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Degradation on polyacrylamides. Part I. Linear polyacrylamide

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Abstract

The stability of linear polyacrylamides (PAAM) under thermal and irradiation conditions were investigated. The study showed that PAAm is stable under fluorescent lights and does not release any detectable acrylamide (AAM) in hot aqueous solution at 95 °C. Hydrolysis of side-chain amide groups to acid groups was observed during the thermal aqueous degradation. Under UV irradiation, small levels of released AAm were observed; however they are generally below 50 parts per million repeat monomer units in the polymer. A drop in viscosity is also observed. This indicates that the acrylamide released is due to chain scission, not a unzipping of the polymer chain. Methods of purifying a linear PAAM are also discussed.

Keywords: Polyacrylamide; Degradation; Hydrolysis

1. Introduction

Polyacrylamides (PAAm) find wide use as water purification flocculants [1–4], as soil conditioning agents [5–8], as hydrogels [9] including contact lenses, and in many biomedical applications [10–13]. In particular, gels or membranes made from polyacrylamides have been extensively used in recent years for protein separations [14–17].

Polyacrylamide is generally, but not universally accepted as being non-toxic. However acrylamide monomer causes peripheral neuropathy. Thus the level of acrylamide monomer in commercial polymers has been an important issue particularly for applications where human contact is involved. For example, polyacrylamide used as a water purification agent has strict specifications on the amount of monomer that is allowed. Similarly, polyacrylamide membranes used in blood purification require no detectable monomer or techniques for removing residual monomer.

Recently it has been suggested that an additional but vitally important concern is the possibility of degradation of commercial polyacrylamide formulations to acrylamide. Such reports have been challenged but the question remains as to whether or not polyacrylamide can release acrylamide monomer and if so the extent of such degradation processes.

In this paper we report on the stability of a number of PAAms, prepared with different initiation systems, when heated, exposed to irradiation of fluorescent light (indoor laboratory condition), exposed to ultraviolet irradiation (outdoor condition), and kept at room temperature. We then use these results to rationalize the conflicting reports in the literature.

2. Experimental and results

2.1. Materials

Electrophoresis-grade (>98%) acrylamide was purchased from ICN Biomedicals Inc.; ammonium persulphate (APS) (>98.8) was obtained from Sigma Chemical Co.; H_2O_2 (AR grade, 30% w/v) was obtained from AJAX Chemicals; and N,N,N',N'tetramethylethylenediamine (TEMED) (>99.5%) from Aldrich. Bromine (AR grade) was obtained from FSE Pty Ltd. Saturated bromine water was made by shaking Milli Q water with bromine followed by standing the solution overnight at 4 °C. The aqueous phase was used. Sodium thiosulphate (>99.5%) was purchased from AJAX Chemicals and 1 M solution sodium thiosulphate was used. Spectrophotometric grade trifluoroacetic acid (TFAA, >99%) was obtained from Aldrich Chemical Co.

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2.2. Glassware and pH measurement

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

pH measurements of polymer samples were taken with a WP-81 digital pH meter (TPS Ltd, Australia).

2.3. Polymerization methods

2.3.1. APS/TEMED redox initiated polymerization

Acrylamide (2.5 g) was dissolved in water, and the total volume adjusted to 50 ml. The monomer solution was degassed (3 times under high-vacuum) using the freeze–thaw technique. Then TEMED (0.25 ml) and APS (0.5 ml) water solutions all with the concentration of 10% (w/w) were added into the monomer solution under argon. Polymerization proceeded overnight at room temperature.

2.3.2. APS thermally-initiated polymerization

Acrylamide (2.5 g) and APS (0.05 g) were dissolved in water, and the total volume adjusted to 50 ml. The monomer solution was degassed (3 times under high-vacuum) using the freeze–thaw technique. Polymerization proceeded for 2 h in an oil bath at 60 °C.

2.3.3. Photo-initiated polymerization

Acrylamide (3.75 g) was dissolved in water (71.25 g) to make up 5% (w/w) monomer solution. Photo-initiators, diphenyliodonium chloride (DPIC), toluene-4-sulfinic acid sodium salt (STS), and riboflavin $5'$-monophosphate sodium salt (RMN-Na), were dissolved in water to achieve initiator solutions at concentrations of 0.025, 0.5, and 0.025 M, respectively. Each initiator solution (0.133 ml) was added to the monomer solution. Then the mixture was degassed (3 times under high-vacuum) using the freeze–thaw technique in the dark. Polymerization proceeded overnight under the irradiation of fluorescent lights (18 W) at room temperature.

2.3.4. H_2O_2 initiated polymerization

Acrylamide (2.5 g) was dissolved in water, and the total volume adjusted to 50 ml. Then 0.17 g of 30% (w/v) H_2O_2 solution (0.05 g pure H_2O_2) was added to the monomer solution. The monomer solution was degassed (3 times under high-vacuum) using the freeze–thaw technique. Polymerization proceeded for 2 days in an oil bath at 60 °C.

2.4. Polyacrylamide purification methods

2.4.1. Precipitation

The polymerization mixture (usually with conversion greater than 99.9%) from each of the polymerization methods was diluted with water from 5% (w/w) to 2–3% (w/w) PAAm concentration, and added dropwise into a large excess of methanol (~ 1.5 l). The precipitated polymer was filtered off and washed with methanol (10 times).

The above procedure was repeated three times and the level of free acrylamide monomer in a 1% (w/w) solution was measured. (see Table 1). The AAm concentrations were presented as the number of AAm molecules per 1,000,000 polymer repeat units (ppm).

2.4.2. Treatment with bromine water

Polyacrylamide (2 g) (purified by the precipitation method as described above) was dissolved in water (100 ml). To the polymer solution saturated bromine water was added until a yellow colour persisted (generally 10 ml saturated bromine water). The solution was left standing overnight. Generally more than 10 ml saturated bromine water was used. The excess bromine was removed by reacting with 1 M sodium thiosulphate solution (~ 0.5 ml) and the polymer was precipitated out with methanol 3 times. Finally, the polymer was dried on a vacuum line at 40–50 °C overnight. No acrylamide was detected using HPLC (see method and Table 1 below). These polymers were used in the degradation studies.

We noted that it was more difficult to remove residual AAm from PAAm prepared using TEMED/APS. This required a heat treatment after the first bromination step (designed to aid in releasing adsorbed AAm), followed by further bromination.

2.5. Acrylamide detection (HPLC method)

2.5.1. Milli-Q water as mobile phase

The acrylamide level was measured 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, column size of 250×4.6 mm). Filtered Milli-Q water was used as the mobile phase and all HPLC samples were made up in water solution using the same filtered Milli-Q water as the mobile phase. The sensitivity of detectable AAm level in this HPLC system is 1 part per billion (ppb).

2.5.2. TFAA solution (0.1% w/v) as mobile phase

Some samples from thermal degradation could not be analysed using Milli-Q water only as the mobile phase due to the increased viscosity of the polymer solution, but could be analysed if 0.1% (w/v) TFAA water solution was used as

Table 1
AAm concentration in a 1% (w/w) polymer (initiated by redox system) solution after purification by precipitation (ppt) and treatment with bromine water

Precipitation from MeOH	AAm conc. (ppb)
First precipitation	91.52
Second precipitation	25.96
Third precipitation	3.68
Third ppt + bromination + three ppt	0.00

mobile phase. All thermal degradation experiments were analysed using this mobile phase.

In order to determine the AAm level in the polymer solution, a standard curve of AAm concentration versus the peak area measured by HPLC was created. Different mobile phases gave similar curves, as shown in Fig. 1.

2.6. Degradation methods

2.6.1. Thermal degradation at 95 °C

Polymer solution (10 ml, 1%, w/w) in a Schlenk flask was placed in an oil bath set at 95 °C. The Schlenk flask was sealed with a Teflon top to prevent water from evaporating. About 0.5 ml solution was withdrawn at specified intervals and the sample solution (50 μl) was injected directly into the HPLC column to determine the AAm level of the solution. TFAA solution (0.1% w/v) was used as mobile phase. For the linear PAAms produced by different initiation systems, thermal treatment at 95 °C showed no detectable AAm after 15 days (exp discontinue after 15 days).

2.6.2. Under fluorescent light

The degradation experiment under fluorescent light was also conducted for 1% (w/w) polymer solution. The polymer solution (10 ml, 1% w/w) in a 28 ml sample vial (75 × 25 mm), covered with plastic film, was consistently irradiated by fluorescent light at a distance of 30 cm. At specific intervals, about 0.5 ml solution was taken out, and 50 μl was injected directly into the HPLC column to determine the AAm level of the solution. Milli-Q water was used as mobile phase for HPLC measurement.

No AAm was liberated from any samples after 15 days (exp discontinue after 15 days). There was no observable change in viscosity and no acid groups were detected by titration.

2.6.3. UV degradation (wavelength of 254 nm)

The UV degradation experiment was conducted on polymer solutions (1% w/w), with a UV lamp set at a wavelength of 254 nm. Polymer solution (10 ml) in a 28 ml sample vial, sealed with plastic film, was placed in a black box, with a UV lamp positioned above the sample. The polymer solution was then irradiated at 254 nm. At specific intervals, 0.5 ml of solution was withdrawn, 50 μl was injected directly into the HPLC column to determine the AAm level of the solution. Milli-Q water was used as mobile phase for HPLC measurement. Results are reported in Fig. 2.

It can be seen in Fig. 2 that AAm was detected when PAAm was exposed to UV irradiation. The PAAm initiated thermally with APS gave the highest level of AAm at about 70 ppm repeat units after 14 days. This is equivalent to 1 AAm out of every 14,285 repeat units.

2.7. Viscosity measurement of polymer solution

The viscosity of polyacrylamide solution (0.5% w/w) was measured at 20 °C using a 1 mm diameter U-tube glass capillary viscometer. 10 ml of polymer solution was used for each measurement. The kinematic viscosity, ν, was calculated from the flow time, t, taken for the meniscus of the liquid to flow between two indicators on the tube using Eq. (1) below

$$\nu = C \times t \qquad (1)$$

where $\nu =$ kinematic viscosity (mm^2/s). $C =$ a constant characteristic of the specified viscometer (mm^2/s^2), $t =$ measured flow time (s).

The viscometer was calibrated with water, which has a known kinematic viscosity of 1 mm^2/s at 20 °C. The constant C of the viscometer used was determined to be 0.0129 mm^2/s^2.

The viscosity of the thermally treated PAAms varied with the initiator used. Typical results are shown in Fig. 3. Fig. 4 shows the increase of pH with duration of heating. Thus all solutions increased in viscosity as predicted if charged COO$^-$ groups are being formed on the polymer backbone. We note that less hydrolysis occurred with the photo-initiation system as evidenced by the lower pH and viscosity.

The viscosity changes of linear polyacrylamides (initiated by different methods) after UV treatment are

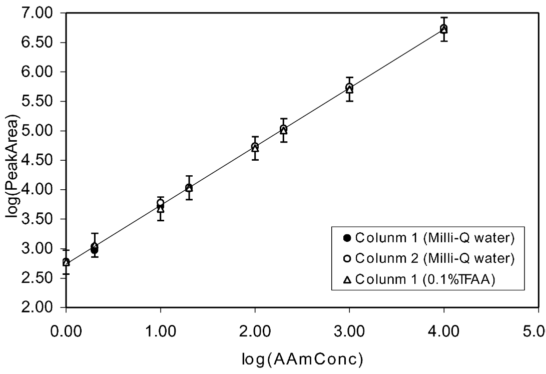


Fig. 1. Standard curves of AAm level determination.

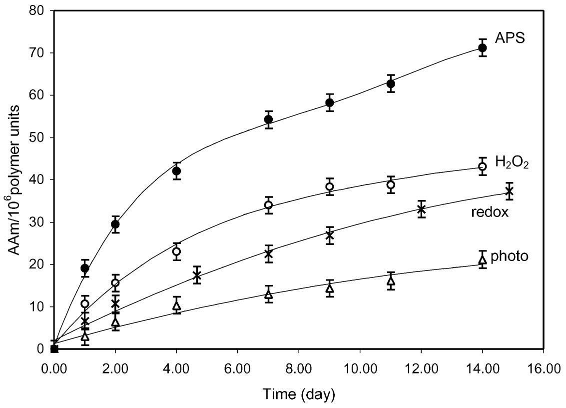


Fig. 2. UV degradation results for different initiators ($\lambda = 254$ nm).

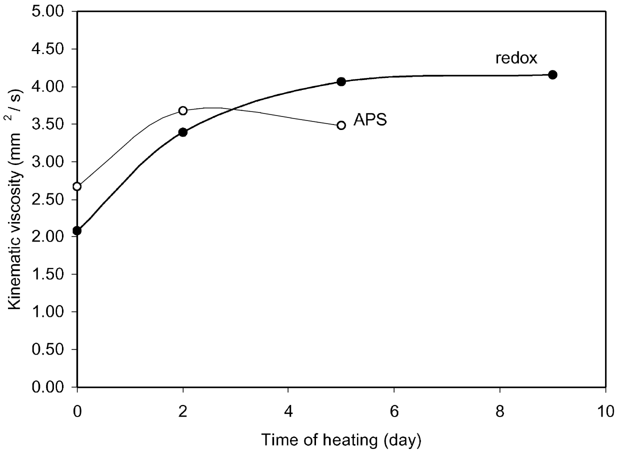


Fig. 3. Effect of heat treatment on the viscosity of LPAAm.

shown in Table 2. Small reductions of the viscosity were observed after the polymer solution was under UV degradation for 5 days.

2.8. Determination of hydrolysis content

The hydrolysis content of polymers was determined by titration. The polymer solution was first acidified by adding a small amount of HCl solution (2.5 M) until a pH of 2 was reached. The polymer was then precipitated into methanol, filtered and dried under vacuum overnight. Polymer solution (1% w/w) was then made up in water. A NaOH solution (0.01 M) was used to titrate the polymer solution. The volume of NaOH solution at the critical point (pH 8) was used to calculate the amount of acid groups, formed by hydrolysis of amide groups in the polymer chain. Results are in Fig. 5.

The hydrolysis content of the H_2O_2 initiated polymer solution is largest, while the photo-initiated polymer gave the lowest amount of hydrolysis. This result is consistent with the pH change of the H_2O_2 initiated polymer solution being large upon heating compared with the other initiation systems used (see Fig. 4).

Table 2
Viscosity change of LPAAm under UV degradation

Initiator	Degradation time (day)	
	0	5
	Kinematic viscosity (mm^2/s)	
APS	2.67	1.15
Redox	2.43	2.22
Photo	1.71	1.56
H_2O_2	1.55	1.31

2.9. Effect of pH on viscosity

The viscosity of polymer solution dramatically dropped down after adjusting its pH value to around 2. The results are shown in Fig. 7.

The viscosity change on acidification implies that the viscosity increase after heating PAAm is not due to molecular weight increase, but the change of functional group along the polymer chain and the consequent change in conformation.

In order to confirm that some amide groups were converted to carboxylic groups upon heating, the viscosity of polymer solutions after 5 days of thermal treatment was measured at different pH values (as shown in Fig. 8). The pH adjustment was carried out using either HCl or NaOH.

It was found that with initial linear PAAm without treatment the viscosity remain constant with changes of pH.

For comparison a sample of PAAm, which has been subjected to UV irradiation for 5 days, has been included.

For the thermally treated polymer solution, the viscosity of the solution was about 2 mm^2/s at the low pH. When the pH was increased to 12, the viscosity increased initially,

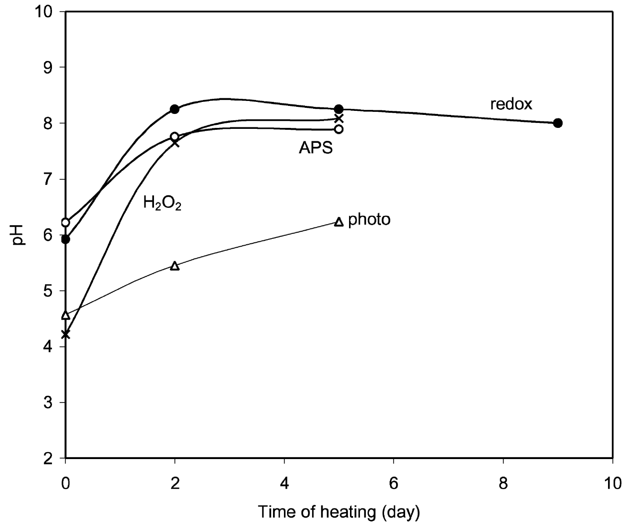


Fig. 4. Effect of heat treatment on the pH of LPAAm solutions.

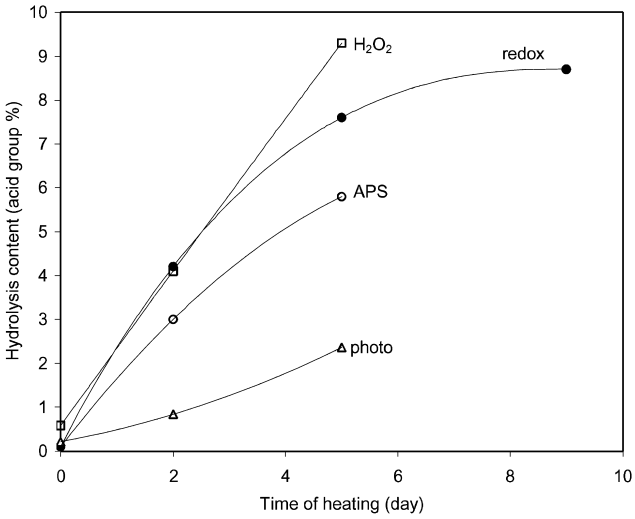


Fig. 5. Effect of heat treatment on the hydrolysis content of LPAAm.

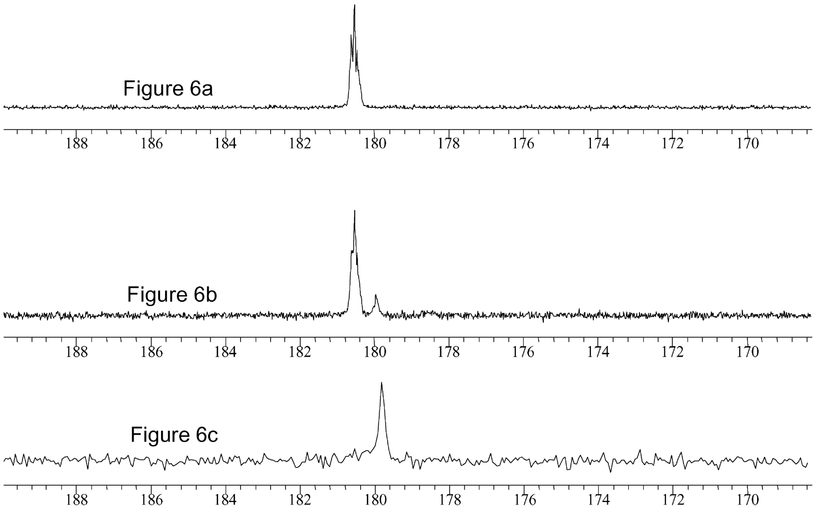


Fig. 6. Extended carbonyl regions of NMR spectra of PAAm and PAA (run overnight at 30 °C, in D_2O). (a) Initial PAAm; (b) PAAm after 10 days heating; (c) PAA.

peaked at a pH value of 8 (where the viscosity is about 8 mm^2/s) before decreasing to about 5 mm^2/s at a pH value of 12. This behavior is typical of a PAA solution as reported in literature [23]. Thus, thermally treated PAAm results in some structures being hydrolysed to PAA moieties.

2.10. NMR measurement

Polymers were dissolved in D_2O at the concentration of 4% (w/w) for polyacrylamide (PAAm) and 0.5% (w/w) for polyacrylic acid (PAA). ^{13}C NMR spectra were obtained on a Unity + 400 NMR machine at 400 MHz using 5 mm broad band probe, for 16 h at 30 °C.

The extended carbonyl region of the NMR spectra is shown in Fig. 6.

The initial PAAm sample gave a ^{13}C resonance in the NMR of the carbonyl group at 180.5 ppm (Fig. 6a). The same polymer after thermal treatment gave an additional peak at 179.9 ppm (Fig. 6b). The carbonyl group from PAA showed a similar chemical shift at 179.7 ppm (Fig. 6c). These NMR measurements confirm that partial hydrolysis of polyacrylamide to a poly (AAm/AA) copolymer did occur during thermal treatment at 95 °C. An integration of the spectrum from the sample (Fig. 6b) shows that about 10% of amide groups in the polymer were hydrolysed after 10 days.

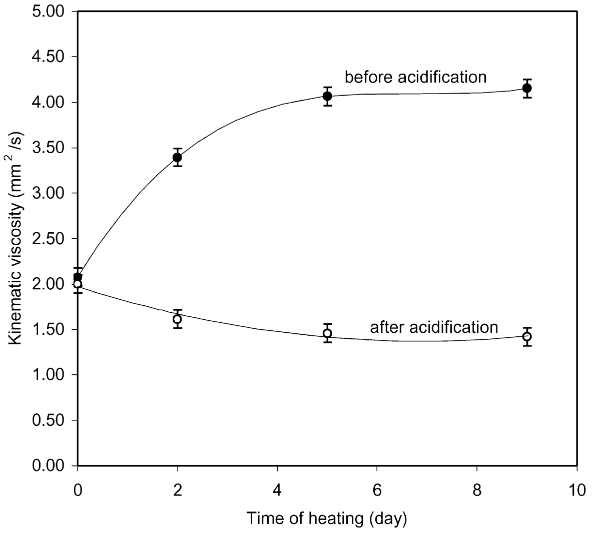


Fig. 7. Effect of acidification on viscosity (redox-initiated PAAm).

3. Discussion

In this work, an effective method for purification of PAAm was studied first. This ensured that the polymer did not contain any detectable acrylamide before any degradation experiments were commenced and would therefore avoid one of the controversial issues of previous work [18,19].

The purification of linear PAAms proved to be extremely

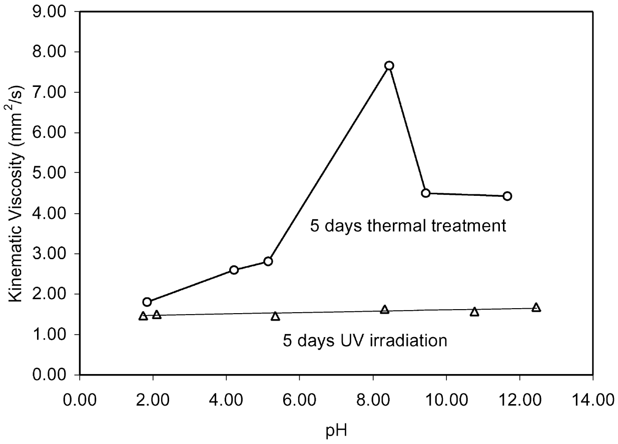


Fig. 8. Viscosity change versus pH value of polymer solutions under thermal and UV degradation (APS as initiator).

difficult. Three precipitations with methanol were not sufficient to reach the target of less than 1 ppb. Additional precipitation further reduced the AAm level but it was still above the desired level. A chemical scavenging process using bromine water was therefore included. This combination of methanol precipitation and scavenging with bromine water eventually yielded PAAm with no detectable AAm monomer.

We suggest that the difficulty of obtaining AAm free PAAm could partly explain some of the controversy in the literature regarding the source of AAm in PAAm after certain exposure regimes. For example the samples used by Smith [18,19] were commercial polymers with no additional purification. These would contain AAm monomer and we suggest that this was a major source of the AAm isolated by Smith and subsequently attributed to unzipping of PAAm chains. A similar explanation of Smith's results has been made by a number of authors [20,21]. Other sources of the AAm isolated by Smith will be discussed in relation to UV degradation.

The PAAms were stable at room temperature and in the presence of fluorescent lights (i.e. laboratory conditions) with no acrylamide or hydrolysis products detected after 15 days.

A possible reason for the viscosity increase of a polymer solution is that the molecular weight of the polymer is increased. Alternatively, the functional groups on the polymer could have changed. In this case, it is most likely that some amide groups on PAAm have hydrolysed to carboxylic groups (Scheme 1). It is known that a polyacrylic acid solution at certain pH values can give a solution of high viscosity [22]. This is due to the extended conformation of the polymer chains [23,24]. Thus, if the amide group of PAAm is hydrolysed, NH_3 will be eliminated which can then form ammonium ions and carboxylate functional groups in water. Hence, it can be expected that the pH of the polymer solution should increase along with the viscosity.

Therefore, when the PAAms were heated at 95 °C, hydrolysis of the side chain amides to acid groups occurred. This was evidenced by the change in pH of the solution, by the titration of the acid groups with base, and by NMR spectroscopy, which clearly showed a second carbonyl peak with the same chemical shift as that of an authentic PAA. The NMR and titration data suggest up to 10% of the amides were converted to acid groups although the number varied between samples.

A consequence of the presence of acid residues in the PAAm was that the viscosity of the polymer varies with pH. Thus at a high pH the polymer was more viscous than at a low pH. The negative charges on the carboxylic group result in the polymer chain extending due to the charge repulsion at high pH values.

No AAm was detected in PAAms subjected to thermal degradation conditions (95 °C).

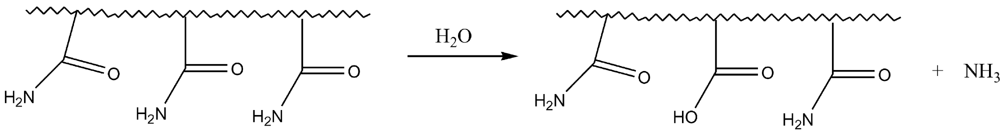
In contrast to the thermal degradation, exposure to UV gave no measurable hydrolysis but did liberate small amounts of AAm monomer. UV exposure also resulted in a reduction in the viscosity of the polymer solution (Table 2), i.e. a lowering of molecular weight (MWt) consistent with chain scission. For example PAAm initiated thermally by APS liberated on average about 70 AAm units per million repeat units of polymer chain. If this were the result of unzipping of a very few molecules, a change in MWt of the polymer solution (i.e. viscosity) would not be expected. Unzipping is also at variance with existing theories on polymer stability and degradation of polymers derived from mono-substituted olefins.

It is envisaged that end groups, chain termination areas, head to head linkages formed from termination and propagation, or any other abnormal groups of the polymer chains might break down under UV irradiation. UV irradiation can cause a carbon–carbon bond to break and form carbon radicals. These could liberate one or two AAm units before the radical ends are terminated again. Some of these termination reactions will involve disproportionation with a consequent lowering molecular weight and viscosity.

It was suspected that different initiator systems might have an effect on the stability of PAAms. The polymers also varied in MWt and in the temperature at which polymerization took place. For example, the APS and H_2O_2 systems were polymerized at 60 °C, whereas the photopolymerized and TEMED/APS initiated polymerizations were conducted at room temperature.

Under UV irradiation, the redox and photo-initiated polymers liberated less AAm than either H_2O_2 or APS initiated polymers. A possible explanation for this is that the higher temperature at which propagation occurred (for the H_2O_2 and APS) would result in less selectivity for head–tail addition with the consequence that the polymer would have more head–head (h–h) linkages. Head–head linkages formed in termination could vary with temperature but also these h–h links could preferentially fragment under UV, liberate an AAm unit and then mutually terminate as discussed above.

Under conditions where hydrolysis is occurring we again note the greater stability of the photo-initiated polymer.



Scheme 1. Hydrolysis of polyacrylamide.

Further work (with more fully characterised polymers and the use of trapping techniques) is planned to elucidate the details of the degradation pathways.

4. Conclusion

Polyacrylamide is difficult to purify by physical methods such as washing or precipitation. Bromination of the residual acrylamide monomers, a chemical purification method used in conjunction with physical purification, has been found to be effective in removing acrylamide. Purified 1% (w/w) polymer solution contains less than 1 part per billion monomers (equivalent to 100 parts per billion monomer repeat units of the polymers) has been prepared.

Polyacrylamide is stable at room temperature and when subjected to continuous exposure to fluorescent light.

When heated at 95 °C, the polyacrylamide carbon–carbon backbone is stable and does not release any detectable acrylamide after 15 days. PAAm does however hydrolyse under these conditions. After 10 days approximately 10% of the amide groups are converted to carboxylic acid residues.

Polyacrylamide can release small amounts of AAm monomers under strong UV irradiation. However, the released amount, normally at about 50 parts per million repeat monomer units after 10 days, is small enough to be able to conclude that polyacrylamide does not unzip under these UV irradiation conditions, but undergoes random chain scission.

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