

Preparation of nonionic polyacrylamide flocculant and its application in removal of clay suspensions

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Nonionic polyacrylamide has been prepared with different molecular weights using the solution polymerization technique to be used in clay suspension removal. The effect of the polymerization conditions on the molecular weight, conversion yield of the prepared polyacrylamide, and its impact on the efficiency of the flocculation process has been studied and partially optimized.

تم تحضير بولى اكليراميد غير مشحون بأوزان جزيئية مختلفه باستخدام تقنية بلمرة المحاليل لاستخدامه فى معالجة الطفله المعلقه فى مياه الصرف الصناعى. تم دراسة تأثير ظروف البلمره على الوزن الجزيئى و معدل تحول المونيمر الى بوليمر للبوليمرات المحضره و مدى تأثير ذلك على كفاءة عملية التجميع.

Keywords: Solution polymerization, Nonionic polyacrylamide flocculant, Flocculation, Colloidal suspensions, molecular weight

1. Introduction

Recently water-soluble polymers of high molecular weight have drawn much attention due to their various practical applications. The nonionic flocculants are large homo polymers of acrylamide with a wide range of molecular weights. The major market for high molecular weights polyacrylamide flocculants is in the treatment of industrial wastewater to affect rapid solid-liquid separation. Their effect as flocculants is due to bridging between particles by polymers chain. The fields of application for using these flocculants depend only on its molecular weight. For example, polyacrylamide with high molecular weight is mainly used as flocculant, while the medium molecular weight is used in paper as dry fortifier, but low molecular weight can be applied as disperser. So the molecular weight of polyacrylamide is the key factor to determine its application [1].

It is well known that high molecular weight polyacrylamides have only been obtained commercially via aqueous solution polymerization of acrylamide. Acrylamide [1, 2] has a very fast propagation rate and a high exothermic heat of polymerization, which leads to the main disadvantage of solution polymerization of acrylamide, increasing solution viscosity. These

limits the synthesis of high molecular weight polymers. Agitation is a problem and polymer degradation can occur. Polymerization is usually stopped at ca. 10-15% conversion.

Alternative polymerization processes such as inverse-emulsion and precipitation polymerization have been studied. In emulsion polymerizations stable water in oil emulsion of the monomer is prepared and polymerized under conditions that are much more isothermal using the oil phase to dissipate the heat of polymerization. Wide ranging polymers can be manufactured using this emulsion polymerization technique, however, the major disadvantages associated could be:

- i. Shelf life of the emulsions, because emulsions are prone to separate especially in high ambient temperatures, and
- ii. When used in application which require potable grade of polymers because the oil used for making emulsion cannot be removed prior to use [3-5].

Precipitation polymerization of acrylamide can approach 100% conversion because the polymer precipitates from the solvent system and the solution never becomes viscous. [6-11]

Free radical initiators, such as peroxides, persulfates, azo compounds, and redox pairs are used for the manufacture of aqueous

solutions. Acrylamide will also undergo polymerization by exposure to heat, high-energy radiation, ultrasonic waves, ultraviolet radiation, and ionic polymerization catalysts to produce water-soluble or swell able polymers. Aqueous solution polymerization is the most common technique.

The presence of trace metal ions can interfere with initiation systems, causing premature polymerization and reduced molecular weight. As a result, the polymerization vessels are glass-lined or stainless steel with de-oxygenation capability, such as vacuum or nitrogen purging.

Polymer molecular weight can be varied by several techniques, including monomer concentration, initiator concentration, polymerization temperature, and chain-transfer agents. Above 15wt % monomer concentrations, there may be enough total heat of polymerization to cause the system to boil rapidly. Boiling can be prevented by running the reaction under pressure or by maintaining a slow rate of free radical generation, which will allow heat removal through the reactor jacket coolant.

The aim of this work is the preparation of polyacrylamide with different molecular weight through controlling of the polymerization conditions and monitoring the impact of molecular weight variation on its flocculation efficiency in the process of clay removal from synthetic wastewater.

2. Materials and experiments

2.1. Materials

1. Acrylamide, was supplied by Fluka chemicals Co. Ltd. (Switzerland), assay $\geq 99\%$. Potassium persulphate [K_2SO_4] supplied by S.D.S. FINE-CHEM Ltd. (England), min assay 98%, chloride not more than 0.04%.

2. Clay powder, Egyptian highly refined Ball clay (smectite- vermiculite) powder of very fine particle size, used mainly for manufacturing refractory bricks and mortar, was obtained directly from Alexandria for Refractories Company. The physical and chemical characteristics of the material (data provided by the manufacturer) are as shown in table 1

Table 1
Characterization of clay powder

| | |
|------------------|------------|
| Particles size | - 325 mesh |
| Moisture | 1% maximum |
| Silica | 51.4% |
| Alumina | 32% |
| Ferric oxide | 2.6% |
| Titania | 2% |
| Calcium oxide | 0.3% |
| Sodium oxide | 0.1% |
| Magnesium oxide | 0.12% |
| Potassium oxide | 0.08% |
| Loss on ignition | 11%. |

2.2. Preparation of clay suspension

Clay suspensions were prepared from clay powder immediately before each set of experiments at 0.25% w/v in distilled water through mixing 2g of clay powder with 800ml of distilled water.

2.3. Preparation of polyacrylamide

Acrylamide monomer is dissolved in distilled water to prepare acrylamide solution of the desired concentration then transferred to 100ml three neck round flask. The solution is purged with nitrogen gas for 30min at room temperature. Predetermined weight of potassium persulphate is added to the monomer solution with continuous bubbling of nitrogen gas for 10 minutes.

Temperature of the reaction medium is adjusted to start the polymerization reaction. After 30 minutes, the stirring is stopped but the nitrogen gas continues to pass through the polymerization vessel atmosphere.

After completion of the polymerization reaction, medium is diluted with distilled water to give the selected flocculant concentration and the medium stirred gently with mechanical stirring until a homogeneous solution is obtained.

2.4. Determination of conversion percent

Polyacrylamide first was precipitated from the polymerization solution by addition acetone to the solution with stirring, then filtrate and dried at 105°C up to constant weight. Estimate the conversion percentage of acrylamide monomer to polymer using the following equation:

Conversion % = $(W / W_0) * 100$.

Where:

W_0 is the weight of acrylamide monomer, and
 W is the Weight of polyacrylamide.

2.5. Determination of relative viscosity

The interstice viscosity of the prepared polyacrylamide was measured using 0.5% homogeneous solution of the previously prepared polyacrylamide by Capillary viscometer (Ubbelohde type). The measurements are made by comparing the efflux time " T " required for a specified volume of polymer solution to flow through a capillary tube with the corresponding efflux time T_0 for the solvent. The relative viscosity of is calculated using the following equation:

$$\text{Relative viscosity} = T / T_0$$

2.6. Flocculation test

A flocculation study of the prepared flocculants was carried out in 0.25 wt% clay suspensions by a standard Jar test procedure, to demonstrate the flocculating ability of prepared polymers. The flocculator used was supplied by J.P. Selecta Company, Spain. Turbidity measurements were carried out using 2100 p Turbidimeter (Hach Co.). The synthetic clay suspension was put in each of six 1L beakers and the flocculant was added in solution form. The following procedure was used for all flocculants. Immediately after the addition of flocculants, the suspension was stirred at a uniform speed of 75 rpm for 2min. this was followed by a slow stirring at 25 rpm for 5min. afterwards; a settling time of 10min was allowed. At the end of the settling period, the turbidity of the supernatant liquid was measured.

3. Results and discussion

3.1. Effect of monomer concentration

The effect of variation of monomer concentration, using 0.001M KPS and polymerization time 4 hours at 50°C, on both the conversion yield of acrylamide monomer to polyacrylamide and the relative viscosity as an indicator for the molecular weight to assess the efficiency of the polymerization conditions was

illustrated in fig. 1. It is clear that both parameters increase with monomer concentration increase. This result could be explained as follow: since the polymerization reaction was carried out using constant initiator concentration and at constant temperature, so the number of the produced free radical as a result of potassium persulphate decomposition is the same in all monomer concentrations. Increasing the monomer concentration will increase the amount of monomer units available for the propagation step and leading finally to longer polymer chains, higher relative viscosity, and higher conversion %.

On the other hand fig. 2 shows the effect of polyacrylamide molecular weight on its flocculation efficiency using the standard jar test procedure. From the figure it is noticed decrease in the residual turbidity with increasing the molecular weight of polyacrylamide. These results are in accordance with those obtained by other authors [12]. They found that higher molecular weight polyacrylamide gave better results, since the effective bridging flocculation require that absorbed polymer extended far enough from a particular particle surface to attach the other particles.

3.2. Effect of polymerization temperature

Since the free radicals are produced from thermal decomposition of potassium persulphate initiator, it is logic to study the effect of

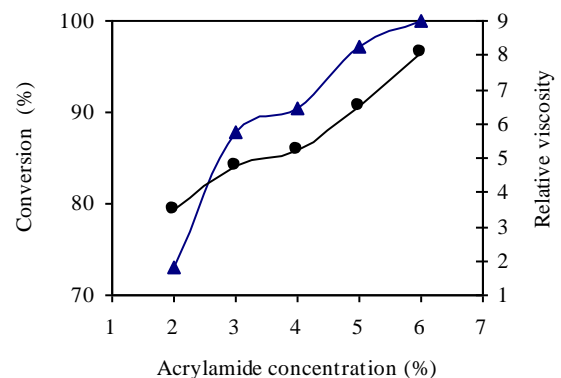


Fig. 1. Effect of monomer concentration on relative viscosity and conversion %: polymerization time = 4 hr; initiator concentration = 0.001M; polymerization temperature = 50°C: (▲) Conversion yield; (●) Relative viscosity.

polymerization temperature on both the characteristic and the efficiency of the prepared polyacrylamide. Temperatures ranging from 50 to 70°C have been investigated. The effect on both conversion % and the relative viscosity are presented in fig. 3. From earlier results we found that polymerization of 6% acrylamide concentration at 50°C, has 100% conversion yield, so increasing the polymerization temperature has no effect on the conversion yield as illustrated in fig. 3. On the other hand, the effect of the polymerization temperature on the relative viscosity or molecular weight of the prepared polyacrylamide is very clear in which the molecular weight decreased linearly with temperature increase. From 50°C to 60°C and dramatically with increasing the temperature above 60°C. A negative impact of the polymerization temperature on the flocculation efficiency has been found fig. 4. The same behavior has been found with different studied monomer concentrations.

The negative effect of the polymerization temperature on the molecular weight of the prepared polyacrylamide and hence on the flocculation efficiency could be explained taking into account that increasing the temperature increase the rate of free radical formation as a result of the thermal decomposition of the persulphate, so the number of chain formed increased. This leads to an increase of polyacrylamide chains, deed the available amount of acrylamide is fixed, so shorter chains, and low molecular weight was obtained.

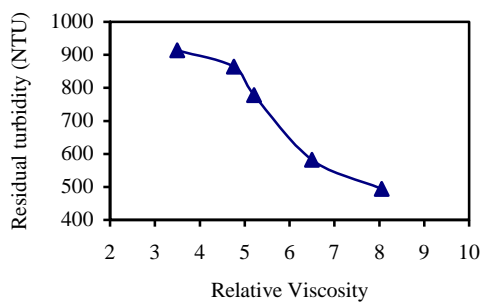


Fig. 2. Effect of monomer concentration on relative viscosity and residual turbidity: polymerization conditions, polymerization time = 4 hr; initiator concentration = 0.001M; polymerization temperature = 50°C: Flocculation conditions, Polymer concentration = 0.5%; polymer dose=1.6ml.

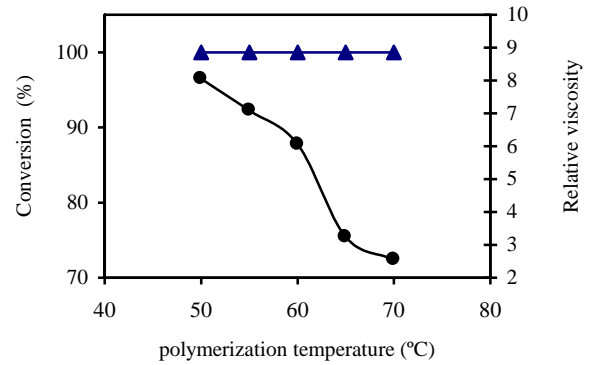


Fig. 3. Effect of polymerization temperature on relative viscosity and conversion %: polymerization time = 4 hr; initiator concentration = 0.001M; monomer concentration = 6%: (▲) Conversion yield; (●) Relative viscosity.

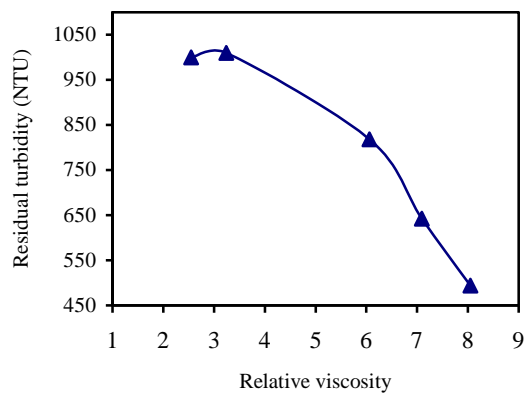


Fig. 4. Effect of polymerization temperature on relative viscosity and residual turbidity: polymerization conditions, polymerization time = 4 hr; initiator concentration = 0.001M; monomer concentration= 6%: Flocculation conditions, Polymer concentration = 0.5%; polymer dose=1.6ml.

3.3. Effect of initiator concentration

From the previous studies the importance of the initiator role in the configuration of the prepared polyacrylamide was deduced. Hence, the effect of the initiator concentration (0.001-0.04M) on the polymerization process was studied fig. 5. The figure shows that increasing the initiator concentration was found to have no effect on the conversion yield since it reaches 100% conversion yield with the lowest initiator concentration. On the other hand, the increase in initiator concentration decreases the relative viscosity of produced polyacrylamide leading finally to decrease the flocculation efficiency (fig. 6).

It is clear that the residual turbidity increased as the molecular weight of polyacrylamide decreased. This decrease is due to the presence of large amount of free radicals in the polymerization media, which consume most of present monomer in initiating new polyacrylamide chains and small amount of monomer, remain for the propagation step. So large number of polyacrylamide chains are produced but with small length or low molecular weight, which is not effective in the flocculation process.

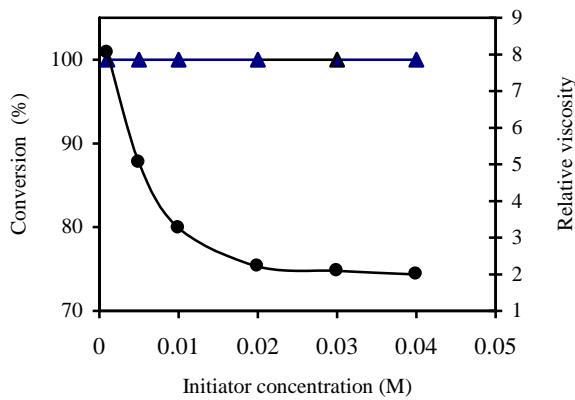


Fig.5. Effect of initiator concentration on relative viscosity and conversion %: polymerization time = 4 hr; polymerization temperature = 50°C; monomer concentration = 6%: (▲) Conversion yield; (●) Relative viscosity.

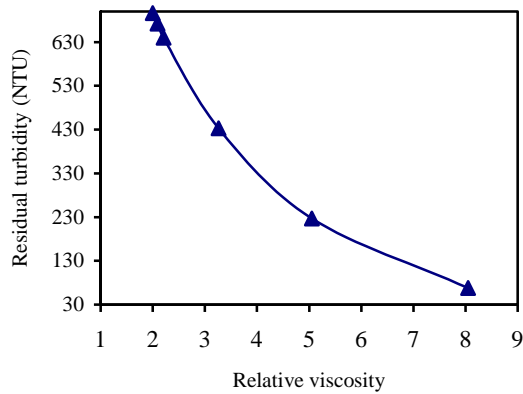


Fig. 6. Effect of initiator concentration on relative viscosity and residual turbidity: polymerization conditions, polymerization time = 4 hr; polymerization temperature=50°C; monomer concentration= 6%; Flocculation conditions, Polymer concentration = 0.5%; polymer dose=1.6ml.

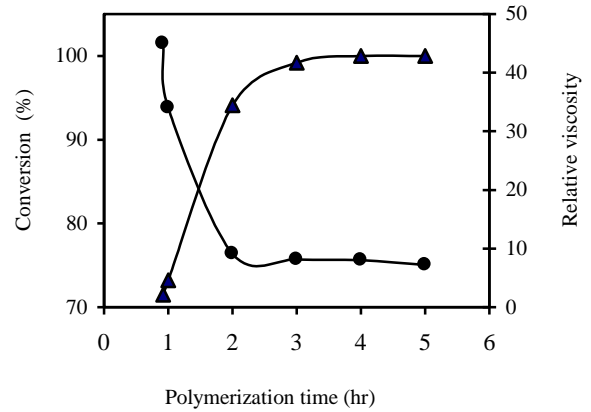


Fig. 7. Effect of polymerization time on relative viscosity and conversion %: initiator concentration = 0.001M; polymerization temperature = 50°C; monomer concentration= 6%: (▲) Conversion yield; (●) Relative viscosity.

3.4. Effect of polymerization time

Gao J. et al. [1] observed that presence of several peroxides such as potassium per sulfate, ammonium per sulfate, and hydrogen peroxide accelerated the degradation of aqueous polyacrylamide at low temperature (40°C), so this study was designed for predict if the presence of the excess initiator concentration at 50°C may degrade the chain length and decrease the flocculation efficiency. Polyacrylamide with higher flocculation efficiency may be prepared in polymerization time shorter than the used time (4 hours).

Various polymerization times has been studied to detect the optimum time for preparing the most effective flocculant figs. 7, 8. The case here is different than that in studying the effect of polymerization temperature & initiator concentration. It was found that reducing the polymerization time to less than 2 hours is very effective in decreasing the conversion %. The case was different for the molecular weight. A mirror image was obtained in which the molecular weight decreased until two hours, then it remained almost constant in the area of 100% conversion. Increasing the polymerization time from 55min to one hour reduces the relative viscosity by about 22%. Further increase beyond 2 hours reduces the relative viscosity again by about 78%.

This is an indication of how much the polymerization time is important in controlling the molecular weight of the prepared poly

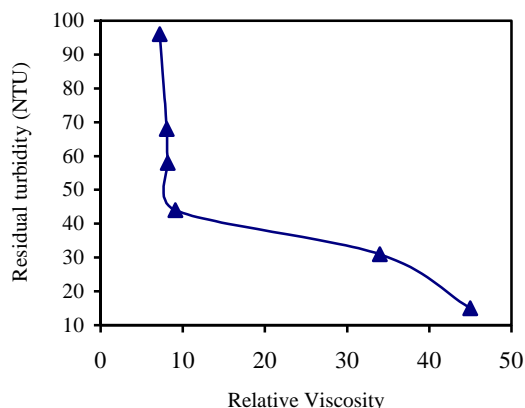


Fig. 8. Effect of polymerization time on relative viscosity and residual turbidity: polymerization conditions, initiator concentration=0.001M; polymerization temperature=50°C; monomer concentration= 6%; Flocculation conditions, Polymer concentration = 0.5%; polymer dose=1.6ml.

acrylamide. On the other hand, fig. 8 represent the effect of the relative viscosity on the residual turbidity. It is noticed that the residual turbidity decreased as the molecular weight increased, and the most effective polymerization time is 55min. This is natural since the relative viscosity was and/or the molecular weight of polyacrylamide dramatically influenced by increasing the polymerization time in negative way, due to the degradation caused by the presence of KPS at such high temperature.

4. Conclusions

1. Increasing the monomer concentration in the studied range increases both the conversion yield and the relative viscosity of the produced polyacrylamide, so increasing the flocculation efficiency of the produced polymer.
2. Increasing the polymerization temperature and the initiator concentration in the studied range, have no effect on the conversion yield of acrylamide but they have a negative influence on the molecular weight of the produced polyacrylamide. Which in turn has a negative impact on the flocculation efficiency.
3. prolongation of polymerization time beyond two hours causes intensive degradation of the

prepared polyacrylamide and/or reducing its molecular weight, hence decreasing its efficiency.

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