

Polyacrylamides Obtained by Redox Polymerization as Flocculants: The Effect of the Polymer Structure on Flocculating Properties

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Redox polymerization of acrylamide using Ce(IV) in conjunction with glycerol, ethyleneglycol and n-propanol was carried out to yield linear and three-armed polymers. The molecular weight depends on monomer and ceric ion concentration. The water soluble polymers obtained and a commercial polymer were tested in the flocculation of suspension of tincal concentrate and the three-armed polymer showed better flocculating properties than linear and commercial polymers.

Introduction

Considerable interest has arisen regarding acrylamide (AA) polymers from an applied standpoint. Especially, polyacrylamides (PAA) have been used as flocculating agents in the treatment of a large variety of aqueous suspension of solids. In these applications, water soluble AA polymers operate by a variety of mechanism including bridging, charge neutralization, complex formation and depletion flocculation [1]. The molecular weight, the charge density of polymer, and the structure of the polymer are the most important characteristics effecting flocculations. The preferred techniques for preparing PAA utilize azo, peroxy or redox initiators in aqueous polymerization. From a practical view point, it is a challenge to prepare high molecular weight PAA without gelation. Several approaches have been reported in the literature for the preparation of soluble high molecular weight PAA [2]. We have recently obtained water soluble PAA with a high molecular weight via a two-step procedure [3]. In this procedure, the polymerization of AA is initiated by 4,4'-azobis(4-cyanopentanol) (ACP)-to yield PAA with hydroxyl terminal groups and then redox polymerization of AA is initiated by hydroxyl-terminated PAA in conjunction with Ce (IV) provided an increase in the molecular weight of the initial polymer. When in possession of an appropriate structural features for the system, water soluble AA copolymers can also be prepared. We have recently used the redox technique to synthesize polyethyleneglycol (PEG)-PAA block copolymers [4]. Their use as flocculants has shown great promise since

attachment of PEG to PAA flocculants may provide additional advantage in practical applications due to the reduced adhesion of flocculated clay during the filtration process.

In this paper, polymerization of AA with glycerol, ethyleneglycol, and n-propanol in the presence of Ce(IV) is investigated to yield polymers with different structures. Their flocculating properties are evaluated and discussed with respect to the effects of their structure.

Experimental

Materials:

Acrylamide, (AA) (Fluka) was recrystallized from ethylacetate; ceric ammonium nitrate (Merck) was used without further purification. The glycerol, ethyleneglycol and n-propanol used for the experiments were of analytical grade (Merck). In flocculation experiments, a sample of tincal concentrate containing 26.8 % of water insoluble material was used.

Redox polymerization:

Schlenk tubes of aqueous solution of AA containing a given amount of hydroxyl compounds were degassed and purged with nitrogen. An appropriate solution of ceric ammonium nitrate in 1 N nitric acid was then added. The polymerization experiments were conducted while stirring in the dark at 30°C. At the end of polymerization, the reaction mixtures were poured into ten-fold acetone and precipitated polymers were filtered and dried.

The molecular weight of polymers, including the commercial one, were determined from the solution viscosities at 30°C in water with the aid of the following equation [5]:

$$[\eta] = 6.8 \times 10^{-4} \overline{Mn}^{0.66} \quad (1)$$

Flocculation Test:

Using a simple laboratory method, the above mentioned polymers were studied in jar-test experiments [6]. PAA-based, conventional polymeric flocculant called Magnoflog 351 supplied by Cyanamide Company was used for comparison. This type of flocculant was chosen because it is recommended for the flocculation of tincal concentrate. An appropriate amount of tincal concentrate, determined from the solubility in water at 15°C was dissolved in distilled water and stirred for 30 minutes at 100 rpm. Different volumes of polymer solution (0.05 %) were added to the suspension while stirring at 70 rpm. The suspension was then mixed for 5 minutes at 100 rpm after the suspension was allowed to settle for 30 minutes. supernatant samples were filtered and the turbidity was determined by using a Hach turbidimeter. In order to determine the visible floc formation time, the 20 ml of polymer solution was added to the suspension while stirring at 70 rpm. The time was measured while the suspension was stirring at 100 rpm.

Results and Discussion

The polymerization of AA with glycerol, ethyleneglycol and n-propanol in the presence of Ce(IV) was carried out by examining the influence of reaction parameters such as Ce(IV) and monomer concentration on the

molecular weight. As stated repeatedly, the control of molecular weight of the polymers is quite important regarding their use in flocculation. As can be seen from Table 1, the molecular weight increases with concentration of ceric ion and then decreases in each case. This behavior may result from the simultaneous effect of the ceric ion concentration on the initiation rate and the oxidative termination of the primary radicals [7]. For this reason, the ceric ion concentration was determined for each alcohol used. As can be seen from Table 2, the molecular weight increases with monomer concentration.

Table 1. The Effect of Ce(IV) Concentration on the Molecular Weights of PAA Obtained by Redox Polymerization ^a

[Ce(IV)]x10 ⁴ (mol/l)	Glycerol ^b	Ethyleneglycol ^c	n-Propanol ^d
	\overline{Mn}	\overline{Mn}	\overline{Mn}
1.5	6.3x10 ⁵	1.3x10 ⁶	6.2x10 ⁵
2.4	1.6x10 ⁶	1.6x10 ⁶	1.3x10 ⁶
3.1	1.1x10 ⁶	1.1x10 ⁶	1.7x10 ⁶
6.9	6.1x10 ⁵	4.3x10 ⁵	2.0x10 ⁶
9.3	-	-	6.5x10 ⁵

a: AA : 2 mol/l in all cases

b: Glycerol : 2.2x10⁻² mol/l

c: Ethyleneglycol : 3.8 x 10⁻² mol/l

d: n-Propanol : 3.8 x 10⁻² mol/l

Table 2. The Effect of Monomer Concentration on Redox Polymerization

[AA] (mol/l)	Glycerol ^a	Ethyleneglycol ^b	n-Propanol ^c
	\overline{Mn}^d	\overline{Mn}^d	\overline{Mn}^c
1.6	1.5x10 ⁶	1.2x10 ⁶	8.9x10 ⁵
2.0	1.6x10 ⁶	1.6x10 ⁶	2.0x10 ⁶
2.4	1.7x10 ⁶	1.3x10 ⁶	1.6x10 ⁶
2.8	1.3x10 ⁶	1.7x10 ⁶	1.8x10 ⁶

a: Glycerol : 2.2x10⁻² mol/l

b: Ethyleneglycol : 3.8x10⁻² mol/l

c: n-Propanol : 3.8x10⁻² mol/l

d: Ce(IV) : 2.4x10⁻⁴ mol/l

e: Ce(IV) : 6.9x10⁻⁴ mol/l

Above obtained polymers with high molecular weight and a commercial polymer were used as flocculants to clear an aqueous solution of colloidal tincal solids. The effectiveness of the polymers listed in Table 3 on the aggregation of the suspension was determined via the jar-test. The results obtained from the flocculation experiments are presented in Table 4 and Table 5. It is observed that the polymers obtained with glycerol are the most effective ones at clearing the suspension in the solution, by given the transparency values, probably due to the three-armed structure of the polymer. Furthermore, it is observed that the visible floc formation times observed with the polymers obtained with glycerol are shorter than those obtained with the other polymers.

These results show that the structure of the polymer as well as molecular weight and charge density of the polymer plays an important role in flocculation.

Table 3. Description of Polymers used as Flocculants

Code	Structure	Molecular Weight
F1	PAA ^a	1.7x10 ⁶
F2	PAA ^b	1.7x10 ⁶
F3	PAA ^c	1.8x10 ⁶
F4	PAA ^d	1.7x10 ⁶

a: Polymer obtained with glycerol

b: Polymer obtained with ethyleneglycol

c: Polymer obtained with n-propanol

d: Commercial Polymer

Table 4. Jar-Test Results of Various Polymers for Suspension of Tincal Concentrate

Flocculant	Supernatant Turbidity (FTU)		
	10 ml	15 ml	20 ml
F1	27	17	10
F2	30	18	15
F3	28	24	16
F4	31	21	16

Table 5. The Results of Visible Floc Formation Time^a

Flocculant	t ₁	t ₂
F1	5	15
F2	8	23
F3	10	25
F4	10	25

t₁: Visible Floc Formation Time (min)

t₂: Large Floc Formation Time (min)

a: Polymer Solution = 20 ml

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