A COMPREHENSIVE KINETIC INVESTIGATION OF THE INVERSE SUSPENSION COPOLYMERIZATION OF ACRYLAMIDE: THEORETICAL AND EXPERIMENTAL STUDIES

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ABSTRACT

A comprehensive theoretical and experimental kinetic investigation of the inverse suspension copolymerization of acrylamide is presented. The experimental work, which included both the homopolymerization of acrylamide and the copolymerization with Dimethylaminoethyl acrylate (DMAEA) at various compositions, was carried out in a 0.25L jacketed reactor. Paraffin oil was employed as the oil phase.

A comprehensive mathematical model was developed based on a detailed kinetic mechanism to simulate the dynamic evolution of the monomer conversion and molecular weight developments (i.e., Mn, Mw, PD). The proposed kinetic mechanism of the acrylamide copolymerization comprises a series of elementary reaction steps, including initiator decomposition, chain initiation, propagation, chain transfer to monomer and termination by disproportionation. The basic kinetic parameters were estimeted using solution polymerization experiments. The resulting kinetic model has been evaluated against experimental data for homo- and co-polymerizations of acrylamide. A very good agreement has been found between model predictions and the experimental data (literature and current work).

INTRODUCTION

Due to their excellent properties, polyacrylamide products are suitable in several applications like water treatment, oilfield and mining as well as paper chemicals. High molecular-weight homopolymers of acrylamide are used as pushing fluids in tertiary oil recovery, as drag reduction agents and as drilling fluids. Copolymers with various cationic monomers such as diallyldimethylammonium chloride (DADMAC) and dimethylaminoethyl acrylate (DMAEA) are used for fines retention in paper making, as flocculants, and, in general, wherever aqueous solid liquid separations are required.

Since acrylamide is solid at normal reaction temperatures it is usually polymerized in aqueous solutions. However, the polymerization of acrylamide is characterized by a very high heat generation rate ($\Delta Hp = 19.5$ kcal/mol) and by the formation of a highly viscous reaction medium. Furthermore, the reaction should be performed in neutral solutions and at moderate temperatures (i.e., less than 70°C) to avoid intermolecular imidization. Thus, industrially, the polymerization of acrylamide is often carried out in heterophase processes like inverse-suspension or inverse-emulsion. The inverse suspension process involves the emulsification of a water-soluble monomer, in solution, in a continuous organic phase. A water-in-oil steric stabilizer is used and the polymerization is carried out with either a water- or an oil-soluble initiator, although the latter is more common. The resulting microsuspensions have lower viscosities, provide easier heat removal and can be used at higher monomer concentrations than the solution process [1].

In the present work, a comprehensive theoretical and experimental kinetic investigation of the inverse suspension copolymerization of acrylamide is presented. The experimental work, which included both the homopolymerization of acrylamide and the copolymerization with DMAEA at various compositions, was carried out in a 0.25L jacketed reactor. Paraffin oil was employed as the oil phase and Span 80 (Sorbitan monooleate) was used as surfactant (HLB = 4.3) to stabilize the water in oil suspension.

A comprehensive mathematical model was developed based on a detailed kinetic mechanism to simulate the dynamic evolution of the monomer conversion and molecular weight developments (i.e., Mn, Mw, PD). The proposed kinetic mechanism of the acrylamide copolymerization comprises a series of elementary reaction steps, including initiator decomposition, chain initiation, propagation, chain transfer to monomer, termination by disproportionation. Basic kinetic parameters were estimated using solution polymerization experiments at low conversion. The resulting kinetic model has been evaluated against experimental data for copolymerization of acrylamide with DMAEA. A very good agreement has been found between model predictions and the experimental data (literature and current work).

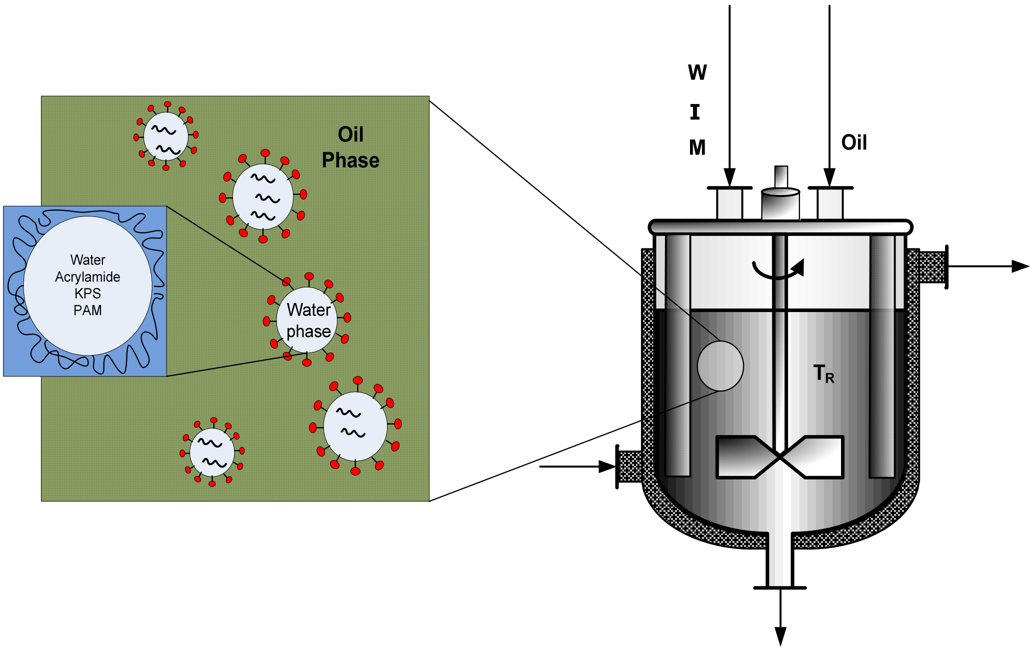

Figure 1. Inverse suspension polymerization of acrylamide.

Historically, the term "inverse" has been used for water-in oil emulsions in contrast to "direct" or "conventional" oil-in-water dispersions. There have been many investigations of the kinetics of heterophase acrylamide polymerizations in different media [1]. These can be divided into three cases depending on the type of the initiator (soluble in water or oil phase) and the chemical nature of the continuous phase (paraffin or aromatic): (i) When water-soluble initiators are used, all components for the polymerization reside in the dispersed droplets (See Figure 1). Each particle acts essentially as a small batch reactor and the kinetics are similar to those for solution polymerization. (ii) When oil-soluble initiators are used with aromatic continuous oil phase the kinetics have been shown to resemble emulsion polymerization with the locus of initiation occurring in inverse micelles. (iii) Finally, when oil-soluble initiators and paraffinic oil phases are used, the locus of initiation is in the monomer droplets. The polymerization therefore physically and kinetically resembles a suspension.

MATHEMATICAL MODELING OF THE ACRYLAMIDE PROCESS

A comprehensive mathematical model was developed based on a detailed kinetic mechanism to simulate the dynamic evolution of the monomer conversion and molecular weight developments (i.e., M_n, M_w, PD). The proposed kinetic mechanism of the acrylamide copolymerization comprises a series of elementary reaction steps, including initiator decomposition, chain initiation, propagation, chain transfer to monomer, termination by disproportionation and reaction with terminal double bond.

Kinetic mechanism of acrylamide polymerization

In 1967, Riggs and Rodriguez [2] observed an unusual rate dependence for aqueous acrylamide polymerizations initiated with potassium persulfate, i.e., $R_p \sim k[M]^{1.25}[I]^{0.5}$. Over the past decades, investigations have confirmed a monomer dependency exceeding first order while maintaining that termination occurs predominantly through a bimolecular macroradical reaction. Riggs and Rodriguez [2] interpreted the high rate order as evidence of monomeric influences on the rate of initiation.

Traditionally, to account for high rate orders with respect to monomer, three mechanisms have been proposed: the cage-effect theory, the complex theory and the solvent-transfer theory. Hunkeler and Hamielec [3] analysed the literature data from the polymerization of acrylamide and other water soluble monomers and showed that the persulfate-initiated polymerization of acrylamide is characterized by the formation of hydrogen-bonded associates between the amide and the persulfate, the decomposition of which proceeds via a donor-acceptor mechanism. The proposed mechanism is described below:

Initiation Reaction (Based on the cage model)

$$S_2O_8^{2-} \underset{k_1'}{\overset{k_1}{\rightleftarrows}} \left(SO_4^{\bullet -}\;{}^{-\bullet}O_4S\right) \quad \text{(compact cage)} \qquad (1)$$

$$\left(SO_4^{\bullet -}\;{}^{-\bullet}O_4S\right) \xrightarrow{k_2} \left[SO_4^{\bullet -}\;{}^{-\bullet}O_4S\right] \quad \text{(diffuse cage)} \qquad (2)$$

$$\left[SO_4^{\bullet-}\ {}^{-\bullet}O_4S\right] \xrightarrow{k_d^*} 2SO_4^{\bullet-} \tag{3}$$

$$\left[SO_4^{\bullet-}\ {}^{-\bullet}O_4S\right] \xrightarrow{k_r} S_2O_8^{2-} \tag{4}$$

$$\left[SO_4^{\bullet-}\ {}^{-\bullet}O_4S\right] + M \xrightarrow{k_a^*} \begin{bmatrix} SO_4^{\bullet-}\ {}^{-\bullet}O_4S \\ M \end{bmatrix} \tag{5}$$

$$\begin{bmatrix} SO_4^{\bullet-}\ {}^{-\bullet}O_4S \\ M \end{bmatrix} + M \xrightarrow{k_b} SO_4^{\bullet-} + HSO_4^{-} + CH_2C^{\bullet}C(O)NH_2 \tag{6}$$

$$\begin{bmatrix} SO_4^{\bullet-}\ {}^{-\bullet}O_4S \\ M \end{bmatrix} + M \xrightarrow{k_c} Q \tag{7}$$

Chain Initiation

$$SO_4^{\bullet-} + M \xrightarrow{k_{i1}} R_1^{\bullet} \tag{8}$$

$$SO_4^{\bullet-} + H_2O \xrightarrow{k_H} HSO_4^{-} + HO^{\bullet} \tag{9}$$

$$HO^{\bullet} + M \xrightarrow{k_{i2}} R_1^{\bullet} \tag{10}$$

Propagation

$$R_n^{\bullet} + M \xrightarrow{k_p} R_{n+1}^{\bullet} \tag{11}$$

Transfer to monomer

$$R_n^{\bullet} + M \xrightarrow{k_{tm}} R_1^{\bullet} + D_n \tag{12}$$

Termination by disporportionation

$$R_n^{\bullet} + R_m^{\bullet} \xrightarrow{k_{td}} D_n + D_m \tag{13}$$

The symbols R_n and D_n identify the respective "live" and "dead" copolymer chains. The subscript n denotes the degree of polymerization for acrylamide. The respective net rates of production of "live" and "dead" polymer chains can be obtained by combining the reaction rates of the relevant elementary reactions, describing the generation and consumption of "live" and "dead" polymer chains.

EXPERIMENTAL PART

The experimental work, which included both the homopolymerization of acrylamide and the copolymerization with the cationic comonomer Dimethylaminoethyl acrylate (DMAEA) at various compositions and temperatures, was carried out in a 0.25L jacketed reactor. Paraffin oil was employed as the oil phase.

Reagent purification: Dimethylaminoethyl acrylate (DMAEA) was obtained as concentrated (80 wt%) aqueous solution, inhibited with 800 ppm of hydroquinone monomethyl ether (MeHQ). The quaternary ammonium monomer was purified to MeHQ levels of <0.5 ppm by repetitive extractions with acetone (reagent grade). Solid acrylamide monomer (Sigma-Aldrich) was recrystallized from chloroform (Sigma-Aldrich). More specifically, acrylamide was dissolved into chloroform heated to boiling point (50°C) and filtered without suction in a warmed funnel through filter paper. Allowed to cool to room temperature and kept at -15°C overnight. The crystals were collected with suction in a cooled funnel and washed with 30ml of cold chloroform. The crystals were dried in vacuum to constant weight and stored in the dark over silica gel in desiccators. Potassium persulphate was recrystallized from analytical grade water. All reagents were dried *in vacuum* to constant weight and stored separately in desiccators over silica gel.

Determination of monomer and polymer composition for inverse suspension polymerization: Copolymer compositions were inferred from chromatographic measurements of the residual monomer concentration. A high-performance liquid chromatography method, developed for the simultaneous detection of acrylamide and quaternary ammonium cationic monomers was employed (see Figure 2). This has a sensitivity of below 1 ppm, with reproducibility (95% confidence intervals) in the range of +/-1%. The analysis was performed using an Agilent 1200 HPLC system equipped with a UV detector. As stationary phase a short/guard SEC column (6x50mm, 10μm particle size) was used. As mobile phase analytical-grade water was used with dissolved electrophoresis-grade SDS at 1 mL/min. Detection wavelength was 220nm. For the preparation of the samples a small drop of a water-in-oil emulsion was weighed in an analytical balance to four decimal places in a clean 20 mL glass vial. Ten millilitres of a solution containing a known concentration of Tergitol TMN-10 in analytical-grade water was then added to the vial and the contents were agitated vigorously for 10 min with a magnetic stirrer. Aliquots of 10 μL of these solutions were then injected into the liquid chromatograph.

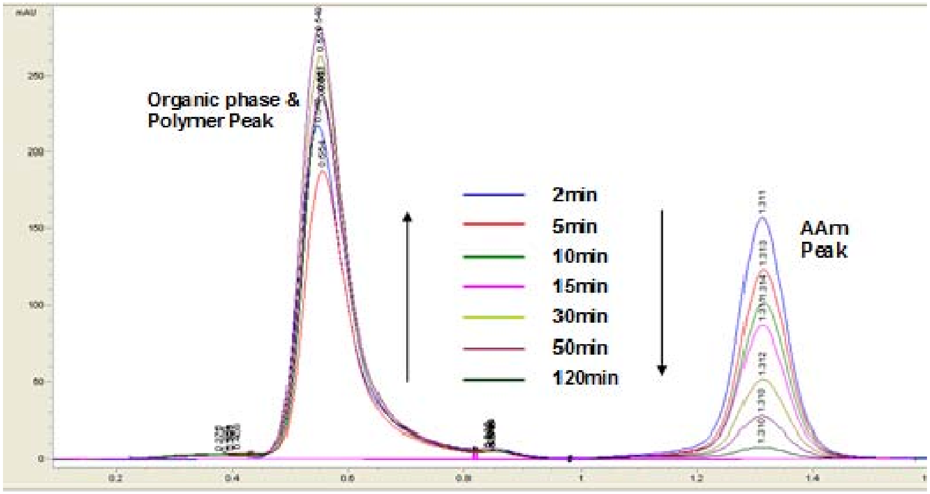

Figure 2. Measurement of monomer conversion using HPLC (inverse suspension polymerization)

Determination of monomer conversion using FTIR: IR spectra collected using the Universal diamond ATR (Attenuated Total Reflection) top-plate accessory at the Frontier FT-IR Spectrometer (Pelkin Elmer) The objective of this research was to demonstrate the feasibility was also used to estimate the individual monomer conversion in a straightforward manner from the recorded IR spectra after subtraction of the contribution of the aqueous phase. More specifically, the profile of C=O stretching peak (1675 cm^{-1}), C= C stretching (1590 cm^{-1}), =C-H bending (1436 cm^{-1}), -C-H bending (1328 cm^{-1}) and =C-H out-of-plane bending (988 cm^{-1}), and the conversion calculated from =C-H out-of-plane bending peak, were recorded for specific reaction times. The intensities of 1590, 1436 and 988 cm^{-1} peaks were weakened steadily. Among these peaks, the 1590 and 1436 cm^{-1} peaks were overlapped with other peaks, but 988 cm^{-1} peak was not overlapped. Therefore, the 988 cm^{-1} peak was used to calculate the conversion of the acrylamide monomer.

Polymerization procedure for inverse suspension polymerization: The purified monomers were removed from their storage desiccators and dissolved at the appropriate concentration in analytical grade water. When dissolved, the monomer solution was covered and purged with rarefied nitrogen (99.999% purity) for 30 min. The initiator solution was prepared by dissolving recrystallized KPS in water and added to the aqueous solution of the monomers. A thermometer was immersed in the solution and the temperature was maintained below 20°C during this procedure. The organic phase was prepared by weighing the appropriate amounts of paraffin oil (Sigma-Aldrich) and sorbitan monooleate (Sigma-Aldrich). Then the organic phase was charged into a well cleaned glass batch reactor and purged with nitrogen for 30min. The temperature was at set point when the aqueous phase was added and the system was emulsified by agitation at 300 +/- 1 r.p.m. Nitrogen sparging at a very slow rate was continued for the duration of the polymerization. The sampling procedure was as follows: A 20 ml syringe was used to take approximately 5ml of sample from the top of the reactor. 50μl of a 2 wt% hydroquinone (Aldrich) solution was added into the sample to stop the polymerization.

Measurement of molecular weight: A Polymer Labs Gel Permeation Chromatograph (GPC), equipped with an on-line viscometer (Viscotek model 210) and a refractive-index (RI) detector, was used for the determination of the molecular weight distribution of the polyacrylamide. A universal calibration curve, constructed with standards of known molecular weights (PolymerLabs), was employed for the determination of the MWD of the unknown polymer sample. The solutions of the polymer samples were prepared using HPLC-grade water. As a mobile phase 0.1N $NaNO_3$ in water was used at 1 mL/min (isocratic elution) at 40^{o}C.

EXPERIMENTAL RESULTS

In order to calculate the kinetic parameters for acrylamide-DMAEA copolymerization a set of solution polymerization experiments were performed. The experimental conditions were: Temperature: 57 and 67 ^{o}C, [M_{total}] = 0.1 and 0.25M, [$K_2S_2O_8$] = 1 and 5 mM, [Am]/[DMAEA] = 100/0, 60/40 and 20/80.

Using literature kinetic rate parameters, very good agreement between the experimental data and the simulations were found both for monomer conversion (Figure 3) and for comonomer composition. The estimated reactivity ratios were found to be well within the literature reported values (Figure 4).

Figure 5 shows the evolution of the Polyacrylamide MWD during polymerization. As it can be seen the average molecular weight decreases with time. This behaviour can also be seen in Figure 6 where a comparison between model prediction and experimental measurements for the number and weight average molecular weight is depicted for the same experimental conditions (T = 67^{o}C, [M] = 0.25M, [KPS] = 5mM).

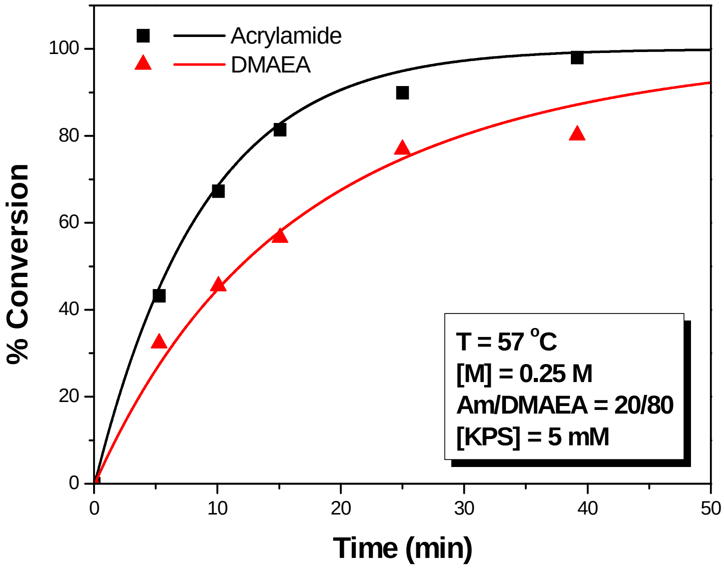

Figure 3. Solution copolymerization of acrylamide with DMAEA.

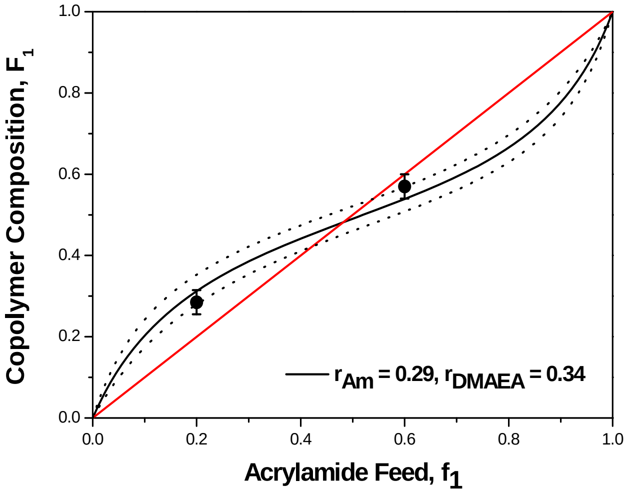

Figure 4. Estimated reactivity ratios using the solution copolymerization experiments.

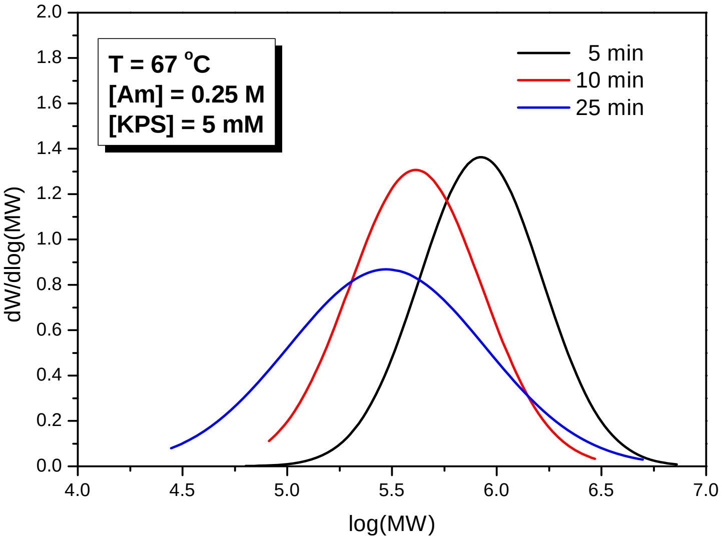

Figure 5. Evolution of MWD of Polyacrylamide (T = 67°C, [M] = 0.25M, [KPS] = 5mM).

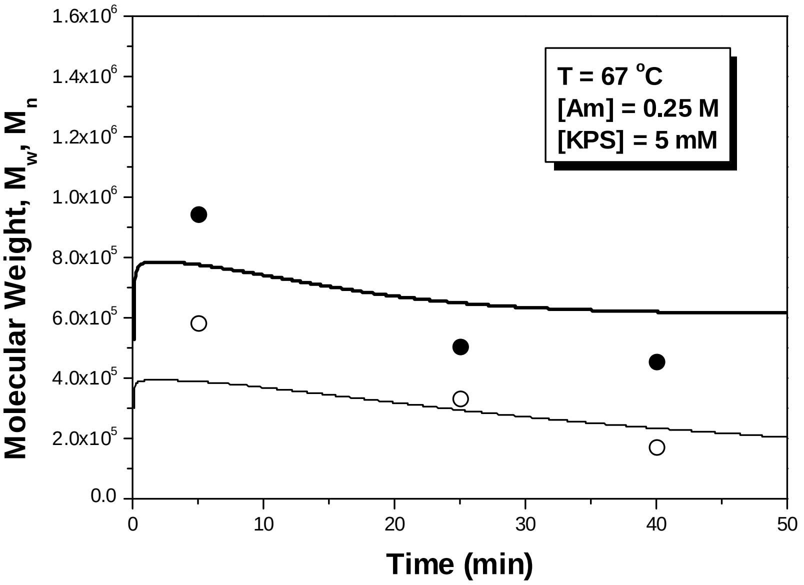

Figure 6. Comparison between model prediction and experimental measurements for the number and weight average molecular weight.

In Figure 7 a comparison between model prediction and experimental measurements for the molecular weight distribution is depicted for the same experimental conditions (T = 67°C, [M] = 0.25M, [KPS] = 5mM). A very good agreement is observed.

SIMULATION RESULTS

Comparison with Literature Experiments

The mathematical model which was developed for the simulation of polyacrylamide copolymerization were employed for the simulation of a large number of experimental data from literature. The comparison was made in a wide range of experimental conditions (temperature, monomer and initiator concentration and type) for the inverse suspension polymerization of acrylamide.

Figure 8 depicts a comparison of model predictions with experimental data by Kang et al [4] for solution polymerization at different reactor temperature (i.e., 40-65 °C). Note that for the data of Kang et al an induction period of ~15 min was used in their work due to presence of oxygen impurities which has been reported. As it can be seen a good agreement is observed between the experiment IR measurements and the model predictions.

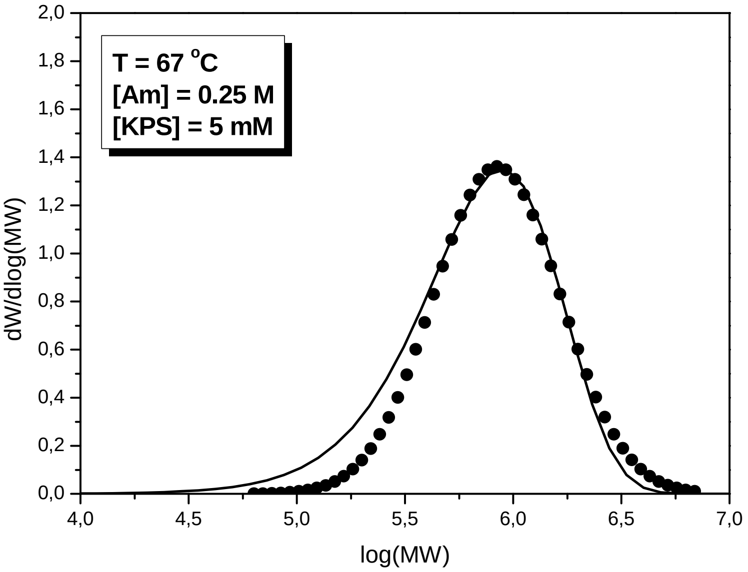

Figure 7. Comparison between model prediction and experimental measurement for the MWD of polyacrylamide.

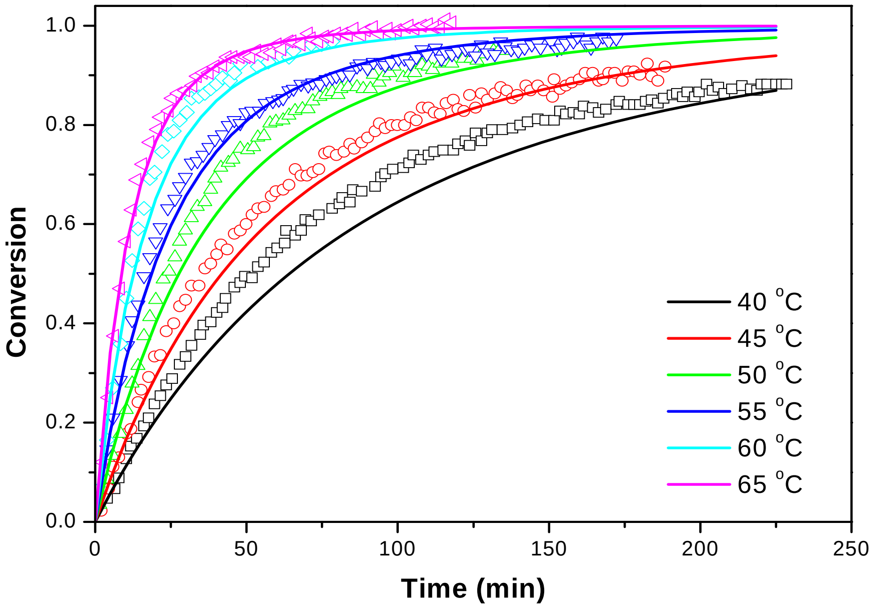

Figure 8. Comparison of model predictions with experimental data (IR measurements) by Kang et al [4], [M] = 0.7 M, [KPS] = 2.25mM

Figures 9 and 10 show a comparison between simulated and experimental acrylamide conversion. The experimental data for the inverse suspension polymerization of acrylamide were reported by Hunkeler [5]. As it can be seen the experimental measurements and the simulation results are in excellent agreement even at very high monomer conventration (i.e., 4.69 and 6.70 M, respectively)

CONCLUSIONS

Due to their outstanding properties, polyacrylamide products play a key role in several markets like water treatment, oilfield and mining as well as paper chemicals: In the water treatment industry, polyacrylamide is mainly used for various solid-liquid separation applications in drinking water and sludge dewatering processes, in the mining industry, polyacrylamide beads are primarily used for mineral extraction processes and water recovery and in the oilfield industry specialty polyacrylamide is primarily used in enhanced oil recovery. Finally, in the paper industry, polyacrylamide copolymers are used for retention and drainage in paper and paperboard machines..

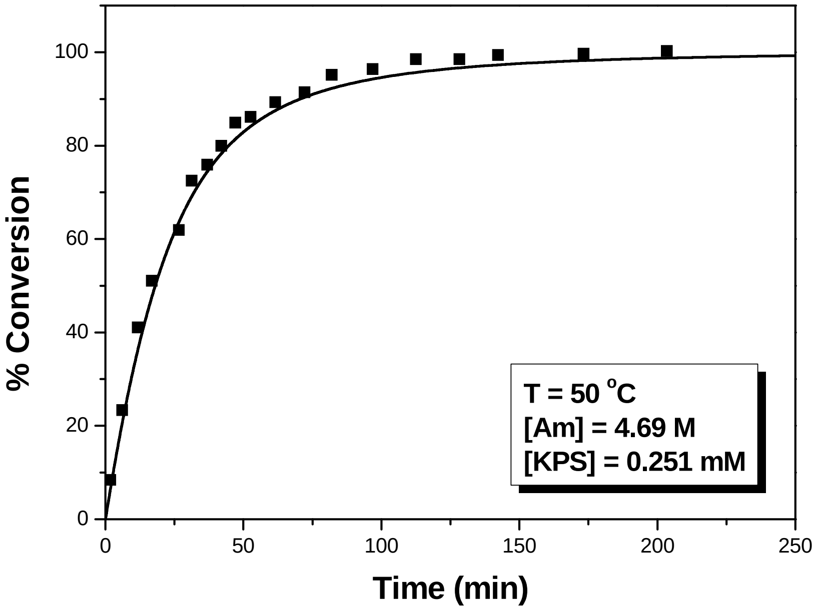

Figure 9. Comparison between model prediction and experimental measurements [5] (T = 50°C, [M] = 4.69M, [KPS] = 0.251mM.

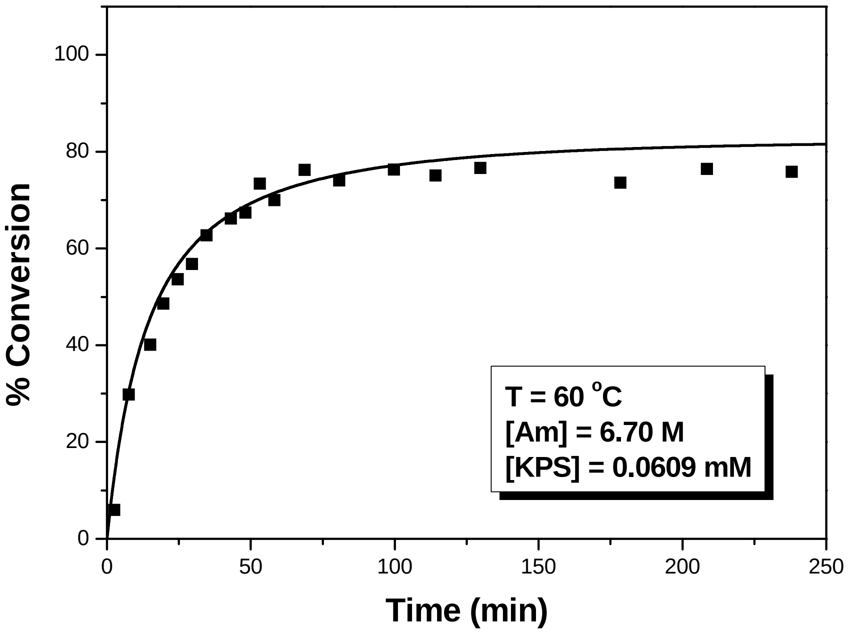

Figure 10. Comparison between model prediction and experimental measurements [5] (T = 60°C, [M] = 6.70M, [KPS] = 0.0609mM.

In the present work, a comprehensive theoretical and experimental kinetic investigation of the inverse suspension copolymerization of acrylamide is presented. The experimental work included the homopolymerization of acrylamide as well as the copolymerization with DMAEA at various compositions, was carried out in a 0.25L jacketed reactor. Paraffin oil was employed as the oil phase and Sorbitan monooleate was used as surfactant to stabilize the water in oil suspension. Monomer conversion was measured using HPLC and FTIR measurements and the molecular properties using GPC. In additon, a comprehensive mathematical model was developed based on a detailed kinetic mechanism to simulate the dynamic evolution of the monomer conversion and molecular weight developments (i.e., Mn, Mw, PD, MWD). The resulting kinetic model has been evaluated against experimental data for copolymerization of acrylamide with DMAEA. An excellent agreement has been found between model predictions and the experimental data. In addition, the model simulations has been compared with experimental measurements from the literature for solution and inverse suspension polymerization of acrylamide.

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