

## **Thermal Stability of Polyacrylamide Solutions: Effect of Residual Impurities in the Molecular- weight-degradation Process upon Heating**

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### SUMMARY

We have investigated the effect of temperature on the chemical (hydrolysis) and thermal (molecular weight) stability of purified polyacrylamide solution. From viscosity and light scattering data we show that no polymer degradation due to oxygen contamination results from heating polymer solutions although higher temperature is responsible for hydrolysis of amide groups.

### INTRODUCTION

Aqueous solutions of commercial polyacrylamides which contain oxygen often lost a great part of their initial viscosity when stored at moderate (60°C) and higher (90°C) temperature for extended periods of time (1). The viscosity loss in salt solution of heated polymers can be due to increase in the ionic character of polymers (hydrolysis of amide groups) and/or to molecular weight degradation. We have shown that molecular weight degradation can occur in temperature (60°C) and pH (7-9) conditions where the hydrolysis increase is found negligible (2). Commercial polymers always contain small amounts of residual impurities (e.g. residual polymerization catalysts, ...) which are thought to have an adverse effect on polymer degradation in solution when oxygen is not excluded from the system (free radical mechanism). Excluding and/or scavenging oxygen is a possible way to reduce degradation (3). An other solution is to remove residual impurities during preparation and recovery of polymers or by treating the aqueous polymer solutions by the way of adequate separation methods (dialysis, percolation through ionic exchange resins, ultrafiltration).

Here we present results concerning the thermal stability of purified polyacrylamides which are not from commercial origin. In all experiences oxygen was not excluded nor scavenged. We show that purified

polyacrylamide solutions exhibit no molecular weight degradation at temperatures between 60 and 100°C although hydrolysis extents are increased upon heating. The good thermal stability is attributed to the absence of residual impurities.

#### EXPERIMENTAL

Purified acrylamide was polymerized with  $\text{Na}_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_5$  as an initiator in aqueous solution. The monomer concentration was 0.42 mole/l and the polymerization time was 15 hours at room temperature. The reaction product was reprecipitated twice in methanol. With initiator concentration between  $3.4 \cdot 10^{-3}$  and  $8.5 \cdot 10^{-4}\text{M}$ , polymers with intrinsic viscosities (in water) in the range 13-125 ml/g were obtained.

A polymer with molecular weight  $\bar{M}_w = 1.57 \cdot 10^5$  was hydrolyzed in the presence of NaCl with 2M potassium hydroxide at 63°C for various times. Samples with hydrolysis extents in the range 4-60% have been prepared. A fully hydrolyzed polyacrylamide (i.e. polyacrylic acid) was obtained from hydrolysis in acidic condition (2M HCl). The reaction products were washed and reprecipitated in methanol.

#### RESULTS

##### Hydrolysis and viscosity data

In Figure 1 is plotted the viscosity dependence (at room temperature) on the extent of hydrolysis for hydrolyzed polyacrylamide samples we have prepared. The viscosity is measured in 0.05M phosphate buffer i.e. at a pH value (=6.8) such as the carboxylic groups are dissociated (the degree of ionization  $\alpha=1$ ).

In buffer without added salt, the viscosity is found to increase with the hydrolysis extent ( $\tau$ ) i.e. with the charge density parameter  $\alpha\tau$ . In the presence of an excess of added salt (0.5M NaCl), the viscosity is lower and less dependent on the hydrolysis extent as the anionic sites of polymer ( $\text{COO}^-$ ) are screened by the cationic species of the salt.

As previously reported (4) hydrolysis of amide groups results from heating polyacrylamides and the rate of hydrolysis increase is strongly dependent on both pH and temperature. In Table I are given the changes in viscosity and hydrolysis extent for a polyacrylamide sample ( $\tau=10\%$ ) heated at 100°C in water solution (the initial pH was 5.0). As already reported, pH variations are observed during heating (5).

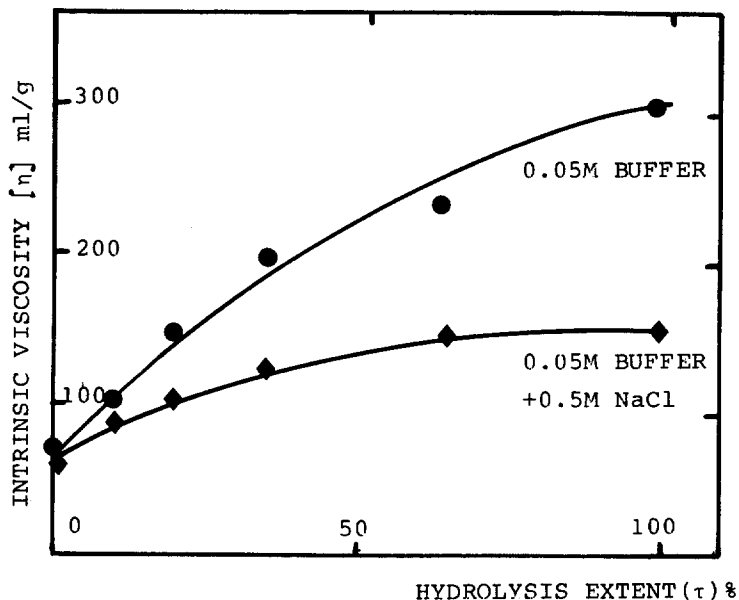


Figure 1. Viscosity (in ml/g) dependence on the extent of hydrolysis for polyacrylamide ( $M_w = 1.57 \cdot 10^5$ ) in buffer (pH=6.8).

TABLE I

POLYACRYLAMIDE ( $\tau_i = 10\%$ ) HEATED ( $100^\circ\text{C}$ ) IN WATER (pH<sub>i</sub>=5.0).

HOURS	0	16	40	88	141	184
pH	5.0	6.2	6.3	6.1	5.9	5.4
$\tau$ (%)	10	16	21	32	45	59
Reduced viscosity (ml/g)	337 76	1070 86	1050 -	1320 -	- -	- (1) 85 (2)

- (1) reduced viscosity measured in water  
 (2) reduced viscosity measured in 0.1M NaCl

The increased viscosity values in pure water (Table I) are in good agreement with the hydrolysis increase i.e. with the increasing ionic character of the polymer. In the presence of salt (0.1M NaCl), the viscosity is only slightly increased as usual.

In Figure 2 is reported the variation of the reduced viscosity (in 0.1M NaCl) versus the charge density parameter  $\alpha\tau$  for unheated polyacrylamide samples (HPAM 10 and 60). By taking into account the pH and  $\tau$  changes resulting from heating (reported in Table I), it can be seen that the charge density of the polymer sample which was before heating of near 5% ( $\text{pH}_i=5.0$ ,  $\alpha=0.5$ ,  $\tau=10\%$ ) has reached a value near 15% after heating for 184 hours ( $\text{pH}_{184\text{h}}=5.4$ ,  $\alpha=0.2$ ,  $\tau=60\%$ ). As indicated in Figure 2, the reduced viscosity of the heated sample (85 ml/g in 0.1M NaCl) is near that of an unheated sample of the same charge density showing thus that no degradation occurred.

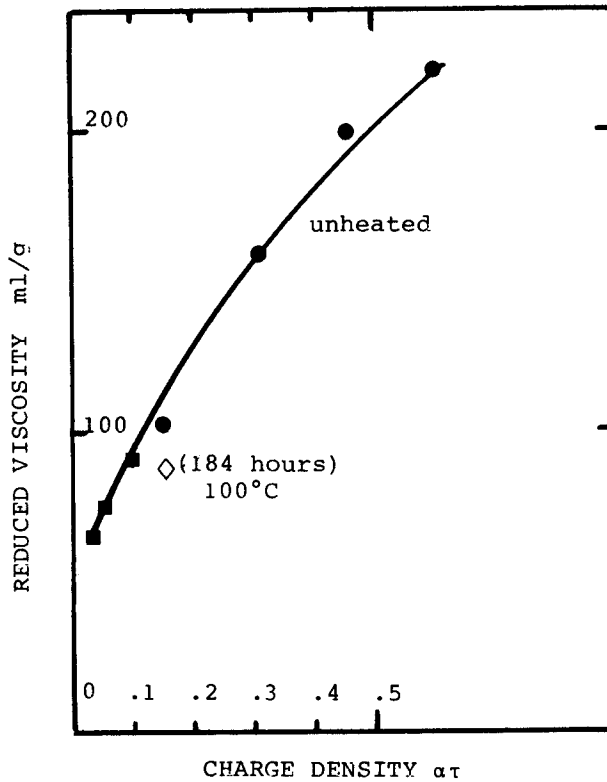


Figure 2. Reduced viscosity (ml/g) measured in 0.1M NaCl versus the charge density of polyacrylamide samples. Unheated samples are in black symbols.

In Table II are reported the hydrolysis and intrinsic viscosity changes for the same polyacrylamide sample heated at 100°C in 0.05M phosphate buffer (pH=6.8).

TABLE II  
POLYACRYLAMIDE HEATED IN BUFFER (100°C)

HOURS	0	40	90	136	208	260	352	640
$\tau$ (%)	10*	16*	25	33	40	50	60	56*
$[\eta]$ ml/g	100	140	166	184	200	218	240	250

The extent of hydrolysis was determined from potentiometric titration (asterisked values) or from viscosity data given in Figure 1 (reference curve).

Similar results are obtained for other polyacrylamide with different initial hydrolysis extents: for a sample with  $\tau_i=34\%$  and  $\eta_i=200$  ml/g (in buffer) we found  $\tau=60\%$  and  $\eta=240$  ml/g after 20 days in buffer at 100°C.

In Figure 3 are reported the differences observed for polyacrylamides hydrolyzed to the same extent but from different origin. Both samples have been heated in the same conditions and in the presence of oxygen. As it is clear viscosity loss is observed for commercial sample (HPAM 35) whereas a slight viscosity increase is observed for the laboratory purified sample (HPAM 34).

#### Low angle laser light scattering data.

Scattered light intensities measured at low forward intensities angles were used to calculate the weight average molecular weight  $\bar{M}_w$ .

Two polyacrylamide purified samples ( $\bar{M}_w=1.57 \cdot 10^5$ ,  $\tau=20\%$ ) were heated in 0.1M KCl (pH=7.1) at 60°C (16 days) and 90°C (32 days).

Light scattering measurement results are given in Table III.

As it can be seen, no change in molecular weight  $\bar{M}_w$  is observed in agreement with the viscosity data reported above. In the same temperature and pH conditions, a molecular weight decrease of about 55% (16 days, 60°C) and 80% (32 days, 90°C) has been found for commercial polyacrylamide (2).

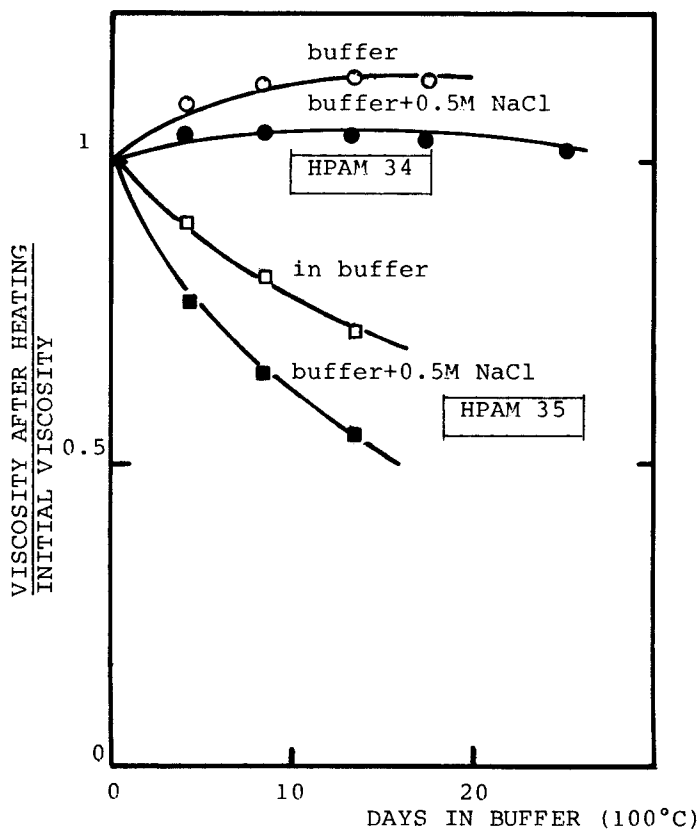


Figure 3. Viscosity retention after heating at 100°C in buffer (pH=6.8):  
 HPAM 35: commercial polyacrylamide ( $\bar{M}_w = 3.4 \cdot 10^6$ )  
 HPAM 34: laboratory purified polyacrylamide ( $\bar{M}_w = 1.57 \cdot 10^5$ )

These experiments indicate that oxygen itself should not degrade polyacrylamide solutions if the solutions are made free of residual impurities. In the case where polymer solutions contain traces of various reducing impurities, oxygen can serve as initiator for a free radical degradation reaction which is found to be accelerated by higher temperature

TABLE III  
LIGHT SCATTERING DATA FOR POLYACRYLAMIDES

DAYS (60°C)	0	4	9	16		
$\bar{M}_w \cdot 10^5$	1.5 <sub>7</sub>	1.6 <sub>3</sub>	1.5 <sub>8</sub>	1.5 <sub>3</sub>		
$A_2 \cdot 10^{-3}$	2.1	2.6	2.3	2.3		
DAYS (90°C)	0	2	4	9	16	32
$\bar{M}_w \cdot 10^5$	1.5 <sub>7</sub>	1.4 <sub>6</sub>	1.3 <sub>7</sub>	1.3	1.5 <sub>3</sub>	1.5 <sub>0</sub>
$A_2 \cdot 10^{-3}$	2.1	2.2	2.4	-	2.9	3.1

Contrary to the case of polyacrylamides from commercial origin, the presence of dissolved oxygen is not detrimental to stability of low molecular weight purified polyacrylamides as shown from viscosity and light scattering data reported here.

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