Precipitation polymerization of acrylic acid in toluene.
I: synthesis, characterization and kinetics

Charun Bunyakan \( ^a \), David Hunkeler \( ^b, ^* \)

\( ^a \)Department of Chemical Engineering, Vanderbilt University Nashville, TN 37235, USA
\( ^b \)Laboratory of Polymers and Biomaterials, Department of Chemistry, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

Received 19 March 1998; received in revised form 10 August 1998; accepted 19 November 1998

Abstract

Acrylic acid was isothermally polymerized by precipitation polymerization in toluene at various monomer and initiator concentrations over the temperature range of 40°C–50°C. 2,2'-azobis (2,4-dimethyl-valeronitrile) was employed as a chemical initiator. The rate of polymerization was found to depend on the monomer and initiator concentration to the 1.7th and 0.6th orders, respectively. The greater than first order dependence on monomer concentration signifies a secondary, monomer-enhanced, decomposition step for the initiator molecules. The approximately 0.5 order dependence of the rate of precipitation polymerization on the initiator concentration indicates that the chain termination process is predominantly bi-macromolecular. The temperature dependence on rate of precipitation polymerization obeys an Arrhenius equation with the activation energy found to be 21.49 kcal/mol. This result agrees well with the literature values of 23.5 and 22.0 kcal/mol obtained for the solution polymerization of partially neutralized acrylic acid (pH = 11) and undissociated acrylic acid (pH = 1), respectively. The weight average molecular weight of the polymer was found to be independent of conversion, indicating that transfer to the monomer is the chain controlling reaction. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Acrylic acid; Polyacrylic acid; Precipitation polymerization

1. Introduction

Polyacrylic acid is an important water-soluble material which is applied in mining, paper manufacturing and oil recovery. It is also, in a lightly crosslinked form, utilized in the personal care sector, most predominantly in diapers. The molecular weight and the ionic character of the polymer are the key factors in determining its utility in particular applications. Polyacrylic acid can also be employed as sequestrants and inhibitors, for molecular weight below 20 000 Da, dispersing agents (MW 20–80 000 Da), and as textile finishing agents and retention aids (MW 100 000–1 000 000 Da).

The worldwide production of polyacrylic acid was 1.44 × 10\(^5\) tons in 1988, with the market divided as follows: 52.9% as superabsorbent polymers, 18.4% as detergent additives, 17.1% as industrial dispersants, 7.8% as water treatment chemicals (primarily sequestrants and scale inhibitors), and 3.8% as coating components and drilling muds [1]. Geographically, 48.2% of the polyacrylic acid was consumed in the United States and Canada, 31.3% in Western Europe and 20.5% in Japan; these data exclude statistics for the former Eastern bloc countries. The polyacrylic acid market is forecasted to grow at approximately 6.5% annually overall in the next decade.

An understanding of the kinetics of the acrylic acid polymerization process is essential for the optimization and control of commercial polymer production. The molecular weight of the polymer, the rate of polymerization, and the conversion are influenced strongly by the polymerization kinetics. The influence of physical variables, such as the agitation conditions and reactor configuration are also crucial for the process design engineer. Although the free-radical polymerization of acrylic acid was investigated by a number of researchers, as is discussed in the following section, relatively little work was conducted on precipitation polymerization in the open literature. Given this, the objectives of this study were to quantitatively understand the precipitation polymerization process. Specifically, this involved an investigation of the influence of polymerization conditions, such as concentration of the initiator, concentration of the monomer, and the temperature on the rate of polymerization, conversion, and molecular weight of the polymer. An additional objective was to provide a kinetic...
model which could predict the rate of a precipitation polymerization as well as the properties of polyacrylic acid up to high conversions. The kinetic model will be derived and evaluated against experimental data in a subsequent article [2].

1.1. Summary of previous kinetic investigations

Acrylic acid was polymerized in bulk via chemical [3] and physical [4] initiation mechanisms. Solution polymerization have found that the reaction rate is dependent on the pH and ionic strength of the aqueous solvent [5,6]. Manickam [7] identified a sesquimolecular (1.5 order) rate dependency on monomer concentration when employing potassium persulfate as an initiator. Gromov [8] reported that the polymerization rate was strongly dependent on the nature of the polar solvent. Polyacrylic acid homopolymer and copolymers can also be produced by reacting the monomer(s) in aqueous or organic media by methods such as inverse-suspension [9–11] or inverse-emulsion [12] polymerization.

1.2. Precipitation polymerization

To overcome the aforementioned problems, the present commercial technologies for the production of polyacrylic acid utilize precipitation polymerization. Therefore, owing to its industrial emergence over the last decade it was selected for the study herein. In a precipitation process, the polymerization takes place in a medium which is a solvent for the monomer and a non-solvent for the polymer. The polymer particles are not stabilized and tend to agglomerate to form a polymer paste or slurry. As the precipitation polymerization produces polymeric solids at very high rates and purity (i.e. free from emulsifier or suspending agent), their popularity is increasing. However, only a limited amount of research was carried out on the mechanism, kinetics, and reaction engineering of the precipitation polymerization of acrylic acid and its copolymers. The precipitation copolymerization of vinyl lactam and acrylic acid in a cosolvent mixture of an aliphatic hydrocarbon solvent and isopropanol have also been studied [13]. Terpolymers of a vinyl lactam, acrylic acid and a hydrophobic monomer, such as lauryl methacrylate, were prepared by precipitation polymerization in aliphatic hydrocarbon solvents (heptane or cyclohexane) [14].

Polyacrylic acid was synthesized via the isothermal precipitation polymerization using 2,2'-azobis(2,4-dimethyl valeronitrile) as an initiator over the temperature range of 40°C–60°C [15]. The viscosity and heat transfer during precipitation polymerization were also monitored [16].

1.3. Discrepancies between dispersion and precipitation/slurry polymerization

The polymerization studied in this article are precipitation or slurries and not classical “dispersions”, such as those described by Bamford [17] or Barrett and Thomas [18]. This implies that the primary particles which were formed did not aggregate into colloids, as in dispersion polymerization, but remained in a loose slurry-like form. In other words, while the polymer was insoluble in the solvent (toluene) and precipitated, these oligopolymers did not aggregate into lattices. One reason for this is that we did not add any stabilizer or block copolymer to the latex to provide a steric barrier, as is common in dispersion polymerization in organic media [19]. A second important difference in our results is that we attempted to perform kinetic measurements under industrially relevant conditions. This always involves some tradeoffs to be associated with the applied benefits. Under such conditions we did not purify the monomer. It was polymerized after degassing, however, the residual inhibitor (200 ppm of hydroquinone) was not removed. Therefore, we can state quite conclusively that there is no nucleation and the lack of initial reaction at low conversion, which is presented in the discussion section is, indeed, owing to induction. Further, direct evidence of this is the following: for a typical reaction which had an induction period of 10 min, the onset of the turbidity was observed after approximately 15 min. Therefore, the initial stages of the reaction are retarded because of the initiator consuming hydroquinone rather than a heterogeneous nucleation mechanism. This is certainly not to say that the interpretation Avela et al. [15] is incorrect, rather only that Avela used a true dispersion polymerization, while the present article is limited to a precipitation. Certainly, under such circumstances, it is not surprising that different methods of polymerization offer disparate kinetic behavior.

2. Experimental

2.1. Chemicals

Glacial acrylic acid, inhibited with 200 ppm of hydroquinone monomethylether, was purchased from the Rohm and Haas Company (Philadelphia, PA). The monomer was degassed but not otherwise purified prior to polymerization. The solvent used, toluene (Certified ACS), was obtained from Fisher Scientific (Atlanta, GA). The initiator, 2,2'-azobis(2,4-dimethyl-valeronitrile) (ADVN), was supplied by Wako Pure Chemicals (Richmond, VA). This had a purity of 99% and was used as delivered without further purification. The water utilized, type I reagent grade, was prepared through a series of deionization and organic purification. The water utilized, type I reagent grade, was used in all of the experiments. Under such conditions we did not add any stabilizer or block copolymer to the latex to provide a steric barrier, as is common in dispersion polymerization, but remained in a loose slurry-like form. In other words, while the polymer was insoluble in the solvent (toluene) and precipitated, these oligopolymers did not aggregate into lattices. One reason for this is that we did not add any stabilizer or block copolymer to the latex to provide a steric barrier, as is common in dispersion polymerization in organic media. A second important difference in our results is that we attempted to perform kinetic measurements under industrially relevant conditions. This always involves some tradeoffs to be associated with the applied benefits. Under such conditions we did not purify the monomer. It was polymerized after degassing, however, the residual inhibitor (200 ppm of hydroquinone) was not removed. Therefore, we can state quite conclusively that there is no nucleation and the lack of initial reaction at low conversion, which is presented in the discussion section is, indeed, owing to induction. Further, direct evidence of this is the following: for a typical reaction which had an induction period of 10 min, the onset of the turbidity was observed after approximately 15 min. Therefore, the initial stages of the reaction are retarded because of the initiator consuming hydroquinone rather than a heterogeneous nucleation mechanism. This is certainly not to say that the interpretation Avela et al. [15] is incorrect, rather only that Avela used a true dispersion polymerization, while the present article is limited to a precipitation. Certainly, under such circumstances, it is not surprising that different methods of polymerization offer disparate kinetic behavior.

2.2. Apparatus and procedures

Precipitation polymerizations of acrylic acid were carried out in a pilot plant reactor. The 5-liter 316-Stainless Steel reactor was equipped with a chilled water/high pressure steam jacket, a nitrogen inlet and outlet for sparging, and
two baffles. Agitation was supplied with a pitched blade impeller which was driven by a speed variable motor through the impeller shaft. The maximum impeller speed was 400 rpm. The reactor was connected to a Macintosh based control system running Labview, an object oriented language. A PID controller was used to control the temperature inside the reactor by adjusting the ratio of flow rates of a high pressure steam to cooling water via a pneumatic control valve. The temperature inside the reactor was measured by a platinum resistance temperature detector (RTD, model PR-12, Omega Engineering Inc., Stamford, CT). The precision of controlled temperature was within ±0.5°C.

The polymerizations were conducted under isothermal conditions at three temperatures: 40°C, 45°C and 50°C. The prescribed amount of the monomer was dissolved in the solvent. This solution was then charged into the reactor and nitrogen was bubbled for 30 min prior to the reaction and throughout the polymerization. After the oxygen purging was completed, the initiator solution was injected into the reactor to start the polymerization. Twenty milliliters of reaction mixture was withdrawn from the reactor at predetermined intervals during the course of polymerization. A sampling interval of once every 5 min was utilized at low conversions. The sampling interval was extended to 10 min at high conversions. These samples were collected in

Table 1  

Experimental conditions

<table>
<thead>
<tr>
<th>Experimental code a</th>
<th>Temperature (°C)</th>
<th>[M]₀ (mol/l)</th>
<th>[I]₀ (ADVN) (mmol/l)</th>
<th>Agitation rate (RPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP1</td>
<td>50</td>
<td>1.252</td>
<td>8.5</td>
<td>400</td>
</tr>
<tr>
<td>PP2</td>
<td>50</td>
<td>1.252</td>
<td>6.5</td>
<td>400</td>
</tr>
<tr>
<td>PP3</td>
<td>50</td>
<td>1.252</td>
<td>4.0</td>
<td>400</td>
</tr>
<tr>
<td>PP4</td>
<td>50</td>
<td>1.252</td>
<td>2.0</td>
<td>400</td>
</tr>
<tr>
<td>PP5</td>
<td>50</td>
<td>0.626</td>
<td>8.5</td>
<td>400</td>
</tr>
<tr>
<td>PP6</td>
<td>50</td>
<td>0.313</td>
<td>8.5</td>
<td>400</td>
</tr>
<tr>
<td>PP7</td>
<td>50</td>
<td>0.156</td>
<td>8.5</td>
<td>400</td>
</tr>
<tr>
<td>PP8</td>
<td>45</td>
<td>1.252</td>
<td>8.5</td>
<td>400</td>
</tr>
<tr>
<td>PP9</td>
<td>40</td>
<td>1.252</td>
<td>8.5</td>
<td>400</td>
</tr>
</tbody>
</table>

a PP1-4: Initiator concentration variation; PP1,5,6 and 7: Monomer concentration variation; PP1,8 and 9: Temperature variation.

Fig. 1. Experimental data for precipitation polymerization of acrylic acid in toluene at 50°C, [M]₀ = 1.252 mol/l, and [I]₀ = 2.0–8.5 mmol/l. (● [I]₀ = 2.0 mmol/l, ▲ [I]₀ = 4.0 mmol/l, ▲ [I]₀ = 6.5 mmol/l, and ■ [I]₀ = 8.5 mmol/l).
presterilized 20 ml glass scintillation vials (Fisher). The polymerization reactions in the withdrawn samples were quenched by adding 0.1 ml of a 2% hydroquinone solution in methanol and shaking it manually. The samples were then immersed in an ice–water mixture for approximately 30 min, and stored in a refrigerator at a temperature below 10°C prior to analysis. At the completion of the reaction, the polymer mixture was withdrawn from the reactor through a sampling valve. The reactor was then immediately washed with water several times, with tap and deionized and isolated for the next reaction.

2.3. Conversion measurements

The conversion from the monomer to the polymer was measured using a gravimetric method.

2.4. Molecular weight measurements

Molecular weight measurements were carried out by static light scattering. The light scattering system consisted of a 2-Watt Lexel argon-ion laser operating at 20 mW and of 514.5 nm length (Lexel, Fremont, CA), a Brookhaven 200SM goniometer (Brookhaven Instruments, Holtsville, New York), a B2FBK/RFI photomultiplier detector (Ruislip Middlesex England), and a computer equipped with a Brookhaven BI9000 correlator. Zimm plots were measured on prefiltered and precentrifuged samples.

The solvent used for molecular weight determination, 0.01 M NaCl, was filtered through a Metricel membrane filter of 0.2 μm (Cole–Parmer Instrument, Chicago, IL), equipped with inline filter holder (Gelman Sciences, Ann Arbor, MI) and peristaltic pump (Cole–Parmer Instrument, Chicago, IL). The polymer solutions were then centrifuged using a Fisher Marathon Model 21 K at 9000 rpm for 4 h. Disposable 10 ml syringes were used to transfer the polymer solutions into clean vials.

2.5. Experimental conditions

Precipitation polymerizations of acrylic acid in toluene were carried out isothermally at three temperatures, 40°C, 45°C, and 50°C, using different concentrations of monomer and initiator. The experimental design and conditions employed in this study are listed in Table 1.

3. Results and discussion

3.1. The influence of the initiator (ADVN) concentration

3.1.1. Rate of precipitation polymerization

The effect of initiator concentration on the conversion-time behavior of the precipitation polymerization of acrylic acid at 50°C, is shown in Fig. 1. As a result of the induction period, the “initial” rate of precipitation polymerization needed to be estimated. The following procedure was employed: the tangent with a maximum slope was drawn on the conversion-time curve. The time-intercept of the tangent provided the total induction period of the polymerization process, with the initial rate of precipitation polymerization then calculated from the slope of the tangent and the initial monomer concentration, [M]₀, using the following equation: slope was drawn on the conversion-time.
curve.

\[ R_{P_0} = [M]_0 \frac{\log(dx/dt)}{\log(I)_0} = [M]_0 \text{ (Slope of the tangent).} \]

A plot of \( \log(dx/dt)_{t=0} \) versus \( \log([I]_0) \), using the experimental data generated herein, is shown in Fig. 2. The slope obtained from Fig. 2 was 0.6, therefore, the initial rate of precipitation polymerization was found to be 0.6th order with respect to the initiator concentration (given the errors estimating rates from slopes, the values of the rate dependencies on monomer and initiator concentration are rounded to the second significant digit). When a plot of the initial rate of polymerization versus the 0.5th power of the initiator concentration was constructed a straight line was observed, implying that the rate data are consistent with a 1/2 order initiator concentration dependence, as is found in the free radical polymerization of acrylic acid in aqueous solutions.

Fig. 3. Induction time versus initiator concentration for the precipitation polymerization of acrylic acid in toluene at 50°C, \([M]_0 = 1.252 \text{ mol/l} \) and \([I]_0 = 2.0–8.5 \text{ mmol/l} \).

Fig. 4. The weight average molecular weight versus the initiator concentration for the precipitation polymerization of acrylic acid in toluene at 50°C, \([M]_0 = 1.252 \text{ mol/l} \) and \([I]_0 = 2.0–8.5 \text{ mmol/l} \). The data were measured at a conversion of monomer to polymer of 82.2 ± 2%.
[7,8,20] as well as in organic solvents such as DMSO and formamide [8]. This is an indication that the chain termination process is predominantly bi-macromolecular. The initiator concentration also affects the induction time as shown in Fig. 3. From this figure, one can see that at lower initiator concentrations, which correspond to reduced polymerization rates, the induction period is prolonged. This is an evidence of the presence of species which
consume radicals and compete with the monomer for chain initiation. As the monomer contained 200 ppm of hydroquinone, this is certainly the cause of the retardation. Residual oxygen levels, which can easily scavenge primary radicals, were reduced to below 1 ppm through purging and cannot account for the induction effects.

3.1.2. Weight average molecular weight

A plot of the weight average molecular weight versus the initiator concentration is shown in Fig. 4. Samples were obtained at a conversion of 82 ± 2%. From this figure, it is clear that at low levels of initiator concentration (less than 4 mmol/l) the weight average molecular weight depends strongly on the initiator concentration. However, the weight average molecular weight is only slightly dependent on the initiator concentration when concentrations greater than 4 mmol/l were employed. It should be noted that the weight average molecular weight at an initiator concentration of 4.0 mmol/l should be, theoretically, greater than at 8.5 mmol/l. The lack of correspondence of this trend in the data is a likely manifestation of the imprecision in light scattering measurement (±10%).

The highly non-linear dependence of weight average molecular weight on initiator concentration is not likely caused by experimental errors in synthesis or the molecular weight characterization, but is rather caused by the presence of radical scavenging species in the initial mixture. Hence, the actual concentration of the initiator at the outset of the reaction is lower than what was prepared owing to radicals scavenging. This is evident from Fig. 3 where effects are pronounced at lower rates ([I]₀ = 2.0 mmol/l). Therefore, the presence of radical scavenging species lowers the true initiator concentration which raises the molecular weight.

3.2. The influence of the monomer concentration

3.2.1. Rate of precipitation polymerization

The effect of monomer concentration on the conversion-time data at 50°C, and initiator concentration of 8.5 mmol/l is illustrated in Fig. 5. From this, one can previous section. Additionally, a plot of the initial rate versus the monomer concentration is shown in Fig. 6. The non-linear nature of this curve is another indication that the rate of polymerization is not first order with respect to monomer concentration. A plot of log(dx/dt)₀ versus log[M]₀ is shown in Fig. 7. The slope obtained from Fig. 7 was 0.7, implying that the rate of polymerization with respect to the monomer concentration obtained in this investigation is virtually the same as that found in solution free-radical polymerizations of acrylic acid in the presence of both alkaline and acidic conditions [7,20], as well as for the solution polymerization of acrylic acid using either DMSO or formamide as the reaction medium [8]. This peculiar order of rate of precipitation polymerization with respect to the monomer concentration is a consequence of the dominance of the monomer-enhanced initiation reaction [21]. The conclusion that an order of 1.7 signifies a secondary monomer-enhanced
decomposition step of the initiator is one explanation especially in aqueous media. However, in the present work, polymerization reactions are performed in a non-aqueous media, i.e. in toluene. Thus, another explanation is that acrylic acid tends to dimerize in toluene and may result in orders being larger than one. The monomer may react with the initiator prior to its reaction with a primary radical and “induce” the decomposition of the initiator. In such cases (e.g. acrylic acid and sodium persulfate), the polymerization rate was shown to depend on the 1.5th power of monomer concentration and the 0.5th power of the initiator concentration [7], as was observed in this investigation. The monomer concentration in the reaction mixture was varied from 0.156 to 1.252 mol/l. The results are shown in Fig. 8 and 9.

Fig. 8. Induction time versus monomer concentration for the precipitation polymerization of acrylic acid in toluene at 50°C, [I]₀ = 8.5 mmol/l and [M]₀ = 0.156–1.252 mol/l.

Fig. 9. The weight average molecular weight versus the monomer concentration for the precipitation polymerization of acrylic acid in toluene at 50°C, [I]₀ = 8.5 mmol/l. Each point represents a polymerization carried out at a different monomer concentration.
Fig. 10. Experimental data for precipitation polymerization of acrylic acid in toluene over the temperature range 40–50°C, $[M]_0 = 1.252$ mol/l and $[I]_0 = 8.5$ mmol/l. ( ● $T = 40^\circ$C, ■ $T = 45^\circ$C, and ▲ $T = 50^\circ$C).

Fig. 11. $\log(R_p)$ versus $1/T$ for the precipitation polymerization of acrylic acid in toluene with $[M]_0 = 1.252$ mol/l, $[I]_0 = 8.5$ mmol/l and $T = 40^\circ$C–50°C.
concentration also has an effect on the induction time as is shown in Fig. 8. This is analogous to the effects observed by varying the concentration of the initiator where higher rates cause processes to lower induction periods.

3.2.2. Weight average molecular weight

Fig. 9 shows a plot of the weight average molecular weight versus the monomer concentration. From Fig. 9, it is evident that the monomer concentration has a strong

![Fig. 12](image_url) Fig. 12. Induction time versus the reaction temperature for the precipitation polymerization of acrylic acid in toluene with \([I]_0 = 8.5\) mmol/l and \([M]_0 = 1.252\) mol/l over the temperature range 40°C–50°C.

![Fig. 13](image_url) Fig. 13. The weight average molecular weight versus the reaction temperature for the precipitation polymerization of acrylic acid in toluene with \([M]_0 = 1.252\) mol/l, and \([I]_0 = 8.5\) mmol/l over the temperature range 40–50°C.
influence on the weight average molecular weight only when high monomer levels are employed. At lower concentrations of monomer, the weight average molecular weight was only slightly dependent on the monomer concentration. As lowering the monomer concentrations correspond to higher amounts of solvent, the difference in the weight average molecular weight of low and high monomer concentrations could be attributed to a transfer reaction to solvent or solvent containing impurities. This will be further investigated in a later section which examines the effect of reaction conversion on the molecular weight.

3.3. The influence of temperature

3.3.1. Rate of precipitation polymerization

The influence of temperature on the kinetics is shown in Fig. 10. It can be seen that the temperature has a significant effect on both the initial rate of polymerization and the induction time, both of which were estimated by using the same procedures as described in the previous section. An Arrhenius plot of log($R_p$) versus $1/T$ was constructed (Fig. 11). The activation energy estimated from this plot was found to be 21.49 kcal/mol. The activation energy for precipitation polymerization of acrylic acid in toluene obtained in this investigation is virtually the same as that reported for polymerization of undissociated acrylic acid in 0.1 M perchloric acid (22.0 kcal/mol) [7] or for polymerization of acrylic acid under alkaline (pH $\approx$ 11) conditions (23.5 kcal/mol) [7]. This influence of the reaction temperature on the induction period is illustrated in Fig. 12. Again, higher rates consume impurities faster and lower the induction period.

3.3.2. Weight average molecular weight

Fig. 13 shows a plot of the weight average molecular weight as a function of the reaction temperature. It can be seen that in the range of the temperatures investigated (40°C–50°C), the weight average molecular weight was only slightly dependent on the reaction temperature, with lower temperatures resulting in higher molecular weights of polymer as is usually observed in free-radical reactions.

3.4. The dependence of weight average molecular weight on conversion

Fig. 14 shows the independence of the weight average molecular weight on the conversion of monomer to polymer. Given that no chain transfer agents were used in this investigation, although toluene is a radical scavenging solvent, this trend implies that transfer to the polymer or long chain branching reactions do not occur to any measurable extent. As the concentration of the initiator employed was very small compared to the concentration of solvent and monomer, and ADVN does not have any significant transfer properties, we can also exclude chain transfer to the initiator. Moreover, the independence of weight average molecular weight on conversion is generally an indication that transfer to the monomer is the chain controlling reaction.
Cutie [22] and Zaldivar [23,24] have shown that it is possible to obtain relative moderate molecular weights during the polymerization of acrylic acid without transfer to solvent. Specifically Cutie [22] found molecular weights as low as 600 000 (with Mn’s down to 100 000 daltons). Also, Zaldivar [23,24] has molecular weights as low as 250 000 Da though they are generally above 450 000 Da. In the present study, we found molecular weights in the range of 80 000–100 000 Da. Therefore, the molecular weights reported herein are not significantly lower than those without the presence of toluene. It seems unlikely that toluene is the main factor controlling molecular weight, rather the low molecular weight is likely caused by the very rapid polymerization rates (50% conversion after 5–20 min).

4. Conclusions

The conclusions from this investigation are:

1. The rate of precipitation polymerization of acrylic acid in toluene was found to vary to the 1.66th power with respect to monomer concentration. The greater than first order dependence signifies a secondary monomer-enhanced decomposition step for the initiator molecules. This secondary decomposition step was first postulated (for acrylic acid) in aqueous media by Manickam [7].

2. The rate of precipitation polymerization of acrylic acid in toluene was found to vary to 0.59th power with respect to initiator concentration. In this case, the approximately 0.5 order dependence indicates that the chain termination process is predominantly bi-macromolecular. The dependence of rate of precipitation polymerization on the initiator obtained in this investigation is slightly higher than that of 0.5 for solution polymerization of acrylic acid [7,8,20], but is likely within the limits of experimental errors.

3. The activation energy for the precipitation polymerization of acrylic acid in toluene was found to be 21.49 kcal/mol. This data agrees well with the literature results obtained for solution polymerizations [7].

4. The induction period was found to be highly dependent on the polymerization rate. Specifically, the induction period increases as either initiator or monomer concentration decreases or the reaction temperature decreases.

5. The weight average molecular weight was found to be independent of conversion. This is an indication that transfer to monomer is the chain controlling reaction.

6. The weight average molecular weight of the polymer was also found to be dependent on the polymerization conditions. The molecular weight decreased as the initiator concentration or reaction temperature was increased, and increased with increasing monomer concentrations.

The experimental data generated herein will be used to elucidate a mechanism for the precipitation polymerization of acrylic acid in toluene in a subsequent publication [2].

References