High Molecular Weight Hydrolyzed Polyacrylamides. III. Effect of Temperature on Chemical Stability

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Synopsis

The effect of temperature (100°C) and heating time (up to 384 hr) on the physicochemical properties of high molecular weight ($\overline{M}_p \simeq 4 \times 10^6$) partly hydrolyzed ($\tau \simeq 31\%$) polyacrylamide (HPAM-25) solutions with initial pH values near 4 and 7, respectively, is reported. Potentiometric and spectroscopy data indicate that upon heating the solutions for 16 days the extent of hydrolysis is increased up to around 90%. The viscosity behavior, especially in the presence of bivalent salt (CaCl$_2$), can be explained by taking such an increase in hydrolysis into consideration. From light scattering data, it is shown that the conformational changes are not correlated with molecular weight degradation.

INTRODUCTION

The conformational properties, the viscosity behavior, and the dimensions of weak polyelectrolytes such as partly hydrolyzed polyacrylamides are very sensitive to pH and the nature and concentration of mineral salts. We recently reported the dependence at room temperature of molecular dimensions on the ionic strength for polyacrylamides ($\overline{M}_w \simeq 4 \times 10^6$) hydrolyzed to various extents.[1] It has been shown that too highly hydrolyzed samples, say, above 50%, are very sensitive to the presence of bivalent salts (CaCl$_2$, MgCl$_2$) leading in some circumstances to gelation and precipitation, which considerably reduces the effectiveness of such polymers, for example, in oil recovery. In the application of polyacrylamides in oil fields it is of primary importance to ensure that the polymer solutions remain effective over long periods of time at elevated temperatures. Some literature data are concerned with the effect of temperature on polyacrylamide solution stability; additives and/or purging with nitrogen are said to prevent oxygen and thermal degradation.[2-10] It should be noted that in most reported data, the loss of viscosity (measured in the presence of salt) for heated samples is attributed to degradation.

It is known that hydrolyzed samples can be obtained from acidic and/or alkaline hydrolysis of polyacrylamide. In slightly acidic medium (pH $\simeq$ 4), the reaction proceeds slowly. Strong acid conditions, therefore, are generally used, and consequently fully hydrolyzed product, i.e., poly(acrylic acid), can be obtained. However, insolubility is observed for intermediate products owing to intramolecular imidization.[11] Moreover, alkaline hydrolysis leads to partly hydrolyzed samples with a limiting value near 70%.[12-14]

Here, we wish to present some results concerning the behavior and properties of polyacrylamides that have been subjected to thermal treatment. We paid particular attention to chemical changes that might occur during such experiments.[15]

EXPERIMENTAL

The investigated samples ($\overline{M}_w \simeq 4 \times 10^6$) were of commercial origin (Calgon Corp.). The effect of temperature was studied by heating 0.1% (1000 ppm) polymer solutions (in distilled water and in $0.1M$ NaCl) to 100°C (reflux temperature) for times up to 384 hr. Samples were then cooled to room temperature. Preliminary tests were performed on unhydrolyzed polyacrylamide (HPAM-0) solutions either purged with nitrogen or not. In both cases the viscosities of cooled samples were of the same order of magnitude and very near that before heating. The following results are thus primarily concerned with the effect of temperature on the properties of polyacrylamide samples hydrolyzed to an extent of about 31% (HPAM-25).

Two solutions were prepared with initial pH values near 4 and 7, respectively. The former (sample of H^+ form, degree of neutralization $\overline{\alpha} = 0$) was obtained by percolation of the sodium salt (pH 7, $\overline{\alpha} = 1$) through a cationic exchange resin. Both samples were then heated in salt-free water (without additives) with special care to avoid evaporation during the thermal treatment. The effect of temperature was checked by removing samples at various time intervals. Potentiometric, spectroscopic, viscometric, and light scattering data of removed and cooled samples were compared to the original properties.[1] The heated samples were percolated through a cation exchange column for performing potentiometric titration to ensure that the degree of neutralization $\overline{\alpha}$ is always 0.

RESULTS

In Table I, the changes in viscosity (measured in water at a shear rate of about 1000 sec^{-1}) and the pH resulting from heating HPAM-25 solutions (initially as the acid or the sodium salt, respectively) are given. From previous data, it was shown that[1] such changes are clearly indicative of increased hydrolysis. In the case where the initial pH is near 4, the degree of neutralization after heating is also higher than the initial one (liberation of NH_4^+ ions), which explains the large viscosity increase. For pH 7 the viscosity and pH changes are primarily because of the variation of the extent of hydrolysis.

TABLE I
Viscosity and pH Changes During Heating at 100°C of HPAM-25 Samples in Distilled Water[a]

Heating time, hr	pH	η_{sp}/C_p, dl/g	Initial $\overline{\alpha}$
		$C_p{}^b = 0.1\%$	
0	3.75	42	0
3	4.96	212	
20	—	438	
45	4.73	260	
360	4.92	202	
		$C_p{}^b = 0.023\%$	
0	7.1	148	1
48	6.5	160	
96	6.5	157	
384	5.9	105	

[a] The solutions were not percolated from ion exchange columns.
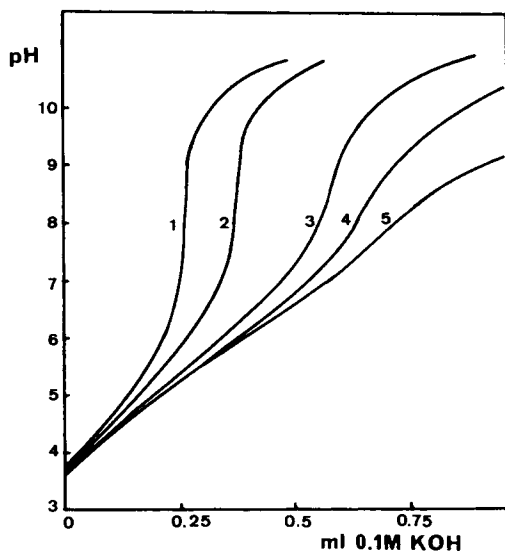[b] C_p = polymer concentration.

Fig. 1. Potentiometric titration (in 0.02M KCl) of HPAM-25 solutions ($\bar{\alpha} = 0$) before heating (1) and after heating for 3 hr (2), 20 hr (3), 48 hr (4), and 15 days (5). The polymer concentration C_p is the same in all cases and the heated solutions are percolated through cationic exchange resin.

Figure 1 shows the titration curves of HPAM-25 (initially at $\bar{\alpha} = 0$) before and after heating to 100°C for various times (the heated solutions are percolated through ion exchange resin). The comparison between titration curves 1 and 2 through 5 at constant polymer concentration C_p indicates clearly that the extent of hydrolysis is increased upon heating (displacement of the equivalent point). The flattening also signifies increased hydrolysis. In this respect, it must be noted that in the case where the heated solutions are not percolated, the initial pH is higher, and, significantly, there is a flattening from pH 8, both in water and/or in the presence of salt. These two points indicate that the heated solutions are no longer at $\bar{\alpha} = 0$ and that KOH is needed to neutralize the released ammonia (pK $\simeq$ 9.25). The hydrolysis increase is otherwise well confirmed by spectroscopic data. The IR shoulder located at 1615 cm^{-1} (NH$_2$) disappears progressively in the heated sample and is replaced by a band near 1710 cm^{-1} (C=O acid). In addition, the differences observed in the far-UV spectra (between 190 and 200 nm) unambiguously show the progressive hydrolysis of the amide groups upon heating. From potentiometric data and changes in the molar extinction coefficient (ϵ), it is found that the extent of hydrolysis of a sample heated to 100°C for 16 days is increased up to about 90% (Table II).

TABLE II
Effect of Heating on UV Spectra of HPAM-25 in Water Solution
($C_p = 1.4 \times 10^{-3}M$, Initial pH 4)[a]

	Heating time, hr						
	0	3.5	24	48	72	216	384
$\epsilon_{192.5\ nm}$, cm^{-1} mole l.$^{-1}$	1424	1280	1043	834	673	378	230
τ, %	31	47	58	68	76	90	95

[a] At $\lambda = 192.5$ nm, ϵ is 2280 for HPAM-0 and 170 for HPAM-100, poly(acrylic acid); τ is calculated from $\tau = (2280 - \epsilon)/21.1$.

As shown in Figure 2, the same behavior is observed when the HPAM-25 solutions are heated in the sodium salt form ($\overline{\alpha} = 1$, pH $\simeq$ 7). In this case the hydrolysis proceeds more slowly, but the conversion limit is nearly the same.

In Figure 3(a), the viscosity changes (measured in 0.1M NaCl) for HPAM-25 samples after heating in 0.1M NaCl are reported. The two samples had initial pH values of 4 ($\overline{\alpha} = 0$) and 7 ($\overline{\alpha} = 1$). In the former case, the viscosity first increases, then reaches a maximum, and decreases upon heating. Such a behavior is closely related to the hydrolysis changes reported above and to the pH increase stated in Table I. For HPAM-25 at pH 7, the viscosity is found to decrease continuously. The difference observed between curves 1 and 2 in Figure 3(a) is understood by taking the different pH values into account, i.e., the number of ionized groups is larger at pH 7. As the viscosity is a measure of the size and shape of the polyions in solution and is strongly dependent on ionization and salt concentration, precautions must be taken in the interpretation of viscosity data.

Figure 3(b) shows the viscosity behavior of two HPAM-25 samples (pH 4 and 7) after heating in water. The viscosity was measured in water and in the presence of $CaCl_2$, respectively. It is important to note that in pure water the viscosity of both heated samples is larger than that of the original one; this is not true in the presence of a bivalent salt. Such viscosity changes are in agreement with increased hydrolysis upon heating. It is obvious that upon heating the chains first assume more extended conformation in water because of the presence of a larger number of carboxylic groups and the resulting electrostatic interactions. In the presence of $CaCl_2$, the viscosity is strongly decreased; this points to collapse of the polymeric coils until precipitation for the highly hydrolyzed samples. The higher the extent of hydrolysis and the pH, the more drastic the decrease in viscosity.

It has been reported in the literature that high molecular weight polyacrylamide undergoes an aging effect leading to a decrease in aqueous solution viscosity, and many explanations have been proposed,[16-25] including chain degradation.[26] Light scattering measurements have been performed to determine if these viscosity changes are correlated with molecular weight variations. In this respect, we have shown previously that hydrolysis of polyacrylamide at 63°C in an excess of KOH yields hydrolyzed samples without a change in molecular weight.[1] Results reported in Table III indicate that the observed viscosity
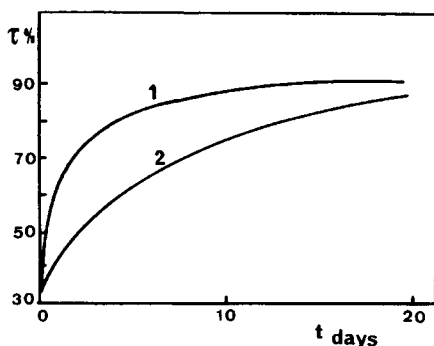

Fig. 2. Effect of heating time (t) on the extent of hydrolysis (τ) of salt-free HPAM-25 solution: (1) initial pH 4 (H^+ form, $\overline{\alpha} = 0$); (2) initial pH 7 (Na^+ form, $\overline{\alpha} = 1$).
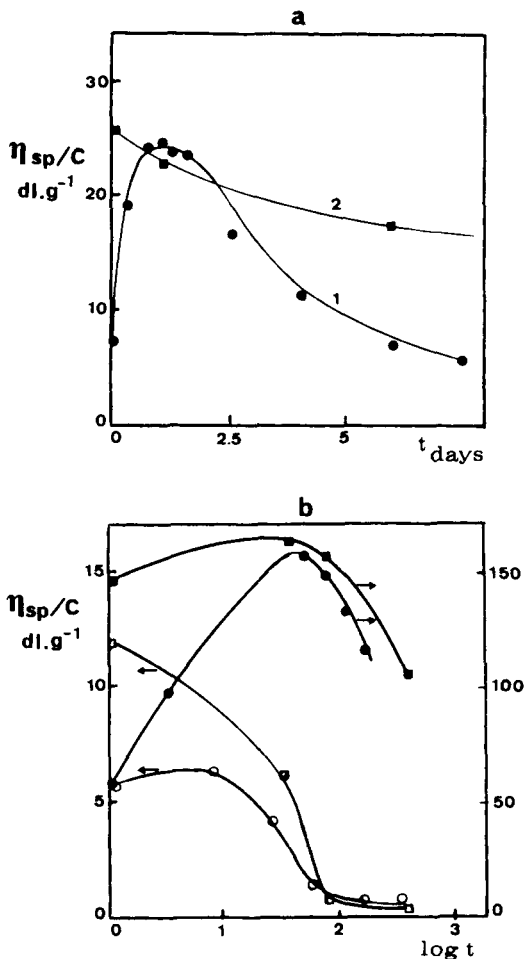
Fig. 3. (a) Reduced viscosity change for HPAM-25 ($C_p = 0.08\%$) heated in $0.1M$ NaCl; initial pH 4 (curve 1) and 7 (curve 2). (b) Reduced viscosity versus heating time in water; reduced viscosity in water (right scale) for HPAM-25 solutions at initial pH 4 (●, $C_p = 200$ ppm) and 7 (■, $C_p = 234$ ppm); reduced viscosity in the presence of CaCl₂ (left scale) for HPAM-25 solutions at initial pH 4 (○, $3 \times 10^{-3}M$ CaCl₂) and 7 (□, $8 \times 10^{-3}M$ CaCl₂) (in both bases $C_p = 800$ ppm).

changes can be explained not by degradation but by conformational changes resulting from an increase in hydrolysis upon heating.

As both the degree of neutralization $[\bar{\alpha}]$ and the extent of hydrolysis (τ) are

TABLE III

Light Scattering and Viscosity Data in $0.1M$ NaCl for HPAM-25 (Initial pH 4, $\bar{\alpha} = 0$) Heated in Water (100°C)

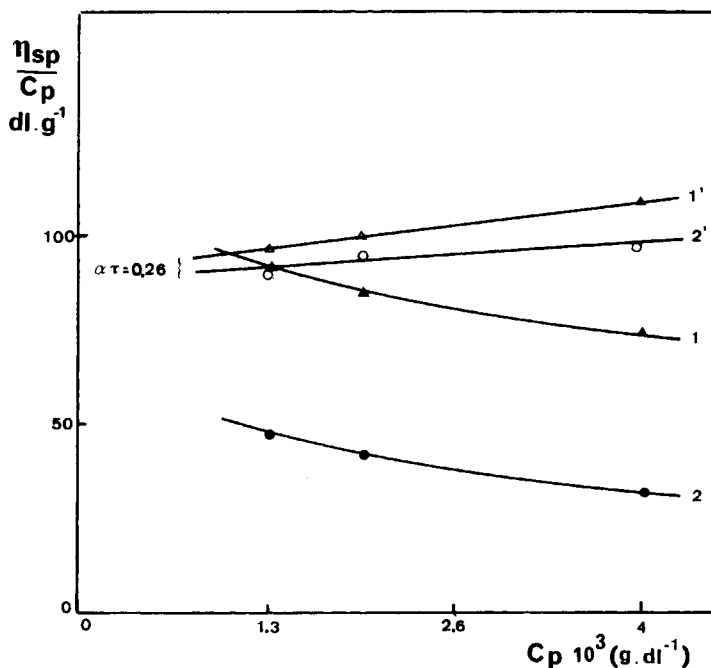|	Heating time, hr						
	0	24	48	72	120	216	384
$[\eta]$, dl/g	8	13	12.2	9.5	8.7	6	5
$(R_g)_z$, Å	1300	—	2000	—	—	—	1550
$\overline{M}_w \times 10^6$	4	—	4	—	—	—	4
$\bar{\alpha}\tau$	0 (31%)						$\simeq 0.25$ (86%)

Fig. 4. Dependence of reduced viscosity η_{sp}/C_p (in dl/g) on polymer concentration C_p for HPAM-25 in water at $\bar{\alpha} = 0$, before heating (1) and after heating for 16 days (2) and at the same charge density $\alpha\tau = 0.26$ before heating (1') and after heating (2').

increased upon heating, the comparison before and after heating must be made at a same value of the charge density ($\alpha\tau$). Under such conditions, we found dimensions of the same order of magnitude for both unheated and heated samples (in $0.1M$ NaCl): unheated HPAM-25 ($\bar{\alpha} \simeq 0.7$, $\tau = 31\%$, $\alpha\tau \simeq 0.21$), $(R_g)_z \simeq$ 1700 Å; heated HPAM-25 ($\bar{\alpha} \simeq 0.25$, $\tau = 86\%$, $\alpha\tau \simeq 0.21$), $(R_g)_z \simeq 1500$ Å.

As illustrated in Figure 4, the reduced viscosities for both initial and HPAM-25 samples heated in water are also close to the same $\alpha\tau$ value (1' and 2'); the difference observed at $\bar{\alpha} = 0$ (for this the heated sample has been percolated through cationic resin) is to be ascribed to the fact that self-ionization (α) is decreasing as the extent of hydrolysis is increased ($\alpha = 0.12$ for $\tau = 31\%$ and 0.06_7 for $\tau = 86\%$).

CONCLUSIONS

Our results show that high extents of hydrolysis (90%) can result from heating (100°C) a partly hydrolyzed polyacrylamide sample under slightly acidic (pH 4) and/or neutral (pH 7) conditions. The viscosity behavior of heated samples is ascribable to the increase in hydrolysis, as clearly shown by potentiometric and spectral data. The results point to conformational changes but are not correlated with molecular weight degradation.

In the application of polyacrylamides, especially in enhanced oil recovery, this chemical instability must be taken into consideration.

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