

# Synthesis of High Molecular Weight Partially Hydrolyzed Polyacrylamide and Investigation on its Properties

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## ABSTRACT

A continuous process for the polymerization of acrylamide and hydrolysis of functional groups in alkaline condition has been carried out. It was found that acrylamide may be polymerized and hydrolyzed in a single consequential step, whereby, both degrees of polymerization and hydrolysis can be carefully controlled. The hydrolysis of polyacrylamide up to 10 and 60% degrees was facilitated in suitable amount of different alkalines. The degree of hydrolysis of samples was determined by a back titration method. We have found that sodium carbonate as an hydrolyzing agent, also acts as a retarder and its addition to polymerization solution reduces the rate of polymerization reaction. The measured molecular weight of samples shows that we have reached a high molecular weight (about 12 million) and excellent water solubility. Another interesting result obtained is that the copolymer solutions showed a non-newtonian shear thinning behaviour. On the other hand, the associative behaviour is observed between the samples.

### Key Words:

polyelectrolytes;  
polyacrylamide;  
partially hydrolyzed;  
high molecular weight;  
anionic flocculant.

## INTRODUCTION

Polyelectrolytes are polymers which possess many ionizable groups. They may be cationic (ionized polymer carrying positive charges), anionic (ionized polymer carrying negative charges) or amphoteric (ionized polymer which may carry both positive

and negative charges). The most common polyelectrolytes are based on polyacrylamide with high molecular weight up to about 20 millions. There are not many papers related to obtaining high molecular weight hydrolyzed polyacrylamide (HPAM). In aqueous

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solution, ionization gives rise to a polyion bearing negative charges, accompanied by small counterions. The degree of ionization for weak polyelectrolytes depends on the pH of the solution. But strong polyelectrolytes are fully ionized over a wide range of pH. Counter ions are not totally independent of the polyion; they tend to concentrate in its vicinity, giving rise to an ionic atmosphere. According to Manning [1], if the charge density on the polyion exceeds a critical value, counter ions condense onto the polyion, limiting the effective charge density. Therefore the polymer chain cannot accept the negative charge more than this critical value.

Many products are colloids (two-phase systems in which one phase has a dimension in the size range 1 nm -10  $\mu\text{m}$  in the matrix phase) or dispersion of larger particles. Colloids or dispersions are used in many processes [1]. Depending on the nature of the polymer such as; charge density and molecular weight, adsorption of a polymer onto the surface of dispersed particles may have either of two effects: stabilization and flocculation.

- During the stabilization process, association and settling of the particles are inhibited and the particles remain in a dispersed state for a long period of time. Application of this phenomenon appears in paints, cosmetics, detergents, pharmaceutical and foods

- During the flocculation process, the particles interact so as to be easily separated from the surrounding medium and form aggregates. Application of this phenomenon appears in water treatment, paper manufacturing, mineral enrichment and recovery from mining.

Water soluble acrylamide (AM)-based polymers are important in a number of industrial applications for such purposes as rheology control agents, adhesives [2] and viscosity control agents for enhanced oil recovery [3,4]. However, the most relevant applications of polyacrylamide (PAMs) with respect to this article are their uses as flocculent, as this might apply to paper manufacturing, mineral enrichment, recovery from mining and water-treatment processes [5]. High molecular weight anionic PAMs with low charge densities are useful as flocculent. In contrast, low molecular weight anionic PAMs with high charge densities are used as dispersants.

## EXPERIMENTAL

### Materials

Acrylamide was used as received. Sodium sulphate,

sodium carbonate and sodium hydroxide were of technical grades. Standard 0.1N hydrochloric acid and 0.1N sodium hydroxide solution were used as received. Potassium persulphate and sodium bisulphite were of technical grades.

### Apparatus

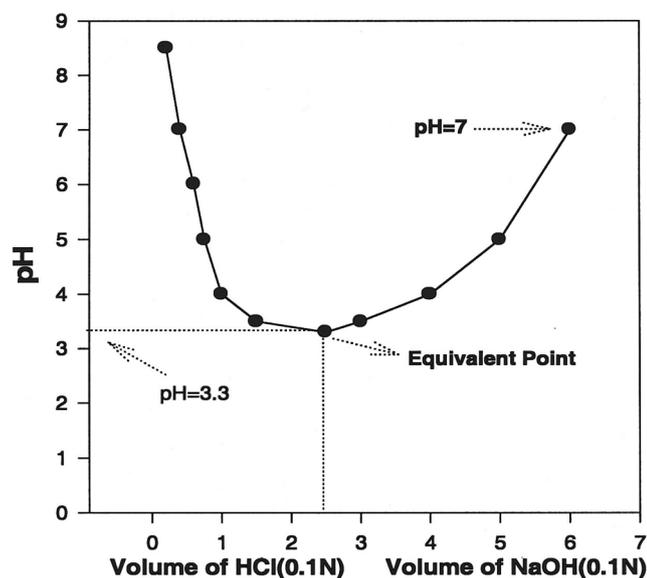
Solution (0.5% w/w) viscosities of polymers were measured by the means of a rotational viscometer, model ST-DIGIT R, Selecta. Depending on the viscosity, various angular speeds and spindles can be used for rheological characterization of polymer solution. The viscometric experiments were carried out using 50, 60, 100 and 200 shear rates at room temperature. IR Spectra are taken with a Bruker model IFS 48 spectrophotometer, taking samples in film forms.  $^1\text{H}$  NMR spectra are taken with a Bruker 500-MHz instrument using TMS as the reference and  $\text{D}_2\text{O}$  as the solvent. The molecular weight of samples was measured with the help of a low-angle laser light scattering photometer model SEMATech 633 at wavelength of 633 nm and  $25^\circ\text{C}$ . The samples were applied in water solvent.

### Polymerization

A random copolymer of poly (AAM-co-sodium acrylate) was prepared by radical polymerization [6]. This copolymer is a partially hydrolyzed polyacrylamide (HPAM) with different degrees of hydrolysis ranging from 10-60%. Various ratios of AAM (0.098 mol. for HPAM 30%) and single or mixture of alkalines (sodium carbonate, 0.0294 mol. for HPAM 30%, caustic soda and sodium sulphate) as hydrolyzing agent were dissolved in 100 mL water and the solution was purged with nitrogen for 30 min. Polymerization reaction was initiated by addition of a mixture of 0.1 gram redox initiator made of potassium persulphate and sodium bisulphite. The reaction mixture was then heated up to  $80^\circ\text{C}$  for several hours. The mixture was stirred by a mechanical throughout the time. In this way high molecular weight polymer was obtained by controlling the initiator concentration at a minimum amount. The product was precipitated by methanol as white and solid mass. The product was air dried and pulverized.

### Quantification of Acrylate Content

A pH meter equipped with a glass and reference electrode quantified the functional groups with different ranges. 0.1 Gram of each HPAM sample was dissolved



**Figure 1.** 0.1 Gram sample was titrated with 0.1N NaOH solution after the pH was lowered to 3.3.

in 200 mL distilled water (Figure 1). The pH of the aqueous solution was about 8.5. Hydrochloric acid (0.1N) solution was dripped until the pH was reached 3.3. This solution dropped titrated with aqueous solution of sodium hydroxide (0.1N) until the pH was raised piecewise to 7. The milliequivalent gram of sodium hydroxide consumed is equal to the number of acrylate content of each samples [7].

## RESULTS AND DISCUSSION

It is known that, as the reaction temperature decreases, the degree of polymerization increases. On the other hand, as the reaction temperature is increased, the degree of hydrolysis increases. Therefore, in order to obtain a desirable product, it is necessary to control the temperature during the polymerization and hydrolysis of acrylamide. We synthesized the polymer through one step polymerization in which the polymerization and hydrolyzing were performed in a single step. In order to be able to investigate and to prepare a hydrolyzed polyacrylamide, we have used different alkalines to examine the behaviour of each alkaline and its effect on the polymerization rate and hydrolysis. By using the different alkalines, we determined the required time to reach lower pH values which is an

indication of alkaline reaction with polyacrylamide. During these experiments it was found that sodium carbonate is a convenient base for lowering to reduce pH to nearly 8.5. We know that sodium carbonate is a hydrolyzing agent, but it also acts as a retarder and its presence to polymerization solution reduces the rate of polymerization reaction [8], although in the case of other alkalines we cannot observe this behaviour. So by this method, the polymer has enough time to go under hydrolysis reaction. Also we used small amount of initiator and suitable temperature of 80°C to reach a high molecular weight polymer. We know that the high molecular weight polymers can bridge better compared to low molecular weight polymers between the particles, thereby causing them to be adsorbed and form flocs. Many commercial polymeric flocculants are, in fact, polyelectrolytes, either anionic or cationic. These polyelectrolytes can destabilize the suspension particles merely through two different mechanisms; charge neutralization and polymer bridging or both of them simultaneously [1]. In polymer bridging, the molecular weight, and in case of charge neutralization, the charge density plays an important role. Also the presence of charged segments along a polymer chain could have a significant effect on bridging flocculation which will be discussed later. Hydrolyzed polyacrylamide is an anionic polyelectrolyte, carrying plenty of negative charges along the polymer chain. Although polyacrylamide is a nonionic polymer, the hydrolysis can occur readily, converting some of the amide groups to carboxylate ions. This gives an anionic polyelectrolyte with a charge density, depending on the degree of hydrolysis and pH value of the solution. The properties of a polyelectrolyte chain in solution are influenced by the repulsion between charged segments, which tend to give more extended configuration. This tendency is most pronounced at low ionic strength, but it is reduced by screening of charges at high salt concentrations. Since more extended chain might be expected to give an enhanced bridging possibility, it might be expected that flocculation would be enhanced at low ionic strength. Also at low ionic strength there would be a greater repulsive distance between the chains, which needs to be spanned. Another important consideration is that anionic polyelectrolytes are frequently used to flocculate negatively charged particles. In order for adsorption to occur some specific affinity must be pres-

ent to outweigh the electrical repulsion which would operate between a negative surface and anionic segment of the chain. Again, ionic strength would be expected to play an important role, since the dissolved salt would effectively reduce this repulsion and promote adsorption. It is known that ionic polyacrylamide will not be adsorbed on many negative particles unless a certain concentration of divalent metal ions such as  $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$  are present. In the absence of such ions, clay particles cannot be flocculated by anionic polyacrylamide because cationic ions promote the adsorption of polyacrylate and produce an enhanced attraction force. The degree of anionic character is also important.

In the case of polyacrylamide, this can be controlled by the degree of hydrolysis and it is found that there is some optimum value, which gives most effective flocculation. This may represent a balance between a certain degree of chain extension and the tendency to be adsorbed on negative surfaces. Michaels[1] found that about 30% HPAM (hydrolyzed PAM) gave optimum flocculation of clay suspensions. He also established that higher molecular weight polymers gave better flocculation. By summarizing all the observed evidence on bridging flocculation, the following general points can be made:

- Higher  $M_w$  polymers are better than lower molecular weight polymers.
- Linear polymers are better than branched cross-linked polymers.
- In the case of polyelectrolytes, there may be an optimum charge density on the polymer chain.
- Ionic strength effects with a possible optimum value are important.
- Very strong flocs can be formed by polymer bridging between different particles.

### Characterization of the Products

The IR and H NMR data of the samples are represented in Table 1 and Figure 2, respectively. As expected, both  $^1\text{H}$  NMR and IR spectra confirm the presence of reacted monomers in the copolymer. The IR spectrum of the copolymer confirms the existence of the carboxylate and amide functionalities indicated by the absorption peaks at 1600, 1667 and  $3347\text{ cm}^{-1}$ , respectively [9]. A typical presentation of  $^1\text{H}$  NMR and IR spectra of one of the copolymers is shown in Figures 2

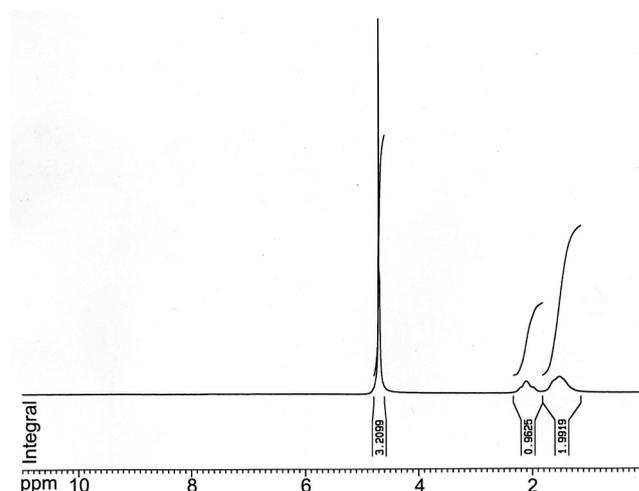


Figure 2.  $^1\text{H}$  NMR Spectrum of sample of HPAM 60%.

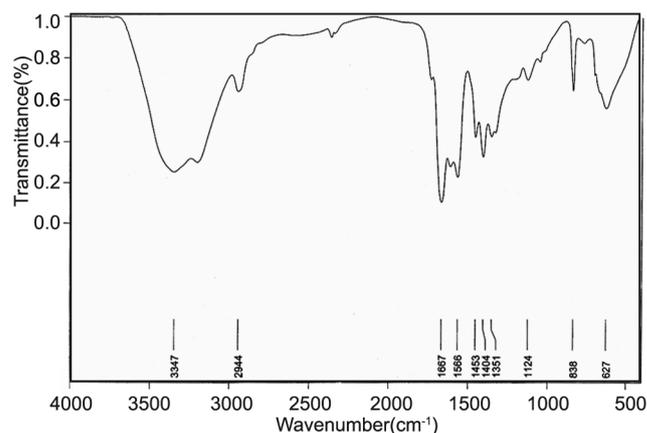


Figure 3. FTIR Spectrum of HPAM 60%.

and 3. The result of light scattering data showed that the  $D_n/dc$  is equal to 0.163 and molecular, i.e.  $11,757,475\text{ g/mole}$ . So we may claim to have obtained a high molecular weight polymer by controlling the ini-

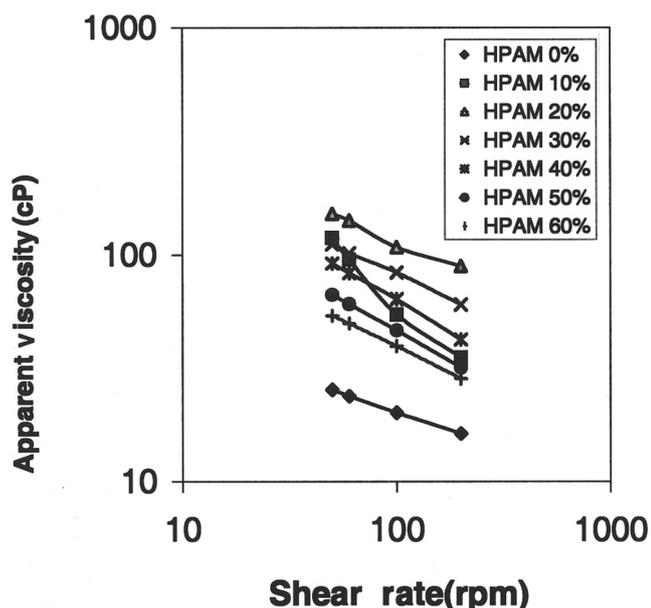
Table 1. IR Data and interpretation.

Peak ( $\text{cm}^{-1}$ )	Interpretation
3347	N-H and O-H stretching
2944	C-H stretching
1667	C=O stretching
1600	O-C-O- stretching
1453	$-\text{CH}_2-$ bending
1404	-C-H bending

tiator concentration of a minimum amount and at optimum temperature. A uniformity in the degree of hydrolysis is observed during the reaction polymerization for the product obtained.

### Effect of Shear Rate on Solution Viscosity

It is apparent from Figure 4 that the copolymer solutions shows a non-newtonian shear thinning behaviour (Table 2) within the experimental range of shear rates. The curves show that the apparent viscosity ( $\eta_{app}$ ) decreases with increasing the shear rate of solutions [10]. A reduction in viscosity as shear rate increases is an indication of the fact that electrostatic interactions between the particles are surpassed by viscous forces applied to the solutions. As a result, at high shear rate the polymer chains are aligned in the direction of flow which results in a viscosity reduction or shear-thinning behaviour. An increase in apparent viscosity is observed with hydrolysis of the sample, however the trend is reversed at around 20% of hydrolysis (Figure 5). The increase in apparent viscosity may be attributed to the association phenomenon which causes an increase in hydrodynamic volume of the polymer chains. The reduction in apparent viscosity is due to the increase of negative charges on the polymer chain resulting in a coil-like configuration. This reduces the hydrodynamic volume of the chains and also the asso-



**Figure 4.** Shear rate dependence of the apparent viscosity of a 0.5%(w/w) aqueous solution of polymers at 25°C.

**Table 2.** Viscosities of samples at different range of shear rates.

Sample no.	Hydrolysis degree (%)	Shear rate (rpm)			
		50	60	100	200
1	0	25.44	23.84	20.16	16.32
2	10	119.04	95.41	54.52	35.18
3	20	152.1	142.18	108.3	89.25
4	30	111.52	101.6	83.62	60.32
5	40	91.68	83.2	63.68	42.25
6	50	66.72	60.64	46.4	31.84
7	60	53.92	49.76	39.52	28.48

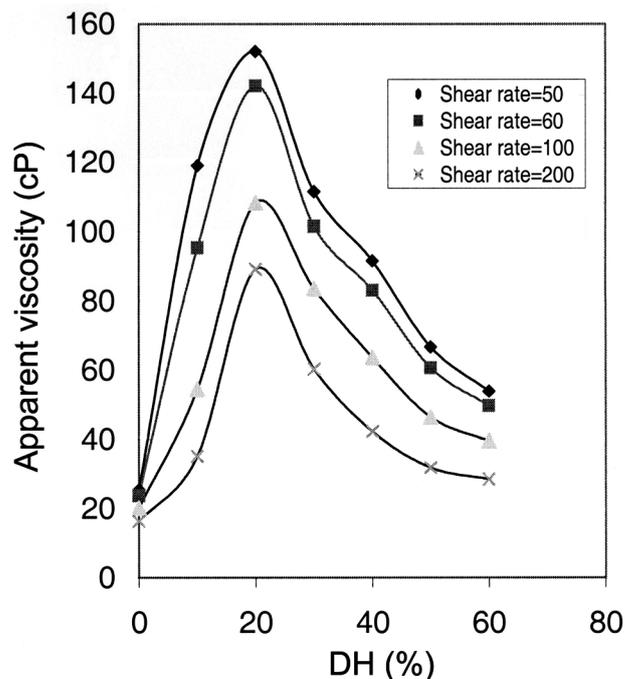
ciation phenomenon, leading to a decrease in apparent viscosity. The viscosity of solutions obey the power-law equation. Power-law as expressed below:

$$\eta = K \gamma^{(n-1)}$$

where, n-1 is the slope of the line,

$\eta$  is called the apparent viscosity,  $\gamma$  is shear rate and K is power-law constant.

According to this equation the slope of the lines



**Figure 5.** 0.5% (W/W) aqueous solution apparent viscosity (cp) of polymers vs. %DH at 25°C.

**Table 3.** Rheological characteristics of polymer solutions at various degree of hydrolysis.

DH (%)	Equation	n-1	n
0	$Y = -0.0574X + 27.324$	-0.0574	0.9426
10	$Y = -0.4981X + 127.09$	-0.4981	0.5019
20	$Y = -0.3976 X + 163.72$	-0.3976	0.6024
30	$Y = -0.3198 X + 122.04$	-0.3198	0.6802
40	$Y = -0.3118X + 102.17$	-0.3118	0.6882
50	$Y = -0.2197X + 73.91$	-0.2197	0.7803
60	$Y = -0.1611X + 59.43$	-0.1611	0.8389

(n-1) and n have been calculated (Table 3). The resulting data derived from shear rate shows that as the quantity of n increases and reaches one, the sample solution behaviour is more newtonian like and also it becomes less shear sensitive.

## CONCLUSION

During polymer hydrolysis with different alkalines, we found that sodium carbonate acts as a retarder and addition of this alkaline to polymerization reaction causes the rate of polymerization reaction to decrease. Wherein, in the case of sodium hydroxide addition, the  $M_w$  decreases and acts as scissors to lowers the  $M_w$  of the final polymerization products. Therefore, the sodium carbonate has two important roles such as in a single step polymerization and hydrolysis of acrylamide. Firstly, it acts as an alkaline to convert the amide group to sodium carboxylate and secondly as a retarder to prevent prepolymerization of monomer. The measured molecular weight of samples shows that we have reached a high molecular weight and excellent solubility. Another result obtained was that the copolymer solutions show a non-newtonian shear thinning behaviour and at high shear rate, the polymer chains are aligned in the direction of flow which result in a viscosity reduction or shear-thinning behaviour. On the other hand, an increase in apparent viscosity is observed with hydrolysis of the sample, however the trend is reversed at around 20% of hydrolysis wherein the sample with 20% degree of hydrolysis has a high associative behaviour.

## REFERENCES

1. Finch C.A., *Industrial Water Soluble Polymers*, The Royal Society of Chemistry, Cambridge CB4 4WF, Cornwall, UK, 62-75 (1996).
2. Thomas W.M., Wang D.W., *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Mark H.F., Bikales N.M., Overberger C.G., Menges G. (Eds.), Wiley, New York, 7, 169-211 (1986).
3. Borchardt J.K., *Oil-Field Chemistry: Enhanced Recovery and Production Stimulation*, Borchardt J.K., Yen T.F. (Eds.), Am. Chem. Soc., Washington, DC, 27-39 (1989).
4. Ibid 446-465 (1989).
5. Klimchuk K.A., Hocking M.B., Lowen S., Water - soluble acrylamide copolymers, IX. Preparation and characterization of the cationic derivatives of poly(acrylamide-co-N,N-dimethylacrylamide), poly(acrylamide-co-methacrylamide), and poly (acrylamide-co-N-t-butylacrylamide), *J. Polym. Sci. Part A: Polym. Chem.*, **39**, 2525-2535 (2001).
6. Salamone J.C., *Polymeric Materials Encyclopedia*, Vol. 1, A-B, CRC, 47-61 (1996).
7. Norris M.V., Snell F.D., Hilton C.L. (Eds.), *Encyclopedia of Industrial Chemical Analysis*, Wiley-Interscience, New York, 4, 160-180 (1967).
8. Kurenkov V.F., Abramova L.I., Homogenous polymerization of acrylamide in solutions, *Polym. Plast. Technol. Eng.*, **31**, 659-704 (1992).
9. Zeynali M.E., Rabii A., Alkaline hydrolysis of polyacrylamide and study on poly(acrylamide-co-sodium acrylate) properties, *Iran. Polym. J.*, **11**, 269-275 (2002).
10. Russel W.B., Saville D.A., Schowalter W.R., *Colloidal Dispersions*, Cambridge University, Cambridge, UK, 258-309 (1991).