



# Synthesis and Characterization of High Molecular Weight Polyacrylamide Nanoparticles by Inverse-emulsion Polymerization

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## ABSTRACT

Polyacrylamide (PAM) and its copolymers are of important polymeric materials in petroleum industry, for example in drilling fluids and enhanced oil recovery. High molecular weights of these polymers are needed to have optimum efficiency in the above given applications. High molecular weight polyacrylamide nanoparticles were prepared by inverse-emulsion polymerization of aqueous acrylamide solution in xylene as a continuous phase under various conditions in the presence of a mixture of non-ionic emulsifiers (Tween 85 and Span 80). Monomer conversion, particle size and its distribution in the final emulsion and molecular weight of the polymer product were analyzed appropriately by gravimetry, dynamic light scattering (DLS) and capillary viscometry techniques. The effect of variables such as stirrer speed, temperature, initiator concentration and type, emulsifier concentration and hydrophilic-lipophilic balance (HLB) value of the emulsifier system on the viscosity-average molecular weight, particle size and its distribution and reaction kinetics were investigated. Depending on the reaction conditions, PAM particles with average particle sizes generally smaller than 200 nm in diameter and particle size distribution in the range of 50-400 nm and viscosity-average molecular weights as high as  $8 \times 10^6$  g.mol<sup>-1</sup> were obtained.

## Key Words:

polyacrylamide nanoparticle;  
inverse-emulsion polymerization;  
high molecular weight;  
reaction kinetics;  
particle size.

## INTRODUCTION

Polyacrylamide (PAM) and its copolymers are of most important synthetic water-soluble polymers. Acrylamide-based polymers are used as coagulants and flocculants in waste and potable water treatment applications, as displacing fluids in the enhanced oil recovery (EOR), drag reduction agents (DRAs) in water and crude oil transportation pipelines, polymeric additive in water-based drilling fluids, and as water clarifier in industries such as mining and paper

making [1-8].

Polyacrylamide and acrylamide-based polymers are commercially produced via heterophase water-in-oil (W/O) polymerization processes such as inverse-emulsion polymerization. Inverse-emulsion polymerization is defined as emulsification of aqueous solution of a water-soluble monomer in a continuous oil medium using a water-in-oil emulsifier with hydrophilic-lipophilic balance (HLB) between 4 and 9 and an oil-soluble or water-soluble

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initiator to give a colloidal dispersion of water-swollen polymer particles in oil [9-11].

Molecular weight of PAM in the above-mentioned applications is desirable to be sufficiently high. The commercial synthesis of high-molecular weight PAM ( $>10^6$  g.mol $^{-1}$ ) needs high monomer loading (about 50 wt% of the aqueous phase). Solution polymerization is limited because of the extremely high viscosity generated at high conversions which result in mixing and heat transfer problems and consequently leading to thermal instabilities [12]. To overcome this problem, it is necessary to use either dilute solutions, with an associated economic trade off due to inefficient reactor utilization, or a heterophase W/O polymerization.

Synthesis of polyacrylamide via inverse-emulsion homopolymerization, producing molecular weight higher than  $10^6$  g.mol $^{-1}$  has been reported in the literature [12-14]. Various oils such as toluene [15-20], heptane [18,21] and isoctane [22,23] are usually used as continuous phase in the inverse-emulsion homopolymerization of acrylamide. The results have shown that properties of final product such as molecular weight and particle size and its distribution can be affected by the type of oil used as a continuous phase [20]. Moreover, photo-initiated, inverse-emulsion polymerization of water-soluble monomers such as acrylamide can be carried out with concentrated monomer solution and a high reaction rate at a lower reaction temperature, which is beneficial to the production of polymer with high molecular weight [18]. There are also other works related to the inverse-(mini)emulsion homopolymerization of acrylamide [24-27]. However, these recent works deal with another type of inverse-emulsion polymerization, i.e. inverse-miniemulsion polymerization of acrylamide. Inverse-miniemulsion polymerization is a heterogeneous type of reaction with different reaction kinetics in comparison with conventional inverse-emulsion polymerization, which is not in the scope of this work.

Reports on using xylene as a continuous phase in the inverse-emulsion homopolymerization of acrylamide are scarce [11]. To our knowledge, there is no report on using mixture of emulsifiers Tween 85 and Span 80 in the inverse-emulsion polymerization of acrylamide to stabilize inverse-emulsion and to

control HLB value of the system. Inverse-emulsion polymerization of aqueous acrylamide solutions in xylene as a continuous phase in the presence of a mixture of non-ionic emulsifiers Tween 85 and Span 80 (for the first time) is investigated in the present study to synthesize stable inverse emulsions of high-molecular weight PAM nanoparticles with average diameters generally smaller than 200 nm and particle size distributions in the range of 50-400 nm (depending on the reaction condition) which lie within the size range of polymer nanoparticles reported in the literature [28,29], where polymer nanoparticles with average diameter up to about 250 nm and particle size distribution in the range of 50-350 nm have been synthesized. Simultaneous investigation of the reaction kinetics and characteristics of the final product in the inverse-emulsion polymerization of acrylamide by using xylene as a continuous phase can be considered as a novelty of this work. Effect of various parameters on the reaction kinetics, average particle size and viscosity-average molecular weight of the product are studied comprehensively. Then, suitable polymerization recipes are determined for synthesis of high-molecular weight PAM nanoparticles up to  $8 \times 10^6$  g.mol $^{-1}$ .

## EXPERIMENTAL

### Materials

Acrylamide ( $\geq 99\%$ , Merck) was recrystallized from chloroform. Xylene (mixture of isomers,  $\geq 99\%$ , Acros) was used as a continuous phase without further purification. 2,2'-Azobis(isobutyronitrile) (AIBN) ( $\geq 99\%$ , Fluka), benzoyl peroxide (BPO) ( $\geq 99\%$ , Merck) and potassium persulphate (KPS) ( $\geq 99\%$ , Merck) were used as initiator systems without further purification. Mixture of emulsifiers, polyethylene glycol sorbitan trioleate (Tween 85 as trade name) and sorbitan monooleate (Span 80 as trade name), were used as received from Merck Company. De-ionized water was used in all the reactions.

### Polymerization Procedure

Inverse-emulsion polymerization of acrylamide was performed in a 0.65 L stainless steel Buchi reactor equipped with a mechanical stirrer, heating system,

**Table 1.** Typical recipe for inverse-emulsion polymerization of acrylamide.

Ingredient	Weight percentage <sup>a</sup>
Acrylamide	15.0
Water	35.0
Xylene	45.0
Span 80	3.5
Tween 85	1.5
Benzoyl peroxide	0.01

(a) Weight percentage of ingredient relative to weight of all ingredients.

reflux condenser, sampling valve and inlets for reaction ingredients and nitrogen gas. Aqueous solution of acrylamide (30 wt%) was dispersed in xylene containing mixture of non-ionic emulsifiers of Tween 85 and Span 80 by stirring at 800 rpm with a six-bladed turbine impeller to form inverse water-in-oil (W/O) emulsion. Highly pure nitrogen gas was bubbled at room temperature into the reaction mixture for about 30 min. Temperature and stirrer speed were set at 60°C and 400 rpm, respectively, and initiator solution in xylene (for oil-soluble initiator) or in water (for water-soluble initiator) was then charged into the reaction mixture. This stage point was set as reaction starting time.

Typical polymerization procedure of acrylamide in the inverse-emulsion system has been given in Table 1. Polymerization was performed for 150 min at 60°C and stirrer speed of 400 rpm. Mixture of non-ionic emulsifiers (Tween 85 and Span 80) was used in all reactions. Xylene was used as a continuous phase.

### Conversion Analysis

To determine conversion of acrylamide as a function of time, samples of approximately 10 g ( $m_1$ ) were removed from reaction mixture at various time intervals. An exact amount of about 0.5 mL of aqueous solution of hydroquinone (1 wt%) was added to each sample in order to stop the polymerization progress. Samples were precipitated with excess amount of acetone and the obtained precipitates were dried under vacuum at 60°C for 24 h until constant weights ( $m_2$ ) were reached. Conversion of acrylamide was then calculated by eqn (1) as follows:

$$\text{Conversion (\%)} = \frac{m'_2}{(m_1 \times m_3)} \times 100 \quad (1)$$

where  $m'_2$  is corrected weight of dried polymer powder (subtracting the amount of hydroquinone added to the samples) and  $m_3$  indicates the weight ratio of initial monomer relative to all the ingredients used in the polymerization procedure.

### Determination of Emulsion Particle Size and its Distribution

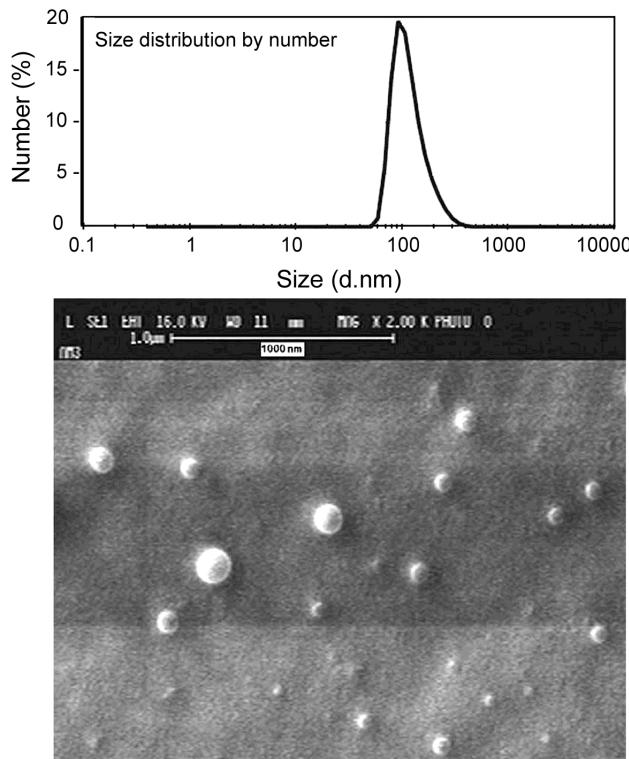
Average-diameter of water-swollen polymer particles ( $d_p$ ) and polydispersity index (PDI) of particle size distribution was measured by Malvern Zetasizer Nano Series dynamic light scattering (DLS) (using a laser as light source with wavelength of 633 nm under scattering angle of 90° at ambient temperature; 25°C) immediately after diluting the emulsions up to ~0.05% solid content by 10 wt% solution of Span 80 in xylene. The polydispersity index (PDI) is defined as the standard deviation of the particle size distribution divided by the average value of the particles' diameter.

In particle size measurements by scanning electron microscopy (SEM) (Model Stereoscanner 360, Cambridge Instrument Co.), one drop of diluted latex was placed on the sample holder and then freeze-dried under vacuum for removing the water. Coating was carried out under reduced pressure in an inert argon atmosphere.

Typical curve obtained from DLS measurement and SEM micrograph for experiment run 10 is given in Figure 1. It is clear from this figure that polymer nanoparticles have average-particle size of 119 nm in diameter and particle size distribution in the range of 50–310 nm. Figure 1 shows that DLS results are in good agreements with SEM observation results. Therefore, DLS technique was used to measure polymer particle size and its distribution.

### Determination of Molecular Weight

Viscosity-average (close to weight-average) molecular weights of the final polymers were determined by Ubbelohde capillary viscometry method using the following Mark-Houwink equation for a 0.5 M aqueous solution of sodium chloride (NaCl) at 25°C [30].



**Figure 1.** Results of particle size distribution of polyacrylamide nanoparticles for run 10 measured by: (a) DLS technique (Table 4, average diameter of polymer particles = 119 nm, particle size distribution = 50-310 nm and PDI = 0.097) and (b) SEM observation.

$$[\eta] = 7.19 \times 10^{-3} \overline{M}_w^{0.77} (\text{mL.g}^{-1})$$

for

$$\overline{M}_w = 5 \times 10^5 - 6 \times 10^6 \text{ g.mol}^{-1} \quad (2)$$

A portion of each final emulsion was precipitated by an excess amount of acetone and washed several times by acetone. Precipitates were then dried under vacuum at 60°C for 24 h. To further purify, dried polymers were dissolved in de-ionized water and then precipitated by an excess amount of acetone. Purified precipitates were again dried under vacuum at 60°C for 24 h. One hundred milligram of the purified polymer powder was dissolved in 100 mL of 0.5 M aqueous solution of sodium chloride within at least one day under stirring. The obtained solution (0.1 g of polymer in 100 mL of solution) was diluted automatically by an automatic capillary viscometer

(Lauda Model PV15) to prepare concentrations of 0.08, 0.06, 0.04 and 0.02 g of polymer in 100 mL of solution. Viscosity of each solution was automatically measured three times by the same automatic viscometer. The intrinsic viscosity,  $[\eta]$ , was determined from intercept value of a linear regression of relationship between the specific viscosity and polymer concentration as well as the reduced viscosity and polymer concentration (in  $\text{g.mL}^{-1}$ ).

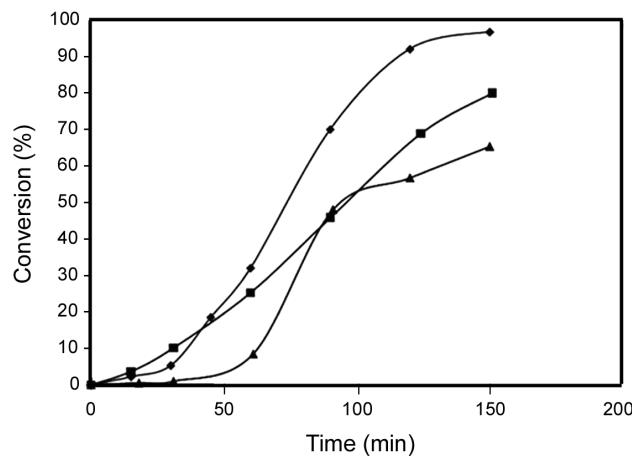
## RESULTS AND DISCUSSION

Inverse-emulsion polymerization of aqueous acrylamide solution in xylene as a continuous phase was performed under various conditions in the presence of mixed emulsifiers of Tween 85 and Span 80. All polymerizations, except those stated in the text, were initiated by BPO initiator at 60°C. The effect of various parameters such as stirrer speed, concentration and HLB of mixed emulsifiers, concentration and type of initiator and temperature on the polymerization rate, particle size and its distribution of final emulsion and molecular weight of final polymer were investigated as in the following section.

### Effect of Stirrer Speed

Stirrer speed has an important role in dispersing aqueous droplets containing water-soluble monomer in continuous oil phase where the formed inverse-emulsion is not thermodynamically stable [31,32]. The effect of stirrer speed on conversion, average particle size of final emulsion and molecular weight of final polymer was investigated in three different stirrer speeds, i.e. 300, 400 and 500 rpm, by using six-bladed turbine type stirrer. Polymerization conditions and experimental results are given in Table 2 and Figure 2.

At the stirrer speed of 300 rpm, final conversion of acrylamide after 150 min reached about 80% (Figure 2). It can be observed from Figure 2 that the conversion curve of run 1 (stirrer speed of 300 rpm) levels off after 150 min (i.e., by an S shaped curve). Hence the linearity of this curve is a consequence of limited final reaction time rather than changes in the kinetic of reaction.



**Figure 2.** Conversion versus time curves for inverse-emulsion polymerization of acrylamide at different stirring rates: (■) 300 rpm, (◆) 400 rpm and (▲) 500 rpm (Table 2).

By increasing the stirrer speed to 400 rpm, final conversion increased and reached about 100%. It is clear that size of monomer droplets and polymer particles decrease by increasing the stirrer speed and thereby interfacial area of emulsion increases. Therefore, polymerization rate increases and average diameter of polymer particles decreases (Figure 2 and Table 2). Moreover, although molecular weight of the final polymer decreases by increasing the stirrer speed, however, its value is still sufficiently high ( $>10^6 \text{ g.mol}^{-1}$ ).

With further increase of stirrer speed to 500 rpm, final conversion decreased to about 65%. Also, a significant amount of coagulum and precipitate was formed during the reaction. It was attributed to the increased coalescence of polymer particles due to the higher stirrer speed. A probable reason is that high stirrer rate leads to desorption of the stabilizer molecule from the particle surface and the particles

become so unstable that coagulation occurs [33]. It should be noted that final polymer obtained at 500 rpm was not fully dissolved in water. Hence, measurement of the molecular weight of final polymer was not possible for this reaction. It is clear from Table 2 that average-diameter of polymer particles decreases by increasing the stirrer speed. Overall, the results show that stirrer speed has a significant effect on the reaction characteristics.

There are some reports in the literature [28,29] which consider polymer particles with diameters as high as 250 nm as polymer nanoparticle because particle size distribution is in the range of 50-400 nm. Therefore, although average particle diameter data in the present work (for example, see average diameter of polymer particles reported in tables) have been reported to be more than 100 nm, however, particle size distribution of the synthesized polyacrylamide particles is in the range of 50-400 nm. About 20-50% (depending on the reaction conditions) of polymer particles have diameters below 100 nm (Tables and Figure 1). Thus, according to the above literature, it is appropriate to consider the synthesized polyacrylamide particles as polyacrylamide nanoparticles.

### Effect of HLB Value of Emulsifier System

It has been observed that using two non-ionic emulsifiers, one with high HLB value and another with low HLB value, would result in improved colloidal stability of an inverse-emulsion system [17,34-36]. Mixture of two non-ionic emulsifiers (Tween 85 with high HLB value of 11.0 and Span 80 with low HLB value of 4.3) was used in the present study to prepare stable inverse-emulsions of aqueous acrylamide solution in xylene. Different weight ratios of emulsifiers were used in the polymerization recipe to attain various HLB values. It should be noted that

**Table 2.** Effect of stirring rate on the inverse-emulsion polymerization of acrylamide<sup>a</sup>.

Run	Stirrer speed (rpm)	X (%) <sup>b</sup>	$\bar{M}_W$ ( $\times 10^{-6} \text{ g/mol}$ )	Particle size (nm)	PSD <sup>c</sup> (nm)	PDI
1	300	79.9	5.62	171	80-350	0.123
2	400	96.7	4.29	146	50-300	0.181
3	500	65.3	-	137	70-280	0.064

(a) Temperature = 60°C, reaction time = 150 min (Table 1); (b) X (%) indicates final conversion (%) at reaction time of 150 min; (c) particle size distribution (PSD).

**Table 3.** Effect of HLB value of emulsifying system on the inverse-emulsion polymerization of acrylamide<sup>a</sup>.

Run	Span 80 (wt%)	Tween 85 (wt%)	HLB value	X (%)	$\bar{M}_W$ ( $\times 10^{-6}$ g/mol)	Particle size (nm)	PSD (nm)	PDI
4	4.5	0.5	5.04	40.3	1.32	-	-	-
5	4.0	1.0	5.64	86.2	4.23	143	60-270	0.116
2	3.5	1.5	6.31	96.7	4.29	146	50-300	0.181
6	3.0	2.0	6.98	85.4	4.05	155	80-310	0.182

(a) T = 60°C, t = 150 min, stirrer speed = 400 rpm (Table 1).

in all reactions the weight ratios of emulsifiers of reaction ingredients was kept at 5 wt%. HLB value of system was set at a desirable value by changing the weight fraction of Tween 85 and Span 80 via eqn (3).

$$\text{HLB value} = [4.3 \times x] + [11.0 \times (1-x)] \quad (3)$$

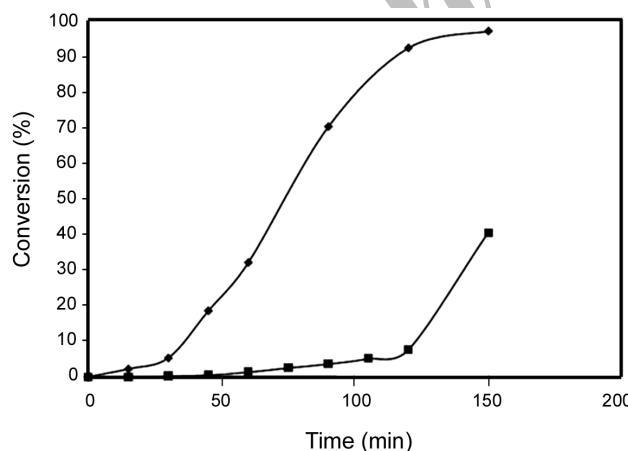
where x is the weight fraction of Span 80. Values of 11.0 and 4.3 denote the HLB values of Tween 85 and Span 80, respectively. Inverse-emulsion polymerization of acrylamide was performed at different HLB values (Table 3). Experimental results are given in Table 3 and Figure 3. It is clear from the results that when reaction is performed at HLB value of 5.04, a significant amount of coagulum and precipitate is formed during the reaction process and polymerization proceeds with slow rate (Table 3 and Figure 3). Due to highly unstable inverse-emulsion system, the

measurement of particle size was ignored for this reaction. Instead, an experiment was performed in the presence of only Span 60 (HLB = 4.7). Similar results were observed and reaction mixture completely coagulated in the initial stage of polymerization. The results showed that emulsifier(s) with HLB value equal or lower than 5 in the preparation of inverse-emulsion are not suitable to obtain a stable system.

Results given in Table 3 indicate that HLB values between 5.64 and 6.98 result in the colloidal stable inverse-emulsions. It is clear from Table 3 that particle size and its distribution as well as the molecular weight of final polymers is not significantly affected by the HLB value of emulsifier system in the region of 5.64-6.98. However, final conversion is affected by the HLB value (Table 3). Moreover, although final conversion was high enough for reactions performed in the HLB region of 5.64-6.94, however, maximum final conversion was observed for the reaction mixture with HLB value of 6.31. Therefore, polymerization recipe with HLB value of 6.31 was used in the next reaction.

### Effect of Emulsifier Concentration

Inverse-emulsion polymerization of acrylamide was performed at various concentrations of mixed emulsifiers under the constant HLB value of 6.31 (Table 4). Results given in Table 4 show that particle size and its distribution (PDI) are reduced by increasing the emulsifier concentration. On the other hand, molecular weight of final polymer increased by increasing the emulsifier concentration up to 5 wt% and then remained almost constant beyond this value. Conversion versus time for polymerizations performed at different emulsifier concentrations is shown in Figure 4. Polymerization rate is reduced by



**Figure 3.** Dependence of conversion on the HLB value of the emulsifying system for inverse-emulsion polymerization of acrylamide: (◆) HLB = 6.31 and (■) HLB = 5.04 (Table 3).

**Table 4.** Effect of emulsifier concentration on the inverse-emulsion polymerization of acrylamide<sup>a</sup>.

Run	Span 80 (wt%)	Tween 85 (wt%)	Xylene (wt%)	X (%)	$\bar{M}_W$ ( $\times 10^{-6}$ g/mol)	Particle size (nm)	PSD (nm)	PDI
9	2.45	1.05	46.5	100.0	2.94	202	120-360	0.218
2	3.50	1.50	45.0	96.7	4.29	146	50-300	0.181
10	4.55	1.95	43.5	100.0	3.91	119	50-310	0.097

(a) T = 60°C, t = 150 min, stirrer speed = 400 rpm (Table 1).

increasing the mixed emulsifier concentration from 3.5 wt% to 5 wt% and then it is increased by further increase in emulsifier concentration to 6.5 wt%. However, final conversion remained almost constant in all experiments. Effect of emulsifier concentration on the inverse-emulsion system is complex and depends on various parameters such as the solvent type used as a continuous phase. For example, it has been reported that polymerization rate increases by increasing the emulsifier concentration when toluene is used as a continuous phase [12,15,20]. Different effects of emulsifier concentration on the conversion were observed in the present study, which can be attributed to the effect of continuous phase (xylene) on the observed behaviours.

Polymerization rate ( $R_p$ ) in the classic emulsion polymerization is expressed as eqn (4) [37,38].

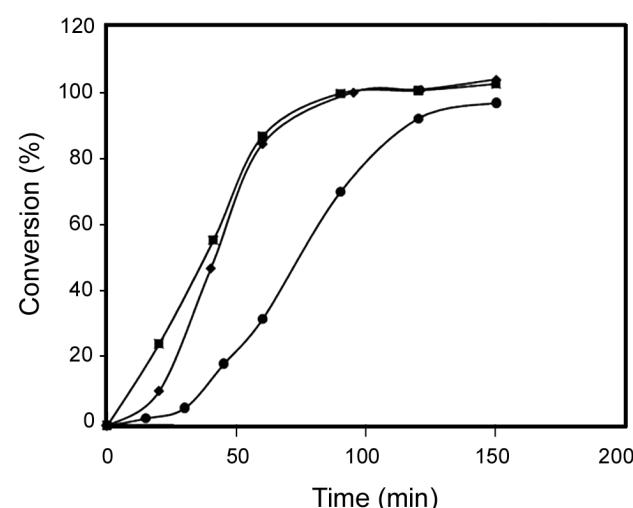
$$R_p = \frac{\bar{k}_p \bar{n} N_p C_{MP}}{N_{av}} \quad (4)$$

where  $\bar{k}_p$  is average propagation rate constant in the particle phase,  $\bar{n}$  indicates average number of growing chains per particle,  $N_p$  indicates number of latex particles per unit volume of the continuous phase,  $C_{MP}$  indicates monomer concentration in the monomer swollen polymer particles at the II interval of emulsion polymerization and  $N_{av}$  is Avogadro's number.

According to eqn (4), there are two kinetic-dependent parameters ( $\bar{n}$  and  $N_p$ ) in reaction condition which may explain the observed results. The higher the emulsifier concentration, the higher the number of polymer particles and the smaller would be the diameter of polymer particles. As a result, the number of growing (macro)radicals per

polymer particles decreases. By increasing the emulsifier concentration to 5 wt%, the overall rate of polymerization is decreased. The result may be due to decreased number of effective growing (macro)-radicals per polymer particle as a result of significant decrease in particle diameters. Therefore, although  $N_p$  increases by higher number of polymer particles, the product of  $\bar{n}$  and  $N_p$  and thereby polymerization rate is dropped in comparison with reaction performed at low concentration of the emulsifier. Furthermore, by emulsifier concentration of 6.5 wt% (run 10), the number of polymer particles increases while  $\bar{n}$  does not decrease significantly. Thus, the product of  $\bar{n}$  and  $N_p$  and thereby  $R_p$  increases. These results show that variations of  $\bar{n}$  and  $N_p$  do not affect  $R_p$  with the same impact.

There are always a competition between termination and chain transfer, especially for acrylamide.



**Figure 4.** Conversion versus time curves for inverse-emulsion polymerization of acrylamide at different emulsifier concentrations: (◆) 3.5 wt%, (●) 5.0 wt% and (■) 6.5 wt% (Table 4).

**Table 5.** Effect of initiator concentration on the inverse-emulsion polymerization of acrylamide<sup>a</sup>.

Run	BPO (wt%)	X (%)	$\bar{M}_W$ ( $\times 10^{-6}$ g/mol)	Particle size (nm)	PSD (nm)	PDI
11	0.005	100.0	4.57	156	80-360	0.129
2	0.010	96.7	4.29	146	50-300	0.181
12	0.020	73.5	3.90	151	80-350	0.065

<sup>a</sup> T = 60°C, t = 150 min, stirrer speed = 400 rpm (Table 1).

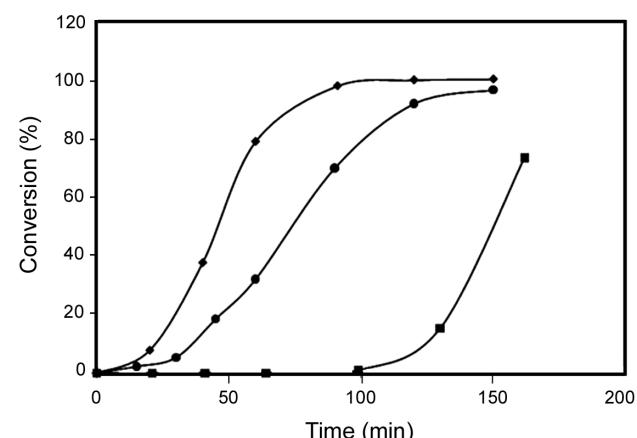
Molecular weight of the polymer increases by increasing the emulsifier concentration (Table 4). Qualitatively, this may be attributed to slower rate of termination reaction as a result of lowering number of growing (macro)radicals per polymer particles. This effect can be seen in run 2 (relative to run 9). However, further increase in emulsifier concentration in run 10 may lead chain transfer reactions inclined towards the emulsifier, resulting in a slightly decreased polymer molecular weight.

### Effect of Initiator Concentration

Inverse-emulsion polymerization of acrylamide was carried out in the presence of various concentrations of benzoyl peroxide (BPO) initiator (Table 5). Results of the reaction kinetics are given in Table 5 and Figure 5. It is clear from Table 5 that particle size decreases slightly by increasing the initiator concentration from 0.005 wt% to 0.01 wt% and then remains constant by further increases in initiator concentration to 0.02 wt%. Results showed that particle size is not significantly affected by the initiator concentration, while the molecular weight of final polymer decreases by increasing the initiator concentration (Table 5) due to higher number of initiator-derived radicals.

Conversion versus time plots for the reactions performed at various initiator concentrations are shown in Figure 5. It is clear from Figure 5 that polymerization rate falls by increasing the initiator concentration. At constant values of C<sub>MP</sub> and N<sub>p</sub> in the interval II of batch emulsion polymerization systems, polymerization rate is generally determined by decomposition rate of initiator in the continuous phase (or equivalently concentration of initiator-derived radicals) and diffusion (or precipitation) of grown oligoradicals into the polymer particles. The unexpected results in Figure 5 may be attributed to the

lower efficiency of oil-soluble initiator at the higher initiator concentration. In these experiments, the micelle concentration as well as number of the polymer particles (Table 5) was almost constant due to equal concentration of the emulsifier. The number of initiator-derived radicals in the continuous phase (xylene) increases by increasing the initiator concentration. Under the condition of higher concentration of initiator and thereby higher concentration of (oligo)radicals in the continuous phase, bimolecular termination of (oligo)radicals may occur before diffusing into the micelles and polymer particles, resulting in the delay in the onset of polymerization until the concentration of initiator and thereby initiator-derived radical decreases in the reaction medium (run 12 in Figure 5). At this time, (oligo)-radicals can enter into the micelles and polymer particle, resulting in the start up of polymerization reactions.



**Figure 5.** Conversion versus time curves for inverse-emulsion polymerization of acrylamide at various initiator concentrations: (◆) 0.005 wt%, (●) 0.010 wt% and (■) 0.020 wt% (Table 5).

**Table 6.** Influence of initiator type on the inverse-emulsion polymerization of acrylamide<sup>a</sup>.

Run	Initiator type	Initiator (wt%) <sup>b</sup>	X (%)	$\bar{M}_W$ ( $\times 10^{-6}$ g/mol)	Particle size (nm)	PSD (nm)	PDI
13	KPS	0.0110	62.4	2.31	124	60-250	0.044
2	BPO	0.0100	96.7	4.29	146	50-300	0.181
14	AIBN	0.0068	100.0	8.03	153	80-240	0.035

(a) T = 60°C, t = 150 min, stirrer speed = 400 rpm (Table 1); (b) equimolar amount of the initiator was used in all experiments.

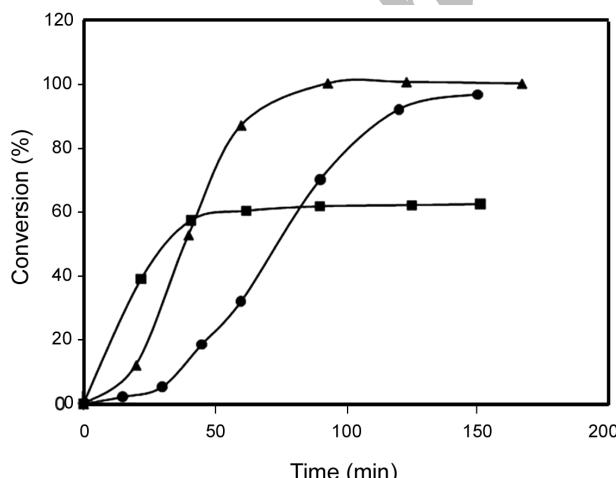
### Effect of Initiator Type

To study the effect of initiator type on the reaction kinetics, three different initiators with the same molar concentrations were used in the inverse-emulsion polymerization of acrylamide. BPO and AIBN were used as oil-soluble initiators with different decomposition rate constants while potassium persulphate (KPS) was used as a water-soluble initiator (Table 6). Conversion as a function of time for experiments given in Table 6 is shown in Figure 6. It is clear from this figure that initial conversion for system initiated with KPS is higher than those initiated with BPO or AIBN. However, conversion reaches a constant value after 40 min, thus the final conversion remains low (about 60%).

High initial polymerization rate and low final conversion in the presence of water-soluble initiator (KPS) may be attributed to the rapid decomposition of

initiator in the aqueous phase where monomers exist. When reaction was performed in the presence of BPO or AIBN, final conversion increased significantly and reached about 100% (Figure 6). However, polymerization rate in the presence of AIBN was higher than that of BPO, which can be attributed to the higher decomposition rate constant of AIBN ( $9.8 \times 10^{-6}$  s<sup>-1</sup> at 60°C) in comparison with BPO ( $2.24 \times 10^{-6}$  s<sup>-1</sup> at 60°C) [39].

Results of particle size analysis (Table 6) showed that although particle size is not affected by the oil-soluble initiator type, yet the particle size distribution (i.e., PDI) is dependent on the oil-soluble initiator type. When the reaction is performed in the presence of AIBN, particle size distribution (PDI) is narrow. This behaviour may be attributed to the rapid particle nucleation and growth as a result of rapid polymerization rate, resulting in the narrow particle size distribution. When the water soluble initiator was used in the system, particle size decreased probably due to the low final reaction conversion. Similarly, the particle size distribution (PDI) was narrowed in the presence of KPS as in the case of AIBN. According to eqn (4), these results indicate that reaction kinetics ( $\bar{n}$  and/or  $N_p$ ) can be affected significantly by the oil or water solubility of initiator. Moreover, the results in Table 6 show that highest molecular weight was observed for the polymerization initiated with AIBN concentration of  $8.03 \times 10^6$  g.mol<sup>-1</sup>.



**Figure 6.** Conversion versus time curves for inverse-emulsion polymerization of acrylamide initiated by different initiators: (●) BPO, (■) KPS and (▲) AIBN (Table 6).

### Effect of Temperature

Inverse-emulsion polymerization of acrylamide was performed at different reaction temperatures (Table 7). Effect of reaction temperature on conversion versus time is given in Figure 7. It is clear from Table 7 and Figure 7 that polymerization rate and final

**Table 7.** Effect of temperature on inverse-emulsion polymerization of acrylamide<sup>a</sup>.

Run	T (°C)	X (%)	$\bar{M}_W$ ( $\times 10^{-6}$ g/mol)	Particle size (nm)	PSD (nm)	PDI
7	50	51.7	5.61	152	90-290	0.139
2	60	96.7	4.29	146	50-300	0.181
8	70	99.4	3.06	161	100-400	0.157

<sup>a</sup> (a) t = 150 min, stirrer speed = 400 rpm (Table 1).

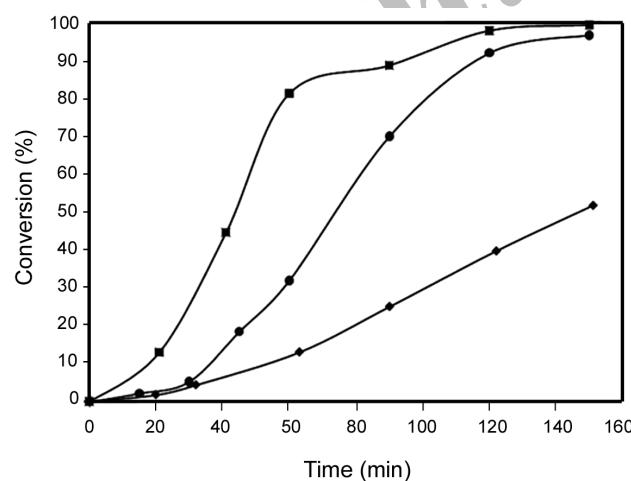
conversion are increased by raising the reaction temperature. It is well known that reaction temperature is an important parameter in the inverse-emulsion polymerization process [40]. Polymerization rate increases with reaction temperature as a result of increase in the decomposition rate constant and decrease in the preventive effect of emulsion interface, resulting in the increased diffusion of oil-soluble initiator-derived radicals into the aqueous phase [40].

It is clear from Table 7 that molecular weight of final polymer drops by rising reaction temperature. This can be attributed to the increased concentration of (macro)radicals and thereby increased probability of bimolecular termination in relation to increased reaction temperature. Results given in Table 7 indicate that diameter of polymer particles is not affected very much by reaction temperature; however, the lower particle size distribution (PDI) due to

increased reaction temperature may be because of rapid particle nucleation and growth processes. Analysis of the final polymers shows that molecular weight decreases by increasing the reaction temperature, however, molecular weight values still remain sufficiently high ( $>10^6$  g.mol<sup>-1</sup>).

## CONCLUSION

Inverse-emulsion polymerization of aqueous acrylamide solution in xylene as a continuous phase was carried out under various conditions in the presence of a mixture of non-ionic emulsifiers (Tween 85 and Span 80). Monomer conversion, particle size and its distribution of final emulsion and molecular weight of the final polymer were analyzed appropriately by gravimetry, DLS and capillary viscometry. The results showed that reaction kinetics, particle size and molecular weight are affected by stirrer speed. It was also observed that more stable inverse-emulsions are obtained when the HLB value of emulsifier system is set at or higher than 5.64. Under these conditions, the conversion rate, molecular weight and particle size are not very much dependent on the HLB value of emulsifier system. Whereas, at constant HLB value the particle size and its distribution were decreased as the emulsifier concentration increased. Molecular weight of the final polymer increased by increasing emulsifier concentration (up to 5 wt%) and then remained almost constant with further increase in the emulsifier concentration. Although polymerization rate was affected by emulsifier concentration, however, final conversion was almost similar for reactions performed at various emulsifier concentrations. The data show that polymerization rate and molecular weight of final polymer are lowered by



**Figure 7.** Conversion versus time curves for inverse-emulsion polymerization of acrylamide at various polymerization temperatures: (◆) 50°C, (●) 60°C and (■) 70°C (Table 7).

increasing the initiator concentration; however, particle size is not affected by the initiator concentration. Results on the effect of initiator type indicated that when oil-soluble initiator with higher decomposition rate constant (i.e., AIBN) is used in the inverse-emulsion polymerization of acrylamide, polymerization rate increases while particle size and its distribution decrease. When the water-soluble initiator (i.e., KPS) was used in the reaction, final conversion and particle size and its distribution decreased while the initial polymerization rate increased. It was also observed that by rising the reaction temperature, final conversion and polymerization rate increase while the molecular weight decreases. Particle size and its distribution were not affected by temperature. In all reactions, polyacrylamide nanoparticles with average diameter of water-swollen polymer particles generally smaller than 200 nm and viscosity-average molecular weight higher than  $10^6 \text{ g.mol}^{-1}$  were obtained.

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## REFERENCES

- Hunkeler DJ, Hernandez-Barajas J, Inverse-emulsion/suspension polymerization. In: *Polymeric Materials Encyclopedia*, Salomone JC (Ed), CRC, New York, 3322-3333, 1996.
- Bajpai AK, Bajpai SK, Kinetics of  $\text{Ce}^{4+}$ /sodium sulphite initiated polymerization of acrylamide, *Iran Polym J*, **4**, 10-16, 1995.
- Jha A, Agrawal S, Mishra A, Rai JP, Synthesis, characterization and flocculation efficiency of poly(acrylamide-*co*-acrylic acid) in tannery waste-water, *Iran Polym J*, **10**, 85-90, 2001.
- McCarty MF, Olson RS, Polyacrylamides for the mining industry, *Mining Eng*, **11**, 61-65, 1959.
- Moody G, The use of polyacrylamides in mineral processing, *Miner Eng*, **5**, 479-492, 1992.
- Vacher CA, Loch RJ, Raine SR, Effect of polyacrylamide additions on infiltration and erosion of disturbed lands, *Aust J Soil Res*, **41**, 1509-1520, 2003.
- Pelton RH, Allen LH, The effect of some electrolytes on flocculation with cationic polyacrylamide, *Colloid Polym Sci*, **261**, 485-492, 1983.
- Lu S, Liu R, Sun X, A study on the synthesis and application of an inverse emulsion of amphoteric polyacrylamide as retention aid in papermaking, *J Appl Polym Sci*, **84**, 343-350, 2002.
- Vanderhoff JW, Bradford EB, Tarkowski HL, Shaffer JB, Wiley RM, Inverse emulsion polymerization, *Adv Chem Ser*, **34**, 32-51, 1962.
- Vanderhoff JW, Wiley RM, Water-in-oil emulsion polymerization process for polymerizing water soluble monomers, *US Patent 3284393* (1966).
- Vanderhoff JW, Distefano FV, El-Aasser MS, O'Leary R, Shafer OM, Vissioli DL, Inverse emulsion polymerization of acrylamide: polymerization kinetics and process development, *J Dispers Sci Technol*, **5**, 323-363, 1984.
- Hunkeler D, Synthesis and characterization of high molecular weight water-soluble polymers, *Polym Int*, **27**, 23-33, 1992.
- Kim KU, Lee HY, Park BH, Inverse emulsion polymerization of acrylamide, *Polymer (Korea)*, **6**, 188-195, 1982.
- Azzam R, Singer K, High molecular weight polyacrylamide prepared by electron beam irradiation, *Polym Bull*, **2**, 147-156, 1980.
- Kurenkov VF, Verizhnikova AS, Myagchenkov VA, Aspects of inversion emulsion polymerization of acrylamide in presence of NaOH and the initiating  $\text{K}_2\text{S}_2\text{O}_8/\text{Na}_2\text{S}_2\text{O}_5$  system, *Polym Sci U.S.S.R.*, **28**, 543-548, 1986.
- Khokhrin SA, Shibalovich VG, Nikolayev AF, Chudnova MV, Soap-free emulsion polymerization of acrylamide in the presence of manganese (III) sulphocomplex, *Polym Sci U.S.S.R.*, **27**, 1901-1904, 1985.
- Graillat C, Pichot C, Guyot A, El-Aasser MS, Inverse emulsion polymerization of acrylamide. I. Contribution to the study of some mechanistic aspects, *J Polym Sci, Part A: Polym Chem*, **24**, 427-449, 1986.

18. Chen LW, Yang W, Photoinitiated, inverse emulsion polymerization of acrylamide: some mechanistic and kinetic aspects, *J Polym Sci, Part A: Polym Chem*, **42**, 846-852, 2004.
19. Zhung D, Song X, Liang F, Li Z, Liu F, Stability and phase behavior of acrylamide-based emulsions before and after polymerization, *J Phys Chem B*, **110**, 9079-9084, 2006.
20. Baade W, Reichert KH, Polymerization of acrylamide in dispersion with paraffinic and aromatic liquids as oil phase, *Makromol Chem Rapid Commun*, **7**, 235-241, 1986.
21. Gromov VF, Osmanov TO, Glazkova IV, Emulsion polymerization of acrylamide, *Polym Sci U.S.S.R.*, **30**, 1210-1215, 1988.
22. Pross A, Platkowski K, Reichert KH, The inverse emulsion polymerization of acrylamide with pentaerythritolmyristate as emulsifier. 1. Experimental studies, *Polym Int*, **45**, 22-26, 1998.
23. Platkowski K, Pross A, Reichert KH, The inverse emulsion polymerization of acrylamide with pentaerythritolmyristate as emulsifier. 2. Mathematical modeling, *Polym Int*, **45**, 229-238, 1998.
24. Capek I, The inverse mini-emulsion polymerization of acrylamide, *Design Monomers Polym*, **6**, 399-409, 2003.
25. Capek I, On the hybrid inverse-emulsion polymerization of acrylamide, *Polym-Plast Technol Eng*, **44**, 539-555, 2005.
26. Qi G, Jones CW, Schork FJ, RAFT inverse miniemulsion polymerization of acrylamide, *Macromol Rapid Commun*, **28**, 1010-1016, 2007.
27. Capek I, On inverse miniemulsion polymerization of conventional water-soluble monomers, *Adv Colloid Interf Sci*, **156**, 35-61, 2010.
28. Liu G, Liu P, Synthesis of monodispersed crosslinked nanoparticles decorated with surface carboxyl groups via soapless emulsion polymerization, *Colloids Surf, A: Phys Eng Asp*, **354**, 377-381, 2010.
29. Ohde H, Wai CM, Rodriguez JM, The synthesis of polyacrylamide nanoparticles in supercritical carbon dioxide, *Colloid Polym Sci*, **285**, 475-478, 2007.
30. Klein J, Conrad KD, Characterisation of poly(acrylamide) in solution, *Makromol Chem*, **181**, 227-240, 1980.
31. Di Stefano FV, Shaffer OM, El-Aasser MS, Vanderhoff JW, Multiple oil-in-water-in-oil emulsions of extremely fine droplet size, *J Colloid Interf Sci*, **92**, 269-272, 1983.
32. Vanderhoff JW, Recent advances in the preparation of latexes, *Chem Eng Sci*, **48**, 203-217, 1993.
33. Liu X, Xiang S, Yue Y, Su X, Zhang W, Son, C, Wang P, Preparation of poly(acrylamide-*co*-acrylic acid) aqueous latex dispersions using anionic polyelectrolyte as stabilizer, *Colloids Surf A: Phys Eng Asp*, **311**, 131-139, 2007.
34. McKechnie MT, *Proceedings of the Conference on Emulsion Polymers*, London, paper 3/1, 1982.
35. Davies R, Graham DE, Vincent B, Water-cyclohexane- Span 80-Tween 80 systems: solution properties and water/oil emulsion formation, *J Colloid Int Sci*, **116**, 88-99, 1987.
36. Renken A, Hunkeler D, Effect of the surfactant blend composition on the properties of polymerizing acrylamide-based inverse-emulsions: characterization by small-angle neutron scattering and quasi-elastic light scattering, *Polymer*, **40**, 3545-3554, 1999.
37. Abdollahi M, Hemmati M, A new method to determine monomer concentration in the polymer particles of emulsion polymerization systems by dynamic light scattering, *J Appl Polym Sci*, **114**, 1055-1063, 2009.
38. Capek I, Fialova L, Berek D, On the kinetics of inverse emulsion polymerization of acrylamide, *Design Monomers Polym*, **11**, 123-137, 2008.
39. Dixon KW, Decomposition rates of organic free radical initiators, In: *Polymer Handbook*, Brandrup J, Immergut EH, Grulke AE (Eds), 4th ed, New York, Wiley, II/1-76, 1999.
40. Baade W, Reichert KH, Kinetics of the dispersion polymerization of acrylamide, *Eur Polym J*, **20**, 505-512, 1984.