

The Inverse Emulsion Polymerization of Acrylamide Using Poly(Methyl Methacrylate)-Graft-Polyoxyethylene as the Stabilizer

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ABSTRACT: Inverse emulsion polymerization of an aqueous solution of acrylamide (AM) in toluene is carried out using poly(methyl methacrylate)-graft-polyoxyethylene (PMMA-*g*-PEO) as an emulsifier. The kinetics of polymerization, morphology of the particle, and particle size of the inverse emulsion have been investigated. The rates of polymerization are found to be proportional to the initiator concentration, the monomer concentration, and the emulsifier concentration. The morphology of particles shows a spherical structure. The mechanism of inverse emulsion polymerization using amphipathic graft copolymer as the emulsifier is proposed. The resulting molecular weights of polyacrylamide are extremely high, and relate to the amphipathic graft copolymer structure. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 528–534, 2001

Key words: inverse emulsion polymerization; acrylamide; amphipathic copolymer; poly(methyl methacrylate)-graft-polyoxyethylene; kinetics

INTRODUCTION

Polymers based on acrylamide (AM) and its derivatives are among the easily available and relatively inexpensive water-soluble materials that offer a unique combination of useful properties. High molecular weight homopolymers of acrylamide are used as pushing fluids in tertiary oil recovery, as drag reduction agents, and as drilling fluids.¹ The main methods of AM-based polymer synthesis are radical polymerization in solution, inverse emulsion, and suspension.² An important advantage of the polymerization in inverse emulsions is the possibility of using concentrated monomer solution under conditions of facilitated

heat removal and the polymerization in low viscosity media. Moreover, the polymerization may occur at a high rate to yield a high molecular weight water-soluble polymeric product.

The mechanism of polymerization in inverse emulsions is still insufficiently studied,³ and no quantitative theory of the polymerization has yet been developed. Detailed knowledge of the kinetics of the inverse emulsion polymerization is important for optimal performance of the polymerization as well as for optimal properties of the polymer. The kinetics of AM polymerization in inverse emulsions and the characteristics of polymers formed depend on the nature and concentration of initiator and emulsifier, on the nature of solvent used as the dispersion medium, on the temperature, stirring rate, etc.² When oil-soluble initiators are used with aromatic continuous phases, the kinetics have been shown to resemble

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Table I Characteristic Data for PMMA-*g*-PEO Copolymers

Sample	\bar{M}_n (PEO)	wt % (PEO)	\bar{M}_n (PMMA- <i>g</i> -PEO)	\bar{M}_w (PMMA- <i>g</i> -PEO)
M-7	2050	26.90	7150	16,500
M-8	3450	26.69	9030	17,160
M-10	3450	17.73	10,950	19,220

emulsion polymerization^{4,5} with the locus of initiation occurring in inverse micelles.

By contrast with many conventional emulsions that remain stable indefinitely, inverse emulsions flocculate quite rapidly. The different nature of the electrostatic forces between direct and inverse emulsion is responsible for this behavior. This problem has led to a study of the polymerization of a water-soluble monomer in a microemulsion^{6,7} rather than in a conventional emulsion.

Amphipathic block and graft copolymers are generally found to be the best steric stabilizers.⁸ Their amphipathic nature provides an opportunity to construct them in such a way that part of the macromolecule exhibits affinity for the dispersed phase, while the other part is soluble in the dispersion medium. March and Napper⁹ have illustrated that for maximum stabilizing effectiveness in colloidal dispersions, the hydrophobic group or anchoring moiety must possess a high affinity for the dispersed phase and the hydrophilic group or stabilizing moiety must be highly soluble in the continuous phase. They have found that for sterically stabilized toluene-in-water emulsions, maximum stability is achieved when the anchor to stabilizing moiety ratio is 0.6 for diblock copolymers. There are multitudes of structural varieties possible for any such molecule, and the amphipathic nature alone does not guarantee efficiency in stabilization of a colloid. These structural variations could be brought about by alterations of the molecular weight of the components or their chemical compositions.

In the last decade, a number of research scientists have synthesized a variety of interesting polymeric amphiphatic materials that can be used as stabilizers in aqueous and organic dispersions.¹⁰⁻¹³ Compared to the more common ionic surfactants, nonionic surfactants offer the advantage of steric stabilization that is not as sensitive to fluctuations and increases in electrolyte concentration.¹⁰ In particular, several block and graft copolymers have been shown to be very effective surfactants in conventional liquid solvents.¹⁰

Amphipathic graft and block copolymers have been used to a considerable extent in colloidal dispersion stabilization. The use of amphipathic block and graft copolymers as stabilizers in colloidal dispersions has received significant attention in both the academic and the industrial arenas.^{12,13} However, very little information is available in the literature about their use as sole stabilizers in aqueous emulsion polymerization.¹⁴ Even less is known about the actual effect of the structural variations of the amphipathic materials on polymerization kinetics and particle stabilization.¹⁵ The mechanism and the kinetics of inverse emulsion polymerization using amphipathic copolymers as emulsifiers have not been thoroughly investigated.

The purpose of this study is to prepare an amphipathic graft copolymer, and to use this material as the sole stabilizer in the inverse emulsion polymerization of acrylamide to examine reaction kinetics, emulsion particle size, and molecular weight of polyacrylamide as a function of surfactant concentration. From these results an effort is made to deduce the mechanism of the inverse emulsion polymerization.

EXPERIMENTAL

Materials

Acrylamide is recrystallized twice from chloroform. Toluene is distilled before use. Azobisisobutyronitrile (AIBN) is recrystallized twice from ethanol. Deionized water is boiled under N₂ before use and then cooled. PMMA-*g*-PEO copolymer is synthesized as previously reported,^{16,17} and characteristic data for the three graft copolymers used are reported in Table I.

Polymerization Procedure

Polymerizations are carried out in a 0.5-L round-bottom reactor equipped with a stirrer, reflux con-

Table II Recipe for Preparation of Inverse Polyacrylamide Emulsion

Ingredient	Weight (g)
Acrylamide	10
Distilled water	30
Toluene	70
PMMA- <i>g</i> -PEO	1.5
AIBN	0.08

denser, sampling device, and inlet system for nitrogen temperature control.

Aqueous solutions of acrylamide are dispersed into toluene with nonionic emulsifiers based on amphiphatic graft copolymer PMMA-*g*-PEO by stirring with a propeller type stirrer to form a w/o emulsion. Purified nitrogen is bubbled at room temperature through the emulsions for about 30-min to eliminate oxygen. Temperature is equilibrated at 50°C using a thermal bath. The initiator dissolved in toluene solution is then added into the reactor. The polymerization is run at constant temperature and in a batch mode. A standard recipe (Table II) is listed.

Determination of Conversion

Inverse emulsions withdrawn periodically from the reactor are added to hydroquinone solution to stop the polymerization. The contents are dried in an oven to constant weight. Conversion of sample can be determined from the original monomer content and polymer weight obtained.

Emulsion Particle Size and Its Distribution

Particle size, i.e., particle median diameter (D_w), and the particle size distribution of these particles are determined using a centrifugal particle size analyzer SA-CP3 (Shimadzu Corporation, Kyoto, Japan).

Transmission Electron Microscopy

Emulsion particle morphologies are determined by transmission electron microscopy using a 100-sx TEM. Internal particle morphologies are examined by drying samples of each emulsion, and the sections are stained with a phosphotungstic acid aqueous solution.

Molecular Weight Analysis

The polyacrylamide emulsion is coagulated and washed with acetone, dissolved in water, and re-

Table III The Effects of AIBN Concentration on R_p

$[I] \times 10^3$ (mol/L oil)	dc/dt $\times 10^2$ (min ⁻¹)	$R_p \times 10^2$ (mol L ⁻¹ min ⁻¹)	ln[I]	ln[R _p]
1.52	0.733	3.438	-6.489	1.235
3.81	1.350	6.332	-5.570	1.846
6.09	1.846	8.658	-5.101	2.158
7.61	2.149	10.079	-4.878	2.310
9.14	2.458	11.528	-4.695	2.445

precipitated with acetone, the polymer is then dried under vacuum, and a solution of 0.1 g polymer/dL is prepared. The viscosity of the polymer solution is measured at 25°C for five different concentrations. The intrinsic viscosity is calculated by extrapolation to zero concentration. The molecular weight of the polymers is determined by applying the Mark-Houwink equation; the k and α values used for polyacrylamide in water are determined by Munk et al.¹⁸

RESULTS AND DISCUSSION

Kinetics of Inverse Emulsion Polymerization

Polyacrylamide inverse emulsions are prepared using AIBN present primarily in the continuous toluene phase. The effects of variations in monomer, initiator, and emulsifier concentrations on the polymerization rate are examined.

Rate Dependence on AIBN Concentration

We have determined the rate of polymerization (at 20–70% conversion) by varying the initiator

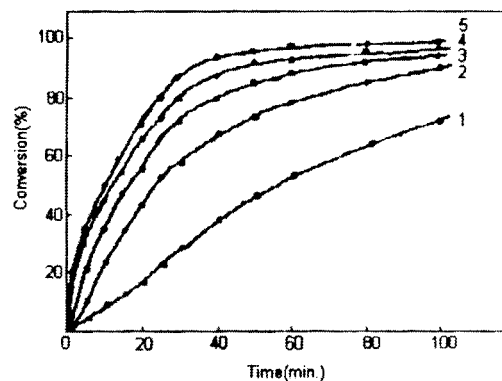


Figure 1 Conversion vs. time at various AIBN concentrations $[AIBN] \times 10^3$ (mol/L oil): 1: 1.52, 2: 3.81, 3: 6.09, 4: 7.61, 5: 9.14.

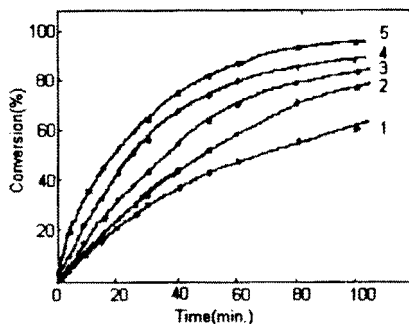


Figure 2 Conversion vs. time at various AM concentrations [AM] (mol/L water): 1: 1.876, 2: 2.814, 3: 3.752, 4: 4.690, 5: 5.628.

concentration. The data are presented in Table III, and the conversion vs. time curve at different AIBN concentration is shown in Figure 1. The relationship obtained from Figure 1 is $R_p \propto [\text{AIBN}]^{0.67}$. The results indicate that the rate of inverse emulsion polymerization of acrylamide is proportional to the two-thirds power of the initiator concentration.

Effect of Monomer Concentration

Figure 2 represents the conversion vs. time curve at different monomer (AM) concentrations; the values for the overall rate of polymerization, R_p , are calculated from the conversion vs. time curves (at 20–70% conversion). The rates of polymerization are listed in Table IV, the relationship obtained from Figure 2 is $R_p \propto [\text{AM}]^{1.04}$.

Effect of Emulsifier Concentration

Leong¹⁹ has reported the inverse microemulsion polymerization of acrylamide using polystyrene-*block*-polyoxyethylene copolymer as an emulsifier. In this article, the selected emulsifier system is amphipathic graft copolymer PMMA-*g*-PEO.

Table IV The Effects of AM Concentration on R_p

[M] (mol/L water)	dc/dt $\times 10^2$ (min^{-1})	$R_p \times 10^2$ ($\text{mol L}^{-1} \text{min}^{-1}$)	$\ln[M]$	$\ln[R_p]$
1.876	1.295	2.429	0.629	0.887
2.814	1.310	3.686	1.035	1.305
3.752	1.335	5.009	1.322	1.611
4.690	1.350	6.332	1.545	1.846
5.628	1.357	7.637	1.728	2.033

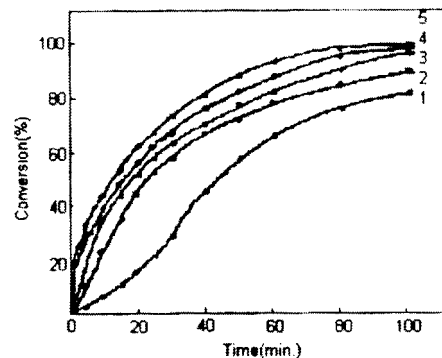


Figure 3 Conversion vs. time at various PMMA-*g*-PEO concentrations $[E] \times 10^3$ (g/mL oil): 1: 7.50, 2: 12.50, 3: 18.75, 4: 25.00, 5: 31.25.

In this work, we have kept constant the overall concentration of (acrylamide + water), initiator, and varied those of the emulsifier (amphipathic graft copolymer PMMA-*g*-PEO). Figure 3 represents the conversion vs. time curve at different emulsifier concentrations; Table V gives the polymerization rates. The rate of polymerization is observed to increase as the emulsifier concentration is increased. The relationship is $R_p \propto [E]^{0.18}$ according to Figure 3.

The interesting feature is the important increase of R_p with increasing emulsifier concentration. Similar to conventional emulsion polymerization, the loci of polymerization is in the amphipathic copolymer aggregates swollen by the monomer (AM) solution. The overall rate of polymerization, R_p , can be expressed as follows:

$$R_p = \frac{k_p N [M] n}{N_A}$$

In this inverse emulsion polymerization system, the aqueous solution of monomer is dispersed in an organic medium; the monomer aqueous drop-

Table V The Effects of Emulsifier Concentration on R_p

$[E] \times 10^3$ (g/mL Oil)	dc/dt $\times 10^2$ (min^{-1})	$R_p \times 10^2$ ($\text{mol L}^{-1} \text{min}^{-1}$)	$\ln[E]$	$\ln[R_p]$
7.05	1.221	5.726	-4.893	1.745
12.50	1.350	6.332	-4.382	1.846
18.75	1.448	6.791	-3.977	1.916
25.00	1.527	7.162	-3.689	1.969
31.25	1.584	7.429	-3.466	2.005

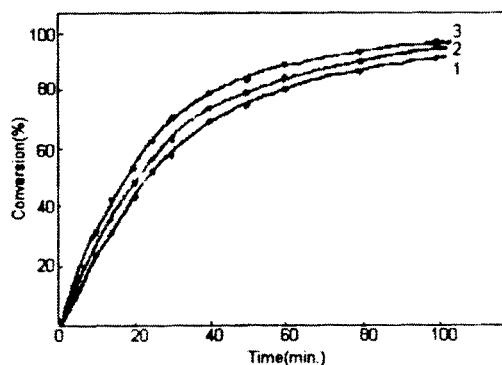


Figure 4 Conversion vs. time at different polymerization temperatures: 1: 40°C, 2: 45°C, 3: 50°C.

let, amphipathic copolymer aggregates, and amphipathic copolymer aggregates swollen by monomer solution coexist at the primary stage. However, the concentration of monomer is different in amphipathic copolymer aggregates swollen by monomer solution and monomer aqueous droplets.²⁰ Increasing the amphipathic graft copolymer concentration leads to locally increasing the monomer concentration ($[M]_n$) in amphipathic copolymer aggregates swollen by monomer solution.¹⁷ On the other hand, the number of amphipathic copolymer aggregates swollen by monomer solution (N) increases with increasing amphipathic graft copolymer concentration also.¹⁷ The observed variation of R_p with the emulsifier is then the results of these two contributions.

Effect of Polymerization Temperature

Figure 4 shows the conversion vs. time at different polymerization temperatures. It can be found that the overall rate of polymerization increases with increasing polymerization temperature.

Overall Mechanisms of Particle Formation and Polymerization

Then amphipathic graft copolymer can aggregate to form polymer aggregates that solubilize both monomer and free radicals as well as provide the

location for polymerization. Many of the properties of the polymer aggregates are similar to those of micelles formed from low molecular weight surfactant, but the size, solubilization ability, and degree of close packing of the hydrophilic inner core of polymer aggregates are different from those of surfactant micelles. Therefore, the behavior and the contribution of polymeric aggregates in inverse emulsion polymerization can be expected to be different from those of micelles.

The difference between the sizes of the initial emulsion particle and final inverse emulsion particle has been analyzed by other authors.⁴ They have found that the particle size decreases with increasing the percent conversions, and conclude that the polymerization site is in the monomer aqueous droplet. To obtain evidence for the system using PMMA-*g*-PEO as the emulsifier, the particle size is measured by a centrifugal particle size analyzer. Table VI shows the result of the inverse emulsion particle size as a function of polymerization time. It is observed that the size of the final inverse emulsion particle is larger than that of the initial emulsion particle. Moreover, with increasing concentration of the emulsifier, the concentration of acrylamide in the aqueous droplet is decreased, but the rate of polymerization is increased (Fig. 3). From these results we can conclude that the main polymerization site is inside the polymer aggregates swollen by the monomer solution, where particles grow by accretion of monomer and polymer aggregates once they have been nucleated. The unnucleated polymer aggregates and monomer aqueous droplets might serve as reservoirs for these components.

Based on these observations, the following mechanism (shown in Fig. 5) is proposed for the inverse emulsion polymerization of acrylamide using PMMA-*g*-PEO as the emulsifier. In the primary stage, there are monomer aqueous solution droplets surrounded by PMMA-*g*-PEO and separated by a continuous phase (toluene); PMMA-*g*-PEO aggregates swollen by the monomer aqueous solution and PMMA-*g*-PEO aggregates. The size

Table VI The Effect of Polymerization Time on the Size of Particle

Time (min)	3	10	15	20	25	30	40	50	60	80	100
Diameter (μm)	1.68	1.77	1.89	2.06	2.21	2.35	2.57	2.63	2.69	2.74	2.78

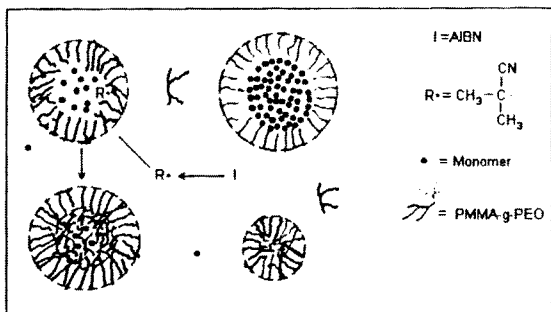


Figure 5 Mechanism of inverse emulsion polymerization of acrylamide using a polymeric emulsifier.

of amphipathic copolymer aggregates swollen by the monomer aqueous solution is smaller than that of the monomer aqueous droplet, but the number of amphipathic copolymer aggregates swollen by the monomer aqueous solution is much more; therefore, the total surface area of amphipathic copolymer aggregates swollen by the monomer aqueous solution is larger. Moreover, the amount of graft copolymer at the surface of the amphipathic copolymer aggregates swollen by the monomer aqueous solution is much more than that of the monomer aqueous droplet. So the amphipathic copolymer aggregates swollen by monomer aqueous solution should be better candidates for capturing the primary radicals, and it is difficult for free radicals to enter the monomer aqueous droplet. In second stage, when the inverse emulsion system is heated in the presence of an initiator, the major source of initiation is from the radicals generated in the toluene phase or possibly at the interface. The radicals diffuse mainly

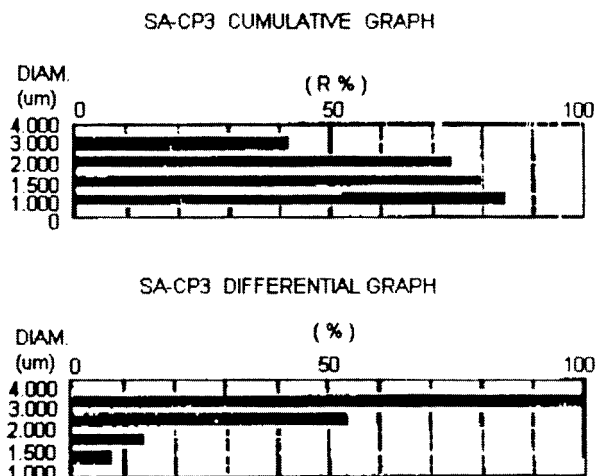


Figure 7 Size distribution of particles.

into the interior of the amphipathic copolymer aggregates swollen by the monomer solution. The nucleate and polymerization loci are mainly in the amphipathic copolymer aggregates swollen by the monomer solution. Particles grow by accretion of monomer and polymer aggregates. The polymer aggregates and monomer aqueous droplets serve as reservoirs. It must be pointed out that there should not be any electrostatic barrier against the radicals entering the particles, because neither radical molecules nor the emulsifier is charged. However, the emulsifier causes a steric barrier against the radicals entry. There are reasons to believe that the diffusion of initiator radicals, and also to a lesser extent initiator molecules, through the boundary layer of the emulsifier into the amphipathic copolymer aggre-

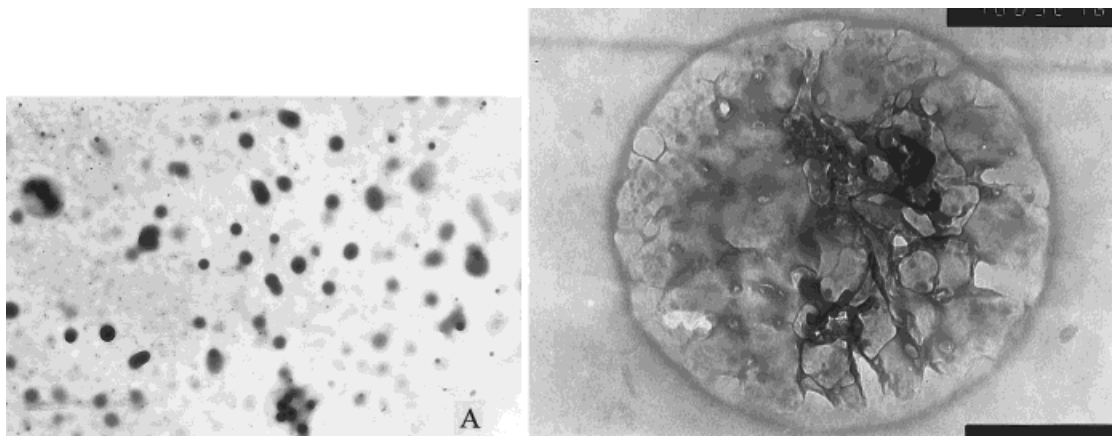


Figure 6 Transmission electron micrograph of inverse emulsion particles. (A) 5×10^3 , B: 4×10^4 .

Table VII The Molecular Weight of Polyacrylamide

Sample	Emulsifier	Molecular Weight
A	Span 80 + Tween 80	1.15×10^6
B	M-7	5.89×10^6
C	M-8	9.25×10^6
D	M-10	1.14×10^7

gates swollen by monomer solution, can be considered as the rate-determining step.

Morphology of Particles

Figure 6 shows the emulsion particles of polyacrylamide at almost 100% conversion photographed by transmission electron microscopy. The particle size distribution of emulsion particles is given in Figure 7, showing average diameters between 2 and 3 μm . Electron micrographs of the final inverse emulsion (Fig. 6) show that the particles are spherical, with a broad size distribution, and multicellular particles consisting of PMMA-*g*-PEO emulsifier molecules surrounding polyacrylamide. Figure 7 also indicates that the size distribution is broad.

Molecular Weights

Table VII shows the results of the average molecular weight of the polyacrylamide obtained from the inverse emulsion polymerization of acrylamide, using different amphiphatic graft copolymers PMMA-*g*-PEO (shown in Table I) as emulsifiers. It can be seen that the average molecular weight of polyacrylamide is higher when the content of the PEO in the PMMA-*g*-PEO is lower or the graft chains (PEO) in the PMMA-*g*-PEO are longer. Moreover, the average molecular weight of polyacrylamide using PMMA-*g*-PEO as the emulsifier is higher than that of the polyacryl-

amide made using the Span 80 and Tween 80 mixture as the emulsifier when the other conditions are the same.

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