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Thermal Stability of High-molecular-weight Polyacrylamide Aqueous Solutions

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INTRODUCTION

Partly hydrolyzed polyacrylamides are among the synthetic polymers considered suitable for mobility control (1) although their flexible coil structure greatly limits the number of reservoirs where they can be used. At room temperature loss of solution viscosity is observed in the presence of salts, the rate of viscosity loss increasing as the extent of hydrolysis increases (2). Moreover the viscosity loss is more drastic in the presence of plurivalent cations (Ca^{2+}) than in the presence of monovalent ions (Na^{+}). Also the effect of temperature on polyacrylamide solution stability is a major problem with regard to the feasibility of using polyacrylamides for long periods of time at elevated temperature (3). Particularly the ease of polyacrylamide hydrolysis, which is strongly dependent on the temperature and the pH, is of great importance for field applications (4). Moreover the presence of impurities in not oxygen-free commercial polymers can be responsible for a molecular weight degradation process involving free radicals with a concomitant viscosity loss (5).

We want to present here data which clearly indicate that hydrolysis of amide groups results from heating polyacrylamides even in moderate pH and temperature conditions. From light scattering measurements we show that molecular weight degradation of polymer chains occurs upon heating in the presence of oxygen. Such a degradation process is not directly related to the hydrolysis of amide groups and is attributed to a synergistic effect of temperature, oxygen and residual impurities.

EXPERIMENTAL

Polymers. Two polyacrylamides from commercial origin have been investigated (Table I).

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TABLE I

HIGH MOLECULAR WEIGHT POLYACRYLAMIDES

Polymer	$\bar{M}_w.10^6$	Hydrolysis extent(τ)
HPAM 25(Calgon)	3.4	31%
Pusher 700 (Lot 06.77)(Dow)	7.5	30%(contains 10% CO_3Na_2)

Measurements. Polymer solutions were made in distilled water with pH in the range 4-10.The investigated temperature was in the range 60-100°C.The polymer solutions were not oxygen free and no additive was added.At various time intervals,samples are removed from the oven,cooled at room temperature and the solution properties of heated solutions were measured and compared to the data before heating.

Hydrolysis extents were determined from potentiometric, conductimetric and spectral measurements on cooled solutions percolated through cationic exchange resins after the heating treatment.

Molecular weights ($\bar{M}_w$) were determined in salt solution from light scattering measurements made by using a low angle laser light scattering photometer KMX6 (Chromatix) at 23°C.Clarification of aqueous solutions was obtained using 0.45 or 1.2 micron filters (type MF,Millipore).

RESULTS

Hydrolysis increase upon heating

As shown in Figures 1 and 2,increase in the extent of hydrolysis of both polyacrylamide samples results from heating at 60°C and 90°C.As it is clear hydrolysis of amide groups into carboxylic groups is observed to be strongly dependent on both pH and temperature. Higher temperature and lower pH result in increasing rate of hydrolysis thus indicating the strong effect of H^+ ions on the kinetics of the hydrolysis process (4).It is interesting to note that hydrolysis occurs even at moderate temperature (60°C) and in pH conditions near the neutrality.Such an evolution of polyacrylamides can be of primary importance in oil field applications as it is known that the salt tolerance is strongly dependent on the extent of hydrolysis. This is particularly important for oil reservoirs containing divalent ions (Ca^{++},Mg^{++}) as precipitation can occur if the extent of hydrolysis is too high (above 40%).We have previously shown that this hydrolysis increase partly explains the decreased viscosity of heated polymer solution when measured in the presence of salts (4,6).The precipitation observed with Ca^{++} is fully consistent with the increasing charge density of polyacrylamides resulting from hydrolysis. This phenomenon has been recently confirmed (3).

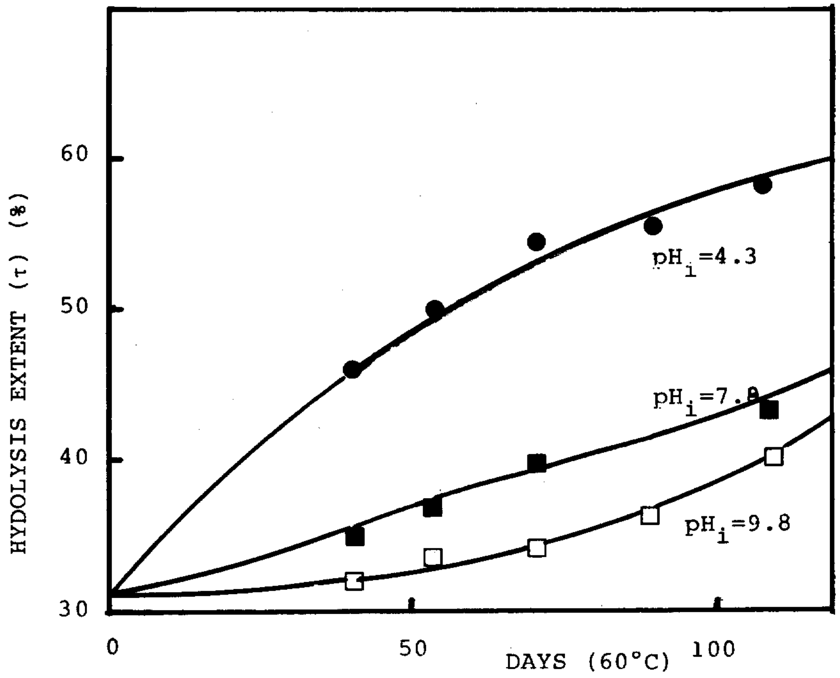

Figure 1. Hydrolysis increase of HPAM 25 (τ_i=31%) during heating (60°C) in water.Effect of the initial pH.

Molecular weight degradation

Scattered light intensities measured at low forward scattering angles were used to calculate the weight-average molecular weight $\bar{M}_w$.$\bar{M}_w$ was obtained from a linear extrapolation to zero concentration of the light scattering data obtained from solutions of different concentrations.Also the absolute second virial coefficient A_2 can be obtained from such measurements (from A_2 changes,informations are available concerning hydrolysis extents and $\bar{M}_w$ changes).

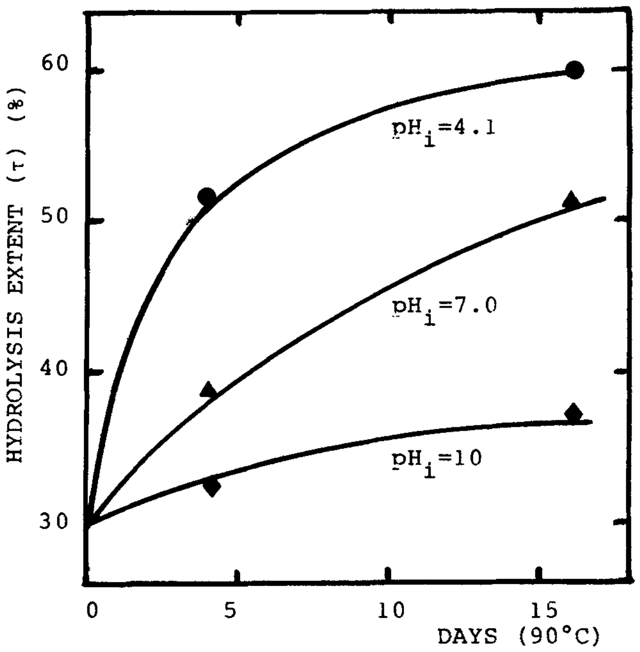

Figure 2. Hydrolysis increase of Pusher 700 (τ_i=30%) upon heating (90°C) in water.Effect of the initial pH.The solutions were made free of the CO_3Na_2 they contained by ultrafiltration.

Figure 3 shows the molecular weight degradation resulting from heating a polyacrylamide sample at 90°C for 6 days in the presence of oxygen.

A molecular weight degradation of near 85% is found. By comparison with data reported in Table II it is clear that higher temperature accelerate polymer degradation due to oxygen contamination.

In Table II are reported the light scattering data for HPAM 25 solutions (0.1M KCl,pH=7.1) heated at 60°C during 100 days.

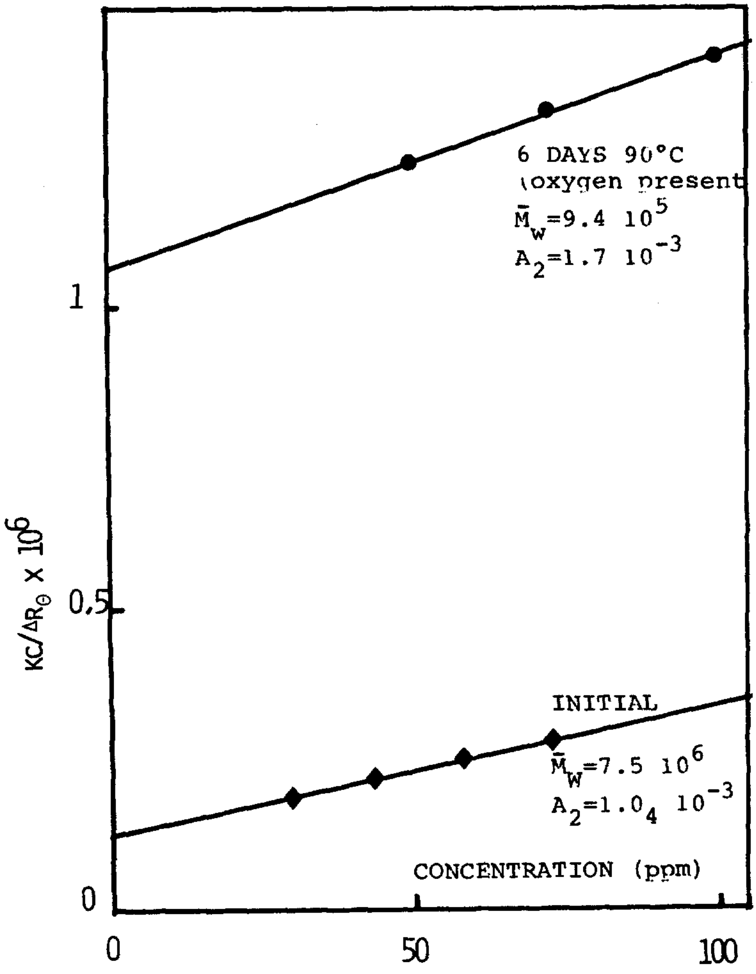

Figure 3. Molecular weight degradation of Pusher 700 (Lot 06.77) (pH_i=9.4;10 g/l NaCl) during heating at 90°C in the presence of oxygen.

TABLE II

THERMAL DEGRADATION OF HPAM 25 IN THE PRESENCE OF OXYGEN (TEMPERATURE:60°C;pH_i=7)

DAYS(60°C)	0	3	10	34	40	51	75	100
$\bar{M}_w \cdot 10^6$	3.4	2.2	1.9	1.5	1.2	0.9	0.7	0.57
$A_2 \cdot 10^{-3}$	1.3	1.2	1.0	2.0	-	1.6	2.0	2.4
$\Delta M_w/M_w$(%)	0	35	45	56	64	73	79	83
τ (%)	31	-	-	-	34	37	39	41

As indicated by data reported in the above table, heating in the presence of oxygen is responsible for a molecular weight degradation of polyacrylamides evidenced by the $\bar{M}_w$ loss (near 80% after 100 days). Also the values of A_2 (a measure of total excluded volume effect) are found to increase upon heating in agreement with the decreasing $\bar{M}_w$ values.
The molecular weight is found to drop sharply in the beginning of heating (0-10 days) and then to decrease more progressively upon further heating (10-100 days). The initial $\bar{M}_w$ drop is dependent on the temperature as indicated by data reported in Figure 3 but the same limiting M_w value is obtained for the two investigated temperatures.
As shown in Table II the molecular weight degradation is not related to the hydrolysis of amide groups:in the first 40 days the molecular weight degradation is near 65% whereas the percentage of hydrolysis increase is only near 10% (31→34%).

It is well recognized that commercial polymers very often contain small amounts of residual impurities which can have an adverse effect on polymer degradation in solution when oxygen is not excluded from the system (oxydation-reduction reactions involving free radicals)(7).From other experimental data not yet published (8) the thermal molecular weight degradation can be ascribed to the synergistic effect of oxygen and impurities.Excluding the impurities and/or scavenging the causes of instability,a good polymer thermal stability can be obtained even in the presence of dissolved oxygen (8).

CONCLUSION

The above reported data show that temperature affects the stability of commercial polyacrylamide solutions in two different ways:

-hydrolysis process of amide groups,which is pH and

temperature dependent.
-molecular weight degradation process which is strngly dependent on the presence of both oxygen and residual impurities.
The first process that increases the anionic character of polymers is responsible for the viscosity loss in the presence of monovalent salts and for eventual precipitation in the presence of divalent salts even if the molecular weight is not changed.Such a process will be governed by pH and temperature of oil reservoirs.
The second process also leading to decreased viscosity values (even if the extent of hydrolysis is not changed) can be avoided or limited by appropriate precautions (excluding oxygen,adding stabilizers).

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