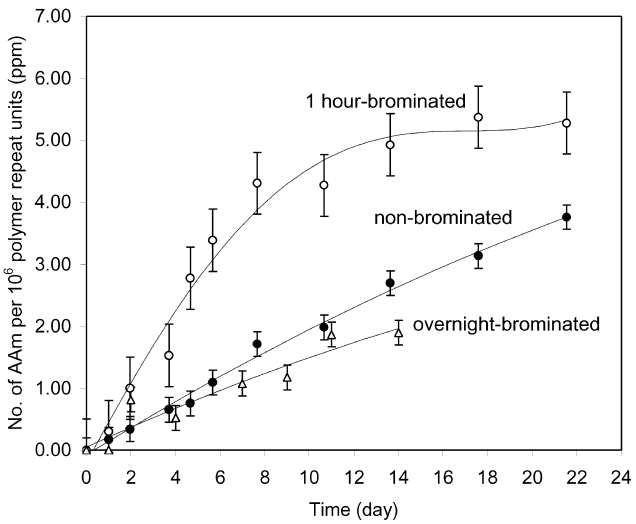


Fig. 6. AAm released from a mAAm/BIS gel (initiated by a thermal method with APS at 60 °C) under UV irradiation at 254 nm.

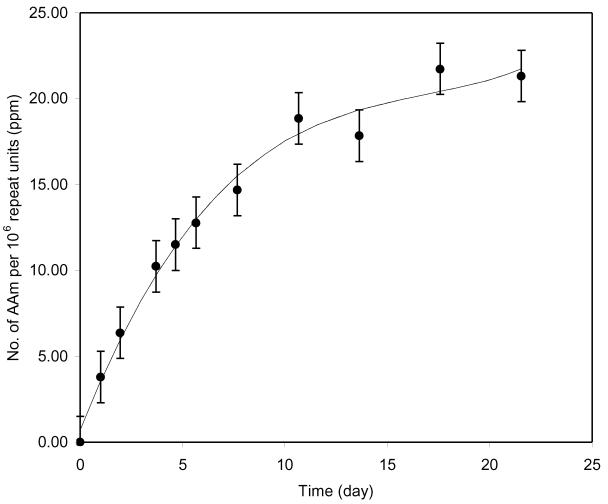


Fig. 7. AAm released from a non-brominated AAm/PIP gel (initiated by a redox method with TEMET/APS at room temperature) under UV irradiation at 254 nm.

3. Discussion

3.1. Purification of gels

The need for careful purification of linear PAAm has been discussed in Part I of this series and a similar situation applies with the gel structures. However, there are distinct and vitally important differences between purifying the soluble linear polymers and the hydrogel networks.

Thus, whilst it was difficult to remove AAm from linear PAAm by precipitation, the insoluble nature of the gels made for easy removal of AAm by simple cold water washing procedures.

The use of a hot water (85 °C) wash, designed to speed-up the washing process, gave an unexpected but nevertheless, very important result; AAm monomer was released from the hydrogel. We will show in the following discussion that this AAm comes from BIS residues in which only one double bond has been incorporated into the network. In other words, there are pendant structures which are the precursors for the release of AAm.

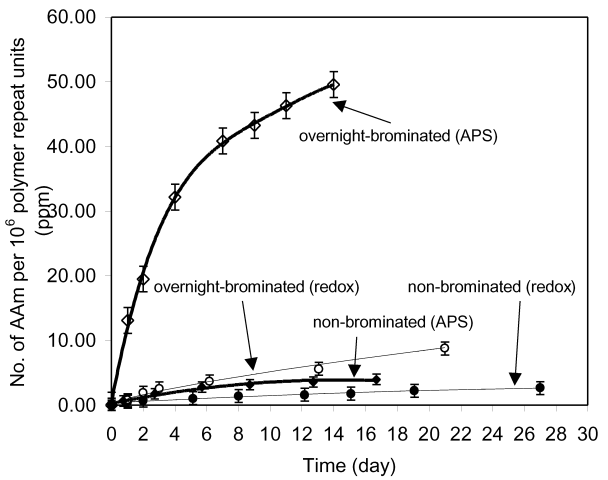


Fig. 8. AAm released from AAm/BIS gels, initiated by a thermal APS and redox APS, under UV irradiation at 254 nm.

As with the linear PAAm, purification with a chemical scavenger, bromine, is also possible. But, with the gels there is an added complication that the pendant unsaturation can also be brominated. And unlike the brominated AAm, which can be removed by washing, the brominated BIS units remain in the gel structure.

Because chemical scavenging is recommended for the commercial purification of PAAm, we have compared systems in which removal of AAm has been by simple washing or by washing followed by various levels of bromine scavenging.

3.2. Stability under laboratory conditions

Gels showed no sign of hydrolysis or of the release of AAm after 60 days exposure in an aqueous environment to continuous irradiation by laboratory fluorescent lights at room temperature. Similar results were obtained for the range of gels, AAm/mBIS, AAm/PIP, mAAm/BIS and for AAm/BIS gels at a range of T and C values.

Thus, the gels are stable under these conditions.

3.3. Degradation in hot aqueous suspension of AAm/BIS gels (thermal degradation)

It was observed from these experiments that non-brominated gels released AAm into the solution during the first 10 days and then the AAm level reached a plateau. The amount of AAm released was within 10 ppm of repeat units. When 1 h brominated gel was used, the amount of AAm released was substantially reduced (Figs. 1 and 2). With an overnight-brominated gel (APS as initiator), no AAm monomer was observed from the polymer solution during the whole degradation period of 13 days. These results suggest that the residual double bond of BIS is the precursor to the released AAm.

3.3.1. Evidence for pendant AAm units in BIS gels

First, we note that the amount of AAm released decreases eventually to zero as the extent of bromination increased.

Secondly, by heating BIS under our thermal conditions a low yield of AAm results. When a 10 ppm BIS solution was heated at 95 °C, AAm formation was observed as shown in Fig. 9. This indicates that BIS itself can hydrolyze and form AAm. Therefore, we would expect that a pendant double bond of BIS in the gel network would undergo a similar degradation. BIS can be synthesized by the condensation reaction of *N*-methylol acrylamide and AAm with the elimination of water. Hydrolysis of BIS is the reverse of this reaction.

We were unable to identify by MS the other products expected from this hydrolysis but note that *N*-methylol acrylamide would be expected to self-polymerize.

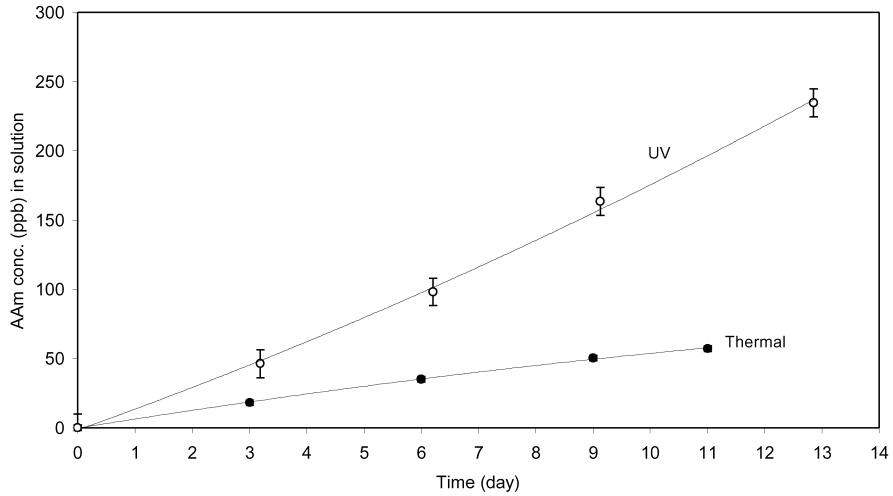


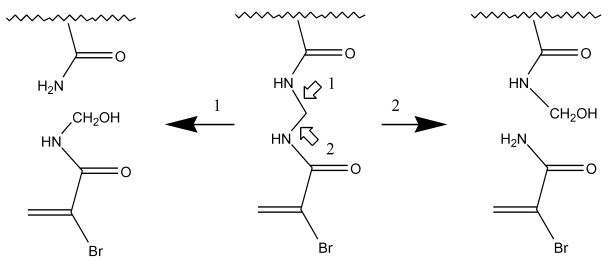
Fig. 9. BIS degradation under thermal degradation condition at 95 °C and UV irradiation at 254 nm wavelength.

In AAm/BIS gels, AAm may be released either by the scission of the main polymer chain or detachment of pendant double bonds in BIS. During bromination, the pendant double bonds in the cross-linkers would react with bromine. If the bromination is complete, all pendant double bonds will be reacted. The above results suggest that the AAm monomer released from the polymer network comes from the pendant double bonds being hydrolyzed to AAm monomer. Therefore, partially brominated (1 h bromination) gels caused the reduction of the AAm released and completely brominated (overnight bromination) gels (APS as initiator) did not give any AAm under thermal degradation at 95 °C. Supporting evidence for this theory is the absence of AAm from linear PAAm, confirming that it is not the result of backbone scission [4].

In the brominated BIS gel we could not identify hydrolysis products which might be expected, the dibromo propionamide and α-bromo acrylamide (amide). It is possible that the brominated product is more resistant to hydrolysis. Alternatively, bromination may alter the pathway of hydrolysis and lead to the unstable *N*-methylol bromoacrylamide. A possible reason is that the electron withdrawing bromine atoms alter the hydrolytic fission as shown in Scheme 2.

Thirdly, in AAm/BIS gels there is a correlation between the amount of BIS and the level of AAm released.

Fourthly, changing the cross-linker from BIS to mBIS or PIP results in no AAm being released, confirming that AAm was released from the cross-linker and not the backbone. These gels are discussed below in further detail.



Scheme 2. Possible hydrolysis pathway of the brominated BIS gel.

Finally, changing to a mAAm/BIS gel still gave AAm, confirming that AAm is not from the backbone (see mAAm/BIS section later).

3.4. AAm/mBIS and AAm/PIP gels (thermal degradation)

If AAm were released from pendant double bonds of an AAm/BIS gel, changing the type of the cross-linker should prevent the formation of AAm during the thermal degradation. Replacement of the BIS cross-linker with either mBIS or PIP gave gels that did not release AAm. This is a further evidence that the PAAm backbone in the gel is stable under the thermal degradation condition and does not release any AAm.

Interestingly, we did not observe the expected hydrolysis products of the pendant unsaturation of these cross-linkers, that is mAAm or acrylic acid (from PIP).

mBIS monomer does yield mAAm (more than BIS) under our degradation condition and we need to address the observation that no mAAm is released from the gels. We note that detection of mAAm by HPLC is less sensitive than AAm but do not favour this explanation. Rather we suggest that because of the difference in reactivity ratios between AAm and mBIS, the cross-linker will enter the chain early and have a much greater chance of both double bonds being incorporated into the network than is the case with BIS. Indeed we have used this fact to prepare unique large pore size gels [5].

PIP was stable when heated at 95 °C for 3 days and hence, we conclude that hydrolysis of pendant PIP units is unlikely.

3.5. mAAm/BIS gel (thermal degradation)

Again, since BIS cross-linker was used in this gel, AAm formation would be expected. When the amount of pendant

double bonds in BIS was reduced by bromination, less AAm formation was observed under thermal degradation, and no AAm was observed with completely brominated gel (overnight-brominated). This is a further evidence that the release of AAm from gels under thermal degradation comes from the pendant double bond of the cross-linker.

The mAAm/BIS gel release more AAm than the AAm/BIS gel and this observation can be explained by the reactivity of mAAm. The mAAm is more reactive than AAm, while AAm has similar reactivity to BIS. Hence, this influences the reaction path and the final structure of the gels [5]. During polymerization of the AAm/BIS gels, since AAm and BIS have similar reactivity, BIS is statistically incorporated to the network. However, in the formation of mAAm/BIS gel, mAAm is more reactive than BIS and BIS will incorporate into the network later in comparison to the AAm/BIS case. Therefore, the chance for the second double bond of the BIS in mAAm/BIS gel being reacted is reduced. This will result in more pendant double bonds in the mAAm/BIS gels.

From the thermal degradation results of the gels with different monomer compositions we can conclude that the carbon–carbon backbone of PAAm gels is quite stable under our thermal condition (95 °C). However, the BIS cross-linker can result in unreacted pendant double bonds that can degrade to AAm. Once these pendant double bonds are eliminated by bromination, no AAm is released.

3.6. Hydrolysis of amide side chain

In the linear PAAms, we have reported on the hydrolysis of the amide units to acid residues. Similar hydrolysis was observed from gels after hot aqueous treatment at 95 °C.

PAAm gels showed less hydrolysis content in comparison with linear PAAm, as shown in Table 2. The gel of mAAm/BIS hydrolysed to a very small extent upon heating, which reflects the known greater stability of methacrylic to acrylic amides/esters. The gels initiated by APS usually produced more acid groups upon heating than ones initiated by redox system. In addition, the AAm/BIS gel with higher C gave less hydrolysis than the one with lower C (Table 2). This aspect is being investigated further.

In summary, under thermal conditions the gels degrade in the same manner as linear polymers, that is they are hydrolysed to form acid residues but no evidence for the carbon–carbon bond of the backbone undergoing scission is found. However, an additional pathway, the hydrolysis of pendant unsaturated in the BIS cross-linker units does give rise to low levels of AAm.

3.7. UV degradation on polyacrylamide gels

At 254 nm, an AAm/BIS gel released AAm monomer (Fig. 6) and it is noteworthy that the amount of AAm is greater than that obtained for the linear PAAm. This suggests that the additional AAm could come from cross-linker residues in which only one double bond has been incorporated into the network. We note that the cross-linker residues were also responsible for the released AAm with the thermal hydrolysis experiments discussed above.

Similar degradation to AAm monomer was observed in our earlier study when a linear PAAm solution was irradiated under UV condition [4]. It was expected that the polymer backbone made from polymerization of AAm in the gel would release AAm. The question here is whether the network structure formed from the cross-linkers will release more AAm.

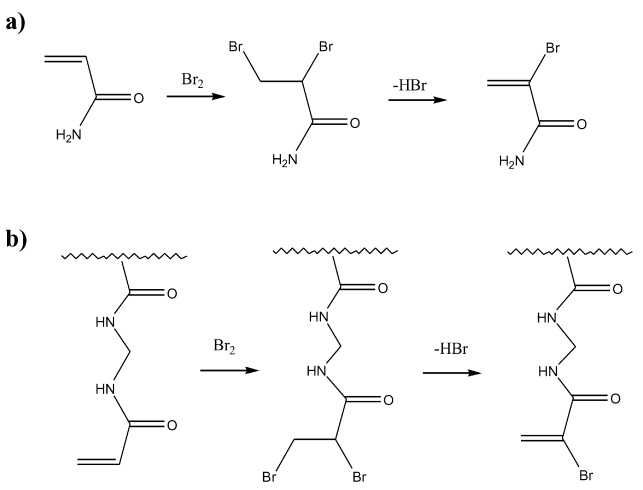
Evidence supporting the conclusion that the pendant double bonds of partially incorporated BIS are the additional source of AAm includes:

1. BIS under UV irradiation yielded some AAm (Fig. 9) and
2. mAAm/BIS gels released AAm, which can only come from the BIS. In this connection, we noted the increased yield of AAm from pendant double bonds, relative to an AAm/BIS gel and this is consistent with the increased amount of pendant double bonds of BIS in mAAm/BIS (see discussion above).

Thus, we conclude that UV irradiation causes scission of the backbone and of pendant unsaturated units forming AAm.

3.7.1. Brominated gels

Brominated AAm/BIS gels showed unexpected properties when subjected to UV irradiation. Rather than reducing the yield of AAm by removing the unsaturated pendant groups, we actually observed an increased yield of AAm. Bromination of AAm converts the monomer to 2,3-dibromopropionamide. It has been reported [6] that under certain condition 2,3-dibromopropinoamide is not a stable derivative and can convert to 2-bromopropenamide by elimination of HBr (Scheme 3a). For the brominated AAm/BIS gel, the dibrominated moieties of the network structure would also be expected to undergo elimination of HBr to



Scheme 3.

form mono-brominated moieties (Scheme 3b). The eliminated HBr could have a catalytic effect and increase the amount of AAm degraded from the polymer. This is suggested as the reason that completely brominated AAm/BIS gel under UV irradiation gave higher AAm levels than the non-brominated gel.

We attribute this to the catalytic effect of bromine entities probably HBr on degradation of the AAm backbone. Evidence for this postulation includes:

1. increased yield of AAm as the amount of bromination is increased, that is, the opposite effect if the pendant groups were the source;
2. increased yield of AAm from an AAm/mBIS gel. That is the backbone is more susceptible to UV degradation in the presence of the liberated bromine entities.

Although the amount of AAm released from the polymer can be as high as 50 ppm per polymer repeat units for a brominated gel, it is still only the release of a few molecules, not a unzipping of the polymer backbone, as only one AAm was released from every 20,000 repeat units.

The mAAm/BIS gel showed unusual results on bromination. Thus, bromination for 1 h gave a gel which released more AAm than the non-brominated gel whereas a brominated (24 h) gel gave a reduced yield of AAm. These results suggest that HBr also catalyses the UV degradation of pendant BIS unsaturation.

The small yield of AAm from the mAAm/BIS gel brominated (24 h) could be due to a small amount of residual unsaturated pendant groups. However, an alternative possibility is the UV catalysed elimination of bromine from the dibromo derivative.

In contrast to the previous two cases, although partially brominated mAAm/BIS gel showed an increase in AAm release, a completely brominated gel caused reduction of the AAm degraded from the polymer. The initial increase may be due to the catalytic effect by elimination of HBr from the brominated product as described before. When the pendant double bonds are completely brominated, there will be no unbrominated double bonds available for degradation to AAm. The fact that there is still a small amount of AAm observed from the completely brominated gels may be due to the reformation of AAm from the brominated moiety of the network structure after being hydrolyzed out of the polymer. In a separate experiment, when 10 ppm water solution of 2,3-dibromopropinoamide, a bromination product of AAm, was subjected to UV irradiation for 3 days, AAm was observed in the solution with a concentration of 450 ppb. This experiment indicates that brominated AAm can revert back to AAm under UV degradation.

It was interesting to find that AAm was released from a mAAm/BIS gel under the same irradiation condition. This result indicates that AAm is also degraded from the moiety of the network formed from cross-linker. In a separate experiment, a 10 ppm BIS monomer solution under UV degradation also produced AAm (Fig. 9). This result confirms that AAm degraded from an AAm/BIS gel is contributed from both the backbone and the pendant double bonds.

3.7.2. Effect of polymerization procedure

Preliminary work comparing APS (thermal) with APS/TEMED (redox) shown a significant differences between the two gels and the APS thermal irradiation resulted in a gel less stable to UV than the redox initiated gel.

In part I [4] of this series, it has been suggested that AAm degraded from a linear PAAm may result from the head to head (H–H) linkages formed during the propagation and termination of the polymer chains. For the cross-linked gels, there should be H–H linkages in the backbone of the network and these H–H linkages could be the source of the AAm units. As described previously, the additional AAm sources are from the network structure formed by cross-linkers. The APS initiation was carried out at 60 °C and the redox at room temperature. The elevated reaction temperature can increase the H–H linkages during the AAm propagation as at a higher temperature, the addition of the monomers to a propagating radical is less selective and more H–H pathway is possible. Therefore, polymerization of AAm/BIS gels with APS at 60 °C would give more H–H linkages in the network and consequently more AAm would be degraded out from the network during the UV degradation of these gels. Further work is under way to test this theory.

4. Conclusion

All the AAm hydrogels were stable at RT and under fluorescent lights. In hot water (95 °C), hydrolysis of the side chain amides to acids occurred although the extent of hydrolysis was less than that observed for linear PAAm.

BIS cross-linked gels, under thermal aqueous condition also yield low levels of AAm. This was shown to come from pendant unsaturation of BIS residues.

Brominated BIS gels, and gels in which the cross-linker was PIP or mBIS, did not yield AAm under hot aqueous degradation conditions.

All the gels gave low levels of AAm when exposed to UV irradiation.

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