Alkaline Hydrolysis of Polyacrylamide and Study on Poly(acrylamide-co-sodium acrylate) Properties

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ABSTRACT

Polyacrylamide is prepared by free radical polymerization mechanism in aqueous solution, using ammonium persulphate as initiator. Poly(acrylamide-co-sodium acrylate) or partially hydrolyzed polyacrylamide (PHPA) with different degrees of hydrolysis was obtained by alkaline hydrolysis of polyacrylamide using sodium hydroxide as hydrolyzing agent. The intrinsic viscosity of copolymers with different degrees of hydrolysis was measured with Ubbelohde capillary viscometer in 0.2 M sodium sulphate solution and related molecular weights ($M_w$) were estimated using Mark-Houwink equation. The results show that the intrinsic viscosity of copolymers increases with increasing the hydrolysis degree. We also found that sodium hydroxide as a hydrolyzing agent influences the $M_w$ of parent polymer and causes significant reduction in product $M_w$ while slight reduction has been reported. The degrees of hydrolysis of copolymers were determined based on a standard back titration method. In addition to titration method, IR spectra bands identified the carboxyl groups.

Key Words: anionic polyelectrolyte, polyacrylamide, degree of hydrolysis, poly(AAm-co-NaAc), alkali hydrolysis

INTRODUCTION

Partially hydrolyzed polyacrylamide (PHPA) molecules carry polar amide groups and ionizable carboxyl groups, which impart water solubility to the polymer. The carboxyl groups dissociate and leave negatively charged macro-ions and positively charged counterions leading to polyelectrolyte property in aqueous solution. In comparison with neutral polymers polyelectrolytes gain some advantages. Their solution viscosity is higher than neutral polymers with same concentration, consequently they present better rheological properties as thickening agent.

Anionic polyelectrolytes based on acrylamide were found to reduce surface charge and enable the particles to coagulate. Anionic acrylamide based polymers, derive their unique properties from the density and distribution of negative charges along the polymer backbone. Anionic functional groups can interact with suspended charged particles and destabilize the suspension thereby causing the coagulation to occur.

As a result of anionic character, PHPA absorbs disperse particles possessing positive charges through ionic attraction and some neutral particles through hydrogen bonding. Therefore, with
appropriate $M_w$ and charge density it can be used as a strong flocculent for waste-water treatment.

It is seen from published papers that PHPA is one of the most widely used and technically important water-soluble polymers. Further uses are for papermaking agents to increase the wet strength of paper, drilling fluid additives for shale stabilizing, pushing fluid and profile modifier in oil recovery.

In general polyelectrolytes can be produced by chemical modification of neutral polymers, homopolymerization of ionic monomers or copolymerization of a non-ionic monomer with an ionic monomer.

In theory for production of PHPA resins there are three different chemical methods as follows [1]:

1. The hydrolysis reaction of polyacrylamide with an acid or base.
2. Copolymerization of acrylamide with acrylic acid.
3. The aminolysis of polyacrylate.

Of these three methods, commercial processes usually use one of the first two reactions. The acid form of PHPA is produced by second and third methods. For industrial applications the sodium salt of PHPA is mainly produced by the first method.

The first method involves polymerization of acrylamide and subsequent alkaline or acidic hydrolysis reaction. Acrylamide is most often polymerized to high molecular weight by free radical addition mechanism in aqueous solution. The polymerization reaction of acrylamide follows the theory of free radical polymerization [2].

Other polymerization techniques such as mixed solvents system; dispersed phase polymerization and inverse emulsion polymerization also have been reported [3,4,5]. In this work, the first method was employed to produce PHPA with different levels in degrees of hydrolysis. The molecular weight of the parent polymer and PHPA were determined and the transport properties in dilute solution were investigated.

**EXPERIMENTAL**

**Material**
The ammonium persulphate, sodium hydroxide, hydrochloric acid and sodium sulphate were obtained from Merck and used without further purification. Acrylamide for polymerization was obtained from Aldrich. The technical grade of methanol was used as precipitating liquid.

**Apparatus**
The Ubbelohde capillary viscometer was used to measure the relative, specific and reduced specific viscosity (dL/g) of 0.02, 0.04, 0.06 and 0.075g/dL of the polymer solutions from the flow times of solutions ($t_i$) and of 0.2M aqueous sodium sulfate ($t_v$) as solvent. The viscosity measurements were carried out at a constant temperature of 25°C. The solution temperature was controlled by a thermostat in a circulating bath and monitored by a thermometer. A stopwatch with a resolution of 0.1 s was used to measure the flow times. By plotting the reduced specific viscosity (dL/g) of polymer solutions against concentration (g/dL), extrapolating to infinite dilution and taking the intercept, the intrinsic viscosity [$\eta$] is determined.

Infra-red spectra were recorded on a Bruker model IFS 48 spectrophotometer.

**Polymerization of Acrylamide**
A 500 mL round-bottom flask was fitted with a mechanical stirrer and thermometer and a nitrogen gas inlet tube. The reaction flask was introduced with 200 mL distilled water, acrylamide (0.14 mol) and ammonium persulphate ($2.19\times10^{-4}$ mol) as initiator. The flask was placed in a water bath and polymerization was carried out at 60°C for about 20 min under nitrogen atmosphere. The reaction mixture was precipitated by adequate methanol. The precipitated polymer was dried in an oven at 50°C for 24 h.

**Alkaline Hydrolysis of Polyacrylamide**
In order to be able to investigate a range of PHPA polymers with an equal degree of polymerization but different levels of ionic groups, polyacrylamide was taken as the parent polymer and subjected to alkaline hydrolysis. Reaction time and amount of added base to the system governed the ratio of the acrylate functional group to acrylamide functional group. The amount of 200 mL of about 10 percent solution of
polyacrylamide was used for hydrolysis. The required amounts of base to achieve various degrees of hydrolysis were calculated based on stoichiometric relationships and are summarized in Table 1.

The hydrolysis reaction started at 60°C by adding aqueous solution of sodium hydroxide to the reactor containing polyacrylamide just before gel formation. A mechanical stirrer adjusted at 200 rpm speed was used for mixing. Measuring the pH of the reactor content monitored the progress of the hydrolysis reaction. When the pH remained on 9, the hydrolysis reaction was stopped. The resulting product was poured into methanol and polymer was precipitated and vacuum dried at 50°C to constant weight. In this way the products with different degrees of hydrolysis ranging from zero to 50% were obtained.

### Determination of Degree of Hydrolysis

To determine the degree of hydrolysis, a weighed portion of sample is dissolved in water and the resulting solution was acidified with 0.1 N hydrochloric acid to a pH = 3 [6]. The acidified solution was back titrated with 0.1 N standard solution of sodium hydroxide to pH = 7, using an electronic pH meter as an indicator. The number of equivalents of base required bringing the polymer solution from PH=3.0 to pH=7.0 was equal to the number of equivalents of sodium carboxylate groups. The neutralization reaction of carboxylic acid groups by sodium hydroxide is as follows:

\[
R-CH_2-CH-COOH + NaOH \rightarrow R-CH_2-CH-COONa + H_2O
\]

From these data, the percent of hydrolysis (carboxyl content) was calculated in accordance with the following equation:

\[
N_1V_1 = N_2V_2 \tag{1}
\]

The results are summarized in Table 2.

### RESULTS AND DISCUSSION

#### Hydrolysis Reaction

The required times for the hydrolysis reaction to be completed are presented in Figure 1. As seen in the Figure, the degree of hydrolysis of polymers increases with increasing reaction time. Theoretically it is possible to produce 100% sodium polyacrylate by starting with polyacrylamide, but in practice it is impossible to achieve [7].

Polyacrylamide shows an abnormal behaviour on alkaline hydrolysis. The reaction rate is quite high at the initial stage and decreases rapidly with increasing conversion. The slowdown of the rate of the hydrolysis of polyacrylamide has been attributed to the polymer structure [8]. In the alkaline medium, accumulation of negative charges on the polymeric chains exerts an electrostatic repulsion effect towards the hydroxyl ion; as a consequence it causes a decrease in the rate of reaction. As a result of retardation phenomena in the hydrolysis reaction, the introduction of carboxyl groups cannot increase beyond 67% even at long reaction times [7].

#### Molecular Weight and Viscosity Determinations

The molecular weight of a polymer is very important in its synthesis and application. A polymer is very rarely monodisperse and any specification of
molecular weight is an average value. It is also important to know how the molecular weight is determined. One of the methods of estimation of molecular weight of a polymer is based on Mark-Houwink equation. Mark-Houwink equation, which can be expressed as follows:

\[ [\eta] = K_{[\eta]} M^{a} \]  

(2)

Where, \( M \) is molecular weight (dalton), \([\eta]\) is called intrinsic viscosity (dL/g), \( K \) and \( a \) are constant parameters.

The intrinsic viscosity is the limit of reduced specific viscosity when the polymer concentration is approaching zero. The molecular weight of a polymer can be estimated using Mark-Houwink equation, if \( K \), \( a \), and \([\eta]\) are known.

The reduced specific viscosity was plotted vs. polymer concentration as a straight line. Plot of reduced specific viscosity vs. concentration of unhydrolyzed polyacrylamide (parent polymer) is presented in Figure 2. The polymerization time for this sample was 20 min. Intrinsic viscosity which was obtained by extrapolating the concentration to zero is 4.32(dL/g), \( K \) and \( a \) are \( 2.43 \times 10^{-4} \) and 0.69 in 0.2 M aqueous sodium sulphate solution at 25°C, respectively (10). By substituting these data in Mark-Houwink equation the molecular weight was found to be 1,438,990 dalton.

Another sample was prepared in 25 min to study the influence of polymerization reaction time on molecular weight. For this sample the intrinsic viscosity was extrapolated to be 6 (dL/g) and the
molecular weight was found to be 2,316,315 dalton.

As it is expected the molecular weight increases significantly with increasing polymerization time. Longer reaction times allow growing radical chains to react with more monomer units to reach higher degree of polymerization. Continuing the polymerization reaction leads to gel formation.

Because of polyelectrolyte behaviour of PHPA in solution the molecular weight of PHPA is very difficult to characterize precisely. The difficulties encountered in viscometry are the variations of Mark-Houwink constants with degree of hydrolysis if all other parameters are unchanged. Meiling et al. [9] described a simple method for determining molecular weight of PHPA using single point method of determination of intrinsic viscosity. In another attempt to find a relationship between Mark-Houwink constants and degree of hydrolysis, Wu et al. [10] obtained two empirical polynomial equations for K and α as functions of degree of hydrolysis, as follow:

\[ \alpha = C_0 + C_1 \text{HD} + C_2 (\text{HD}^2) + C_3 (\text{HD}^3) \]  

where, \( C_0 = 0.625, C_1 = 8.86 \times 10^3, C_2 = -2.40 \times 10^4 \) and \( C_3 = 2.48 \times 10^6 \).

\[ \log k = d_0 + d_1 \text{HD} + d_2 (\text{HD}^2) + d_3 (\text{HD}^3) \]  

where, \( d_0 = -3.36, d_1 = -2.39 \times 10^2, d_2 = 6.96 \times 10^4 \) and \( d_3 = -7.37 \times 10^6 \).

One can calculate the values of K and α precisely at any polymer composition of interest, over the range of 6-40% acrylate content from polynomial expressions. The reduced specific viscosity vs. concentration for PHPA samples with different degrees of hydrolysis are presented in Figure 3.

Using \([\eta]\), extrapolated from Figure 3, K and α from polynomial expressions the molecular weights were determined and summarized in Table 3.

The molecular weight of parent polyacrylamide, which hydrolyzed to PHPA as determined before, is 1,438,990 dalton. It is observed that the molecular weight of PHPA has been decreased markedly in comparison with parent polymer. The chemical hydrolysis reaction causes a significant degradation of polymer chains in contradiction to the other report [11]. Mechanical mixing and grinding operation also affect the molecular weight of the polymer.

The Effect of Degree of Hydrolysis on Intrinsic Viscosity \([\eta]\)

Partially hydrolyzed polyacrylamide molecules contain randomly distributed polar carboxyl groups and behave as polyelectrolyte in aqueous solution.

The carboxyl groups carry negative charges and polymer solution becomes an anionic polyelectrolyte. Polyelectrolyte properties originate from the combination of macromolecular and electrolyte behaviour. Because of the repulsion forces between ionized carboxyl groups, polymer chain extends and uncoils in the solution. Therefore, the effective size or volume of the polymer molecules increase which leads to larger hydrodynamic interactions between polymer chains and water molecules. This influences

![Figure 4. Intrinsic viscosity vs. degree of hydrolysis.](image-url)
transport properties of the polyelectrolyte and increases the intrinsic viscosity.

The above analysis has been supported by our experimental work as it is seen in Figure 4. With increasing the hydrolysis degree or fraction of ionizable carboxyl groups on the backbone of the polymer chain, the intrinsic viscosity increases (data in Table 3). By increasing hydrolysis degree the intrinsic viscosity first rises sharply due to the electrostatic repulsion between charged groups along the polymer chains. In other word because of the repulsion forces between the negative charges (carboxyl groups), the original coiled molecules of polyacrylamide uncoil as hydrolysis proceeds, and molecules become more extended, thereby increasing the flocculation ability as well as viscosity of solutions [12]. Further increase in hydrolysis degree leads to smoothness of the slope of the curve because the rate of reaction decreases. The decrease in reaction rate is due to accumulation of negative charges on polymeric chains; hence the hydrolysis cannot go to completion [8]. The height of this maximum is strongly influenced by the polymer concentration, the salt concentration, the chain length and the molecular weight distribution. It must be noted that information discussed so far applies to dilute solution. Very dilute solutions in water contain only individual, unassociated polymer coils.

Characterization of Functional Groups of PHPA by FTIR

The functional groups of the synthesized copolymers were investigated by Fourier transform infrared spectrophotometer. The spectrum of the copolymer confirms the existence of the carboxylate and amide functionalities evidenced by the absorption peaks at 1560, 1400, 1615, 1660 and 3350 cm\(^{-1}\), respectively [13]. The region between 1500-1800 cm\(^{-1}\) shows that the band located at 1615 cm\(^{-1}\) (amide group) disappears, whereas a band near 1660 cm\(^{-1}\) (acid group) becomes more important as the samples become more hydrolyzed (Figure 5).

CONCLUSION

Polymerization of acrylamide, initiated with ammonium persulphate, was carried out in aqueous medium. Hydrolyzed polyacrylamide (PHPA) resins were prepared under alkaline condition with various degrees of hydrolysis varying from zero to 50%. The degree
of hydrolysis of PHPA resins was determined by back titration with 0.1 N sodium hydroxide solution. IR spectrophotometer was employed for the confirmation of chemical structure of resins.

The intrinsic viscosity \([\eta]\) and related molecular weight of PAM and PHPA resins were studied.

The results of this research work are summarized as follows:

- As the number of acrylate groups per unit of the polymeric chains increases, the solubilizing effect of these groups increases
- As the degree of hydrolysis increases, the number of anionic groups on polymer chains increases. By increasing the anionic groups, the polymer chain becomes more straightened, thus the intrinsic viscosity of polymer solutions would increase as well.
- It is believed that, molecular weight of PAMs would decrease during alkaline hydrolysis with sodium hydroxide.
- At high degree of hydrolysis, the rate of reaction decreases due to repulsion forces between the carboxyl and hydroxyl groups, therefore the hydroxyl groups cannot diffuse into the polymeric chains and hydrolysis cannot go to completion.

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