SYNTHESIS AND CHARACTERIZATION OF POLYACRYLAMIDE WITH CONTROLLED MOLAR WEIGHT

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ABSTRACT

High molecular weight poly(acrylamide) (PAM) samples were synthesized using our solution polymerization technique. The reaction was initiated using thermal initiators potassium and ammonium persulphate (KPS and APS), and redox system comprising APS-TMEDA or N,N,N’,N’-tetramethylethylenediamine. The effects of process parameters such as the severity of mixing during polymerization, the ratio of TMEDA/APS in redox system and the polymerization temperature for the thermal initiators on molecular weight of synthesized PAM were investigated. The results obtained showed the distinctive features of the initiation modes. In particular, ultra-high molar mass of PAM were obtained with the redox system at low temperatures. The synthesized polymers were characterized using 1H NMR spectroscopy for their chemical structures and the differential scanning calorimetry (DSC) for their thermal properties.

Introduction

Water soluble polymers find varied types of industrial applications, such as in flocculants, dispersants, retention aids, steric stabilizers and associated thickeners in as diverse areas as municipal and industrial wastewater treatment, flotation, paper making, enhanced oil recovery (EOR) among others (Tripathy & De, 2006; Behari et al, 2001; Sharma et al, 2006; Sastry et al, 1999; Morris & Penzenstadler, 1978). In particular, poly(acrylamide) or PAM finds widespread use in industrial processes such as solid-liquid separation, for example in waste- water treatment, a process in which finely dispersed particles are aggregated to form large flocs that settle readily for ease of separation.

Several mechanisms are suggested with flocculation; among them bridging is the predominant one where PAM having high molecular weight ($M_w > 1$ MDa) is required. In flocculation, polymer chains adsorb onto particle surfaces to form bridges between one or more adjacent particles. Thus, with increasing polymer chain length (molecular weight), more particles are involved, and as a result flocculation improves (Sharma et al, 2006; Taylor, 2005).

This is why substantial interests exist to synthesize high molecular weight PAMs as flocculants.

Various methods have been investigated for the synthesis of polyacrylamides including solution (Okada et al, 1979; Tanaka, 1986; Mabire et al, 1984; Rabiee et al, 2005; Ariffin et al, 2004), emulsion (Cabestany & Trouve, 1983; Davies & Healy, 1999; Coville & Dai, 1999), and dispersion polymerization (Ye et al, 2003; Chen et al, 2006).
Solution polymerization, however, received scant attention for synthesising high molecular weight polyacrylamide despite its advantages and wide use in industry.

The objective of this work was to investigate the solution polymerization technique and the effects of process parameters on molecular weight during synthesis of PAM. The key parameters of interest are monomer concentration, initiator concentration, reaction time, reaction temperature and type of initiator that influence the molecular weight of PAM during solution polymerization.

**Process Parameters and Molar Mass Control**

Typically, molecular weight can be increased by raising either the monomer concentration or the reaction time (Tripathy & De, 2006). However, monomer concentration is typically kept less than 10 wt%, because otherwise a hydrated polymer product insoluble in water forms (Ye et al, 2003). Moreover, if monomer concentration is >15 wt%, the mixture may boil due to high heat generation during polymerization (Morris & Penzenstadler, 1978). Oxygen even at 1 ppm scavenges off free radicals during acrylamide polymerization (Caulfield et al, 2002). For this reason, the polymerization reactions are typically conducted under nitrogen atmosphere.

Low temperatures promote synthesis of high molecular weight PAM (Lin, 2001). Actually, elevating the reaction temperature causes decrease in molecular weight on account of increase in the rate of radical generation. In addition, polymerization of acrylamide must be conducted below 70°C due to the possibility of intermolecular imidization reactions that result in water insoluble polymers (Escudero Sanz et al, 2007).

The type of initiator has profound influence on the polymer product. Increase in initiator concentration leads to increase in conversion and consequent decline in molecular weight (Lin, 2001). When initiator concentration is increased, the number of active sites to react with monomers goes up. Thus, not only do growing oligomers have better contact with monomers, but also the possibility of termination reaction increases; thus, conversion increases while final molecular weight decreases.

In this work, potassium persulfate (KPS), ammonium persulfate (APS) and a redox system (APS-TMEDA) were deployed as initiators at variable temperatures to determine their effect on molecular weight of PAM. The synthesized polymers were characterized using the NMR and Differential Scanning Calorimetry (DSC).

**Experimental**

**Materials and Methods**

Acrylamide monomer (AM, 99%), potassium persulfate (KPS), ammonium persulfate (APS) and N,N,N’,N-tetramethylethylenediamine (TMEDA) of analytical grade were obtained from Merck. All reagents were used without further purification. 1H NMR spectra of dried synthesized polymers were obtained in D2O with a Bruker (500 MHz) NMR spectrometer at 25°C. Differential Scanning Calorimetry (DSC) (Perkin Elmer Pyris 1, Germany) was used for the polymers characterization (10 °C/min, from 50 to 350 °C).
An Ubbelohde viscometer was used to measure the intrinsic viscosity of synthetic polymers. The viscometer was placed in a thermostated bath with temperature controlled within ±0.1°C and a digital chronometer with ±0.1s accuracy for measuring the flow time. Intrinsic viscosity values were calculated using the following equation:

\[
[\eta]_{ml/g} = \lim_{c \to 0} \left[ \frac{(\eta - \eta_0)}{\eta_0 \times c} \right]
\]

where \(\eta, \eta_0, c\) and \([\eta]\) are solution viscosity, solvent viscosity, concentration of polymer solution and intrinsic viscosity, respectively.

The weight average molecular weights (Mw) of synthesized polymers were calculated at 20°C in water (Munk et al, 1980):

\[
[\eta]_{ml/g} = 3.09 \times 10^{-2} \ M_w^{0.67}
\]

**Polymerization Procedure**

For all experiments, a mixture of acrylamide and initiators in deionized water were utilized in measured proportions. Monomer concentration was 1.565 mol/L and the ratio of the initiator to monomer was set at 0.00035 mol/mol. The reaction mixtures were purged by nitrogen for half an hour, and later the reactions were conducted under nitrogen atmosphere. The synthesized polymers were washed with acetone, placed in a vacuum oven for 24 hours and later pulverized in preparation of analysis.

**Results and Discussion**

**Effects due to initiator and mixing**

The effects due to three initiator systems and mixing were investigated on molecular weight of PAM using two types of mixers: a magnetic and a mechanical stirrer. The results are shown in Table 1. In the case of thermal initiators (KPS or APS), the temperature was increased at 10°C/h until an exothermic reaction was observed and thereafter the temperature was kept constant. Using this procedure, KPS and APS initiators were activated at 40°C and 50°C, respectively. However, for the redox system (APS-TMEDA), the exothermic reaction developed immediately on introduction of TMEDA to the reaction mixture at room temperature. The TMEDA/APS ratio was set at 1.486 \(\mu\text{L/mg}\) for our experiments.

Table 1 indicates that when thermal initiators were used, increased shear during the reaction, achieved by using a mechanical agitator, the molecular weight of PAM was increased. However, with the use of our redox initiator the trend was found to be converse. The observed behavior can be attributed to differences in the initiation mechanisms of these two types of initiator.

Thermal initiators are dissociated by thermal energy for generating radicals while with redox systems, radical generation takes place through reactions between the components of the system (Escudero Sanz et al, 2007). Thus when thermal initiators are used, increasing the severity of mixing leads to temperature rise and increased interactions for oligomers. However, when redox systems are involved, the severity of mixing enhances oligomer-monomer interactions and the reaction between the redox components. This
consequently improves the rate of radical generation, early termination and thus precludes high molecular weight formation. The results show that the latter effect predominates in case of the redox system.

Among the two thermal initiators, KPS appears to be more efficient than APS in increasing molecular weight. This can be attributed to lower activation temperature of KPS compared to APS, and this allows lower polymerization temperature.

Table. 1: Mixing effect on molecular weight (MDa) of PAM

<table>
<thead>
<tr>
<th>Type of Mixer</th>
<th>Initiator</th>
<th>KPS</th>
<th>APS</th>
<th>APS-TMEDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic stirrer (250 rpm)</td>
<td>KPS</td>
<td>3.2</td>
<td>1.8</td>
<td>2.6</td>
</tr>
<tr>
<td>Mechanical stirrer (250 rpm)</td>
<td>APS-TMEDA</td>
<td>5.8</td>
<td>2.9</td>
<td>2.2</td>
</tr>
</tbody>
</table>

TMEDA/APS redox system

Table 1 indicates that higher molecular weights may be obtained via redox initiation with minimal stirring. In this step, our redox systems with variable ratios of TMEDA/APS were examined. For all experiments, after addition of TMEDA, the reaction mixtures were kept at room temperature under nitrogen atmosphere overnight. With time, gradually viscous layers were formed on the bottom of the vessel and their thicknesses increased with TMEDA/APS ratio. Synthesized PAMs were extracted from these layers with washing several times by acetone. The results are shown in Table 2.

With a TMEDA/APS ratio of 0.355 µL/mg, even though three days, no layer was formed; though, using ratio of 2.897 µL/mg reaction mixture became entirely viscous overnight. On the other word, with raising the amount of TMEDA, required time of polymerization declined, but molecular weight of synthesized PAM increased. The above observations indicate that with increasing TMEDA amount, the possibility of reaction of two components of the redox system goes up, so the rate of radical generation levels up. As a consequence, both time of polymerization and molecular weight descend.

Table. 2: Effect of TMEDA/APS redox system on molecular weight of PAM at 25°C

<table>
<thead>
<tr>
<th>TMEDA/APS (µL/mg)</th>
<th>0.4976</th>
<th>1.486</th>
<th>2.897</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (MDa)</td>
<td>14</td>
<td>5.2</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Polymerization temperature with thermal initiators

The rate of radical generation in thermal initiators is directly related to the absorbed energy. Therefore, at higher temperatures, since the rate of energy absorbance increases, radical generation is increased and molecular weight reduces.
We conducted polymerization in an oven without stirring under nitrogen atmosphere overnight. Using this method, gel-like viscous layers were formed and their thicknesses increased on raising polymerization temperature. The results are shown in Table 3. Using KPS as initiator, no layer was formed at the bottom of the vessel at 30°C overnight, however the mixture became highly viscous at 40°C. Moreover, with APS no layer was formed below 40°C. We note that by lowering polymerization temperature, molecular weight increased.

Table 3: The effect of thermal initiator and temperature of polymerization on molecular weight of PAM without agitation (MDa)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>KPS</th>
<th>APS</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>9.1</td>
<td>n/a</td>
</tr>
<tr>
<td>40</td>
<td>2</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Product Characterization

To characterize synthesized polymers, $^1$HNMR and Differential Scanning Calorimetry (DSC) measurements were performed. The results are illustrated in Figures 1 and 2, respectively. For the NMR spectrum, the peak at 1.3 - 1.7 ppm and 2.0 - 2.3 ppm denote the methyne and methylene protons in PAM structure. The $^1$HNMR spectrum confirms the presence of the acrylamide chain and thus the occurrence of polymerization to form desired product. For the DSC, the thermogram indicates that degradation reactions start at about 200°C and are completed at 250°C. This is in agreement with reported results (Caulfield et al, 2002).

![Fig. 1: 1H NMR spectrum of PAM of 2.2 MDa in D2O](image)
Conclusions
In synthesizing high molecular weight poly(acrylamide) products, we investigated the effects of variable initiation and polymerization process conditions. In particular, with the thermal initiators, the rate of radical generation depends on the rate of supplied thermal energy whereas in the case of the redox system, the reaction rate of its two components plays a predominant role. The increase in severity of mixing during polymerization with the thermal initiators and the redox system showed different behavior. The molecular weight was increased by severity of mixing when thermal initiators were used, while a decrease was observed when the redox system was employed. Among the thermal initiators used in this work, KPS surpassed its counterpart APS in enhancing molecular weight.

With the redox system, when TMEDA/APS ratio was increased, the molecular weight decreased due to increase in the reaction between two components with reduced rate of radical generation. In the case of thermal initiators, polymerization at lower temperatures produced higher molecular weight product. Thus, the rate of radical generation plays a major role in synthesizing high molecular weight PAM. For thermal initiators, the rate of thermal energy input and for the redox system, the reaction rate of the reactive components should be decreased to achieve high molar mass poly(acrylamide).

REFERENCES


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**BRIEF BIOGRAPHY OF PRESENTER**

Zohreh Abdollahi is a Ph.D candidate of the University of Sydney working under supervision of Prof. Vincent Gomes. Her main focus of studies has been synthesis and characterization of high molecular weight non-ionic and cationic polyacrylamide.