

PROJECT ADMINISTRATION DATA SHEET

ORIGINAL  REVISION NO. \_\_\_\_\_

Project No. E-19-639 (R5963-0A0) GTRC/~~GIT~~ DATE 6 / 21 / 85

Project Director: F. J. Schork School/~~Lab~~ ChE

Sponsor: National Science Foundation

Type Agreement: Grant CBT8419914

Award Period: From 6/1/85 To 11/30/86\* (Performance) 2/28/87 (Reports)

Sponsor Amount: This Change Total to Date

Estimated: \$ \_\_\_\_\_ \$ 91,128

Funded: \$ \_\_\_\_\_ \$ 44,709

Cost Sharing Amount: \$ 1,930 Cost Sharing No: E-19-331

Title: Continuous Polymerization in Miniemulsions

ADMINISTRATIVE DATA

OCA Contact John Schonk x4820

1) Sponsor Technical Contact: Maria K. Burka 2) Sponsor Admin/Contractual Matters: Altie H. Metcalf

National Science Foundation National Science Foundation

ENG/CPE DGC/ENG

Washington, DC 20550 Washington, DC 20550

202/357-9606 202/357-9602

Defense Priority Rating: N/A Military Security Classification: N/A

(or) Company/Industrial Proprietary: N/A

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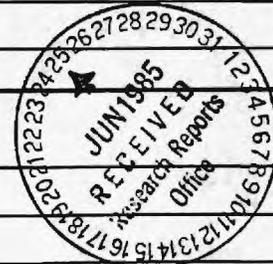
approval where total will exceed greater of \$500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT

COMMENTS:

\*Includes a 6 month unfunded flexibility period.

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Date 3/9/88

Project No. E-19-639 School/Dept ChE

Includes Subproject No.(s) N/A

Project Director(s) F. J. Schork GTRC/~~GTF~~

Sponsor National Science Foundation

Title Continuous Polymerization in Miniemulsions

Effective Completion Date: 11/30/87 (Performance) 2/28/88 (Reports)

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May 6, 1986

Dr. Maria Burka  
Program Director  
Process and Reaction Engineering  
Division of Chemical, Biochemical  
and Thermal Science  
Washington, D.C. 20550

Reference: NSF Grant No. CBT 8419914

Dear Dr. Burka:

Enclosed is a progress report and continuation proposal for the subject grant. I believe the research is progressing well.

Please let me know if you need additional information.

Sincerely,

F. Joseph Schork  
Assistant Professor

FJS/jvl

**CONTINUOUS POLYMERIZATION IN MINIEMULSIONS**

A Report Prepared

for

**National Science Foundation**

by

**F. Joseph Schork, Ph.D**

School of Chemical Engineering  
Georgia Institute of Technology  
Atlanta, GA 30332

under

**NSF Grant Number CBT 8419914**

April, 1986

CONTENTS

	PAGE
I. INTRODUCTION.....	1
II. SYSTEM DESCRIPTION.....	2
III. LITERATURE REVIEW.....	4
IV. EXPERIMENTAL PROCEDURE.....	11
V. RESULTS.....	14
VI. MATHEMATICAL MODELING.....	29
VII. CONCLUSIONS.....	29
VIII. FUTURE WORK.....	29
REFERENCES.....	30
APPENDIX.....	33
Publications	
Presentations	
Research Students	
Other Support	
Financial Report	

## I. INTRODUCTION

NSF Grant Number CBT 8419914 has helped provide funding for the Miniemulsion Research Program at Georgia Tech. Financial support for this work has also been provided by the 3M Company and by the Plastics Institute of America.

This report will focus on continuous heterogeneous polymerization systems in which an oil-soluble monomer is dispersed as monomer droplets in a continuous aqueous phase. This is the basis for classical emulsion polymerization. This report, however, will focus on the effects on the system kinetics, of substantially reducing the monomer droplet size. If this reduction is accomplished by the addition of surfactant and the application of shear forces, the system will be termed dispersion polymerization. If a cosurfactant is employed as well, the system will be termed miniemulsion polymerization.

In this report, a brief description of the miniemulsion (or dispersion) polymerization system will be given followed by a short survey of past work in this area. Included in the literature survey is a brief review of topics of indirectly related to the present work. After describing the experimental aspects of the research, a discussion of the results obtained during the past year will be given. Finally, the significance of

these results with regard to their impact on future work will be examined.

## II. SYSTEM DESCRIPTION

Miniemulsion polymerization is a term used to describe heterogeneous polymerization in those systems in which monomer droplets are substantially smaller than found in a typical classic emulsion polymerization. It is similar to the more familiar suspension and emulsion polymerization techniques. In each type of polymerization, monomer droplets are dispersed in a continuous phase in which monomer is insoluble or only slightly soluble. In most cases, the continuous phase is aqueous. Surfactants and other colloidal stabilizers are used to stabilize the droplets and prevent particle agglomeration.

While both suspension and emulsion polymerizations are free-radical reactions, each proceeds by a unique mechanism. Initiators for free-radical suspension reactions are oil-soluble. Each monomer droplet behaves like a small batch reactor, with all the monomer reacting to produce polymer. Thus, the kinetics are those of a bulk free-radical polymerization.

Emulsion polymerization, on the other hand, is heavily dependent upon mass transfer among the various phases. The initial emulsification leads to the formation of a stable emulsion containing 10 micron monomer droplets and surfactant micelles about 100 Å in diameter. These micelles are formed from

excess surfactant in the continuous phase and have a small amount of monomer at their cores.

Because the micelles greatly outnumber the monomer droplets, the surface area of micelles is much greater than the total surface area of the droplets. Thus, initiator free-radicals enter micelles much more frequently causing them to be the main locus of polymerization. As the micelles begin to react and become polymer particles, monomer molecules diffuse from the monomer droplets, and through the continuous phase to the polymer particles to supply the polymerization reaction. Termination occurs when either a second radical enters the particle or when all the monomer has been reacted. Note that it is possible for the polymerization reaction in any particle to start and stop many times due to diffusion of the free-radicals. The particles eventually grow to a size of about 0.01 microns, forming a final product, referred to as a latex, which is a stable dispersion of polymer particles in the continuous phase.

In miniemulsion polymerization, high shear is used in combination with surfactants and cosurfactants to produce a fine emulsion of monomer droplets. As mentioned previously, the monomer droplets are smaller than those found in a typical emulsion polymerization. Reduction of the monomer droplet diameter causes a corresponding increase in the total droplet surface area. This has the effect of making the monomer droplets competitive with the micelles for radical capture since radical absorption is assumed to be competitive on the basis of relative surface area. Additionally, a slight reduction in the total

number of micelles will occur because the increased surface area of the droplets requires additional surfactant molecules for stabilization purposes.

Given the above considerations, the question arises as to the nature of the kinetics of miniemulsion polymerization. The overall reaction mechanism is thought to contain elements of both the suspension and emulsion mechanisms. However, the extent to which one is prevalent over the other is not known. For example, when using a water-soluble initiator the relative surface area of droplets to micelles may be such that significant nucleation in the droplets can occur in addition to normal micellar nucleation. Questions to be answered include the effects on the overall reaction rate, and on the final particle size distribution. Use of an oil-soluble initiator leads to similar questions and will be addressed later.

### III. LITERATURE REVIEW

While there is not much in the literature that deals with miniemulsion polymerization directly, there are several subject areas which are of interest to this project. One of these involves the study of polymerization reactor dynamics. This involves the unsteady-state behavior of continuous stirred tank reactors (CSTR).

Jaisinghani and Ray (1) have studied the solution polymerization of methylmethacrylate (MMA) under a wide variety

of operating conditions. Their results show that, while multiple steady states may be possible, only unstable limit cycles were obtained for the systems studied. At isothermal reaction conditions, multiple steady states refer to the multiplicity of monomer conversions for a fixed residence time. A limit cycle is the observed oscillatory behavior of conversion about a fixed steady state value. Jaisinghani and Ray point out that it may be impossible to observe stable limit cycles for this particular reaction.

Schmidt and Ray (2) developed a model which proved the existence of multiple steady states for the solution polymerization of MMA in a CSTR. Their model accurately predicts both steady-state and dynamic behavior of the reaction. Their results show that "psuedo-steady-states" may be the result of interactions between reaction kinetics and the dynamics of the reactor system.

As noted above, suspension polymerization proceeds by a bulk, free-radical reaction mechanism. However, several models have been proposed to describe emulsion polymerization. The earliest model was that of Smith and Ewart (3,4,5). Designed for batch emulsion reactions, this model was based upon the number of particles present. Results for water-insoluble monomers were predicted well by the model. Nomura and others (6,7,8,9,10,11) extended the Smith-Ewart model to include continuous polymerization. The extended model accurately fits both transient and steady-state data in all cases except continuous oscillations.

Other models in emulsion polymerization involve particle size distributions. For batch reactions, Min and Ray (12,13,14,15) have developed a model which requires detailed knowledge of the various mechanisms of the polymerization reaction in question. Their model shows good agreement with the available data. Kiparissides and others (16,17,18,19,20,21) have developed a model for continuous emulsion polymerization reactions and experimental studies such as those of Schork (22) show that multiple steady-states and oscillatory dynamic behavior occur.

Another area of concern to this project is in the field of particle size control. Winslow and Matreyek (23) examined the effects of various stabilizers on the particle size obtained during the suspension polymerization of divinylbenzene. Specifically, they examined the effectiveness of polyvinyl alcohol (PVA). Use of PVA that was almost completely hydrolyzed was found to give larger polymer particles and more particle agglomeration than the use of partially hydrolyzed PVA. Reduction of stabilizer viscosity was found to give similar results. Lower stabilizer concentration led to a wider particle size distribution and a larger average particle size.

Church and Shinnar (24) studied the effects of agitation on the formation of stable liquid-liquid dispersions. They first presented a series of conditions necessary for the formation of a stable dispersion and then developed a mathematical model to predict the stability of a given dispersion. Agitation, they stated, must be strong enough to form the dispersion initially

and to break up particle aggregates but must not be so strong that the droplets are destroyed by shear. Their mathematical model involves the solution of three equations. When these equations are plotted on log-log paper as the particle size versus the stirrer speed, a zone of stable dispersions is defined. Among the parameters involved in these equations are the particle and agitator dimensions, physical characteristics of the dispersion components, and the energy needed to separate aggregate particles.

Azad and Fitch (25) examined the effects of hydrocarbon additives in the suspension polymerization of MMA. Using straight-chain hydrocarbon additives, their results showed an increase in the amount of emulsion polymer formed as the chain length rose from eight to sixteen followed by a decrease as the chain length exceeded sixteen. At no point did the amount of latex formed in the presence of additive exceed that formed in the absence of additive. Increasing the additive chain length also produced a shift toward larger particles for those particles lying in the 0.4 to 10 micron size range. They stated that the additives reduced the ability of the monomer to dissolve in the aqueous phase and thus produced the results described above.

Vanzo (26) studied the dispersion polymerization of vinyl acetate. He found that the initial dispersing conditions were most important for obtaining a particular particle size. Stirring speed, he found, did not have to be high throughout but could be reduced to a speed which retarded particle settling after initial dispersion. He also reported that the type of

monomer was very important to the particle size obtained. Other factors affecting the particle size were interactions between the two phases and the amount of shear forces placed upon the monomer.

Almog and Levy (27,28) have studied the dispersion polymerization of styrene. Their results show that particle size decreases as the rate of stirring increases and as the time of mixing is increased. Negligible effects were observed for varying the water to organic phase ratio. Increasing the viscosity of the styrene was found to increase the mass median diameter but caused the number median diameter to decrease. They reached the conclusion that this last result is explained by the fact that more particles of smaller size are formed from the breakup of large particles at high viscosity. Increasing surfactant concentration led to smaller particles because of decreases in surface tension and viscosity.

Almog and Levy also reported bimodal molecular weight distributions and examined these in light of surfactant effects. These bimodal distributions are indicative of two competing mechanisms in the polymerization process. They found that PVA was adsorbed on droplet surfaces but that, after initial dispersion, the excess PVA could be washed away, thus reducing the amount of latex formed. Enough PVA remained however to prevent particle agglomeration. Adsorbed PVA on the dispersion droplets was observed to stabilize some latex at the surface which could not be removed upon reaction completion. Use of an electrostatic stabilizer, sodium dodecyl sulfate (SDS), led to as

much as 25% of the polymer in the latex form. However, the latex was easily removed from the dispersion polymer by centrifugation and washing. At very low concentrations of SDS, almost no latex was observed. Mayoral and Levy (29) examined the dispersion polymerization of styrene with photoinitiation and found similar results.

As mentioned earlier, the use of cosurfactants is one of the things that differentiates miniemulsion polymerization from emulsion polymerization. A good deal of work has been done in an attempt to identify the best cosurfactants and to quantify the stabilization effects of the cosurfactants. The stability of monomer droplets can be broken down into two areas, shear stability and diffusional stability. Shear stability is a measure of the droplets ability to resist coalescence in the presence of shear forces. Diffusional stability refers to the droplets ability to resist degradation via diffusion to the continuous phase or other droplets.

Jansson (30) demonstrated that small droplets are diffusionally unstable in the presence of larger droplets. Lack et al. (31) examined the interfacial aspects of miniemulsion stability and concluded that the overall droplet stability is not comprised solely of diffusional stability. Liquid crystals forming at the oil-water interface apparently increase the droplets shear stability.

Choi et al. (32,33) and Ugelstad et al. (34) studied various cosurfactants, recipes and methods of preparation. Cosurfactants are usually water-insoluble, monomer-soluble and operate on the

principle of eliminating the thermodynamic driving force for diffusion. The studies of Choi and Ugelstad indicate that long-chain hydrocarbons and alcohols are favored as cosurfactants. Further, the order of mixing appears to be an important factor in the stability of the miniemulsion. For example, use of a long-chain alcohol dictates that the alcohol, water and surfactant be thoroughly mixed prior to the addition of the oil phase.

Most of the other work in miniemulsion polymerization deals with the particle size distribution of the product latex. Several authors (35,36,37) have reported a particle size distributions that are markedly different from those obtained in emulsion polymerization. These show polymer particles that are several orders of magnitude larger found in miniemulsion polymerization than found in emulsion polymerization.

Kinetic data for the miniemulsion system has been obtained from batch polymerizations by Gilbert et al. (35) and Choi et al. (38). Gilbert's results indicate a rate of polymerization lower than the emulsion case. Choi has attempted to translate some kinetic data on the miniemulsion system into a series of regions. Choi's primary results indicate the absence of Interval II kinetics and a longer than normal period of polymer particle formation. While there does not appear to be any kinetic data on the continuous miniemulsion system, Chen et al. (39) have derived a mathematical model based on theoretical considerations for a miniemulsion polymerization using an oil-soluble initiator.

The main objective of the current work is to investigate the kinetics and dynamics of miniemulsion polymerization in a CSTR.

These topics were the main items of interest during the past year. The ultimate goal of the current work is to use the multiple nucleation mechanisms to obtain desired multimodal particle size distributions.

#### IV. EXPERIMENTAL PROCEDURE

##### 1. Apparatus

The experimental setup is based upon a CSTR with a usable volume of about 430 ml. Heat is supplied via an internal coil heat exchanger. Temperature control in the reactor is achieved by manipulating the temperature of the water flowing inside the coil. Two feed tanks are used, one for an oil-in-water emulsion and the other for the initiator solution. High shear is applied to the emulsion via a sonicator equipped with a flow cell. This device utilizes a vibrating tip to emit intense sound waves which serve to break up the monomer droplets.

The product latex is analyzed by pumping it to two on-line instruments. The first of these is a digital densitometer. This device measures the emulsion density and thus allows on-line determination of monomer conversion (40). The second unit is a surface tension meter or bubble tensiometer. This device makes it possible to monitor the presence or absence of micelles via solution surface tension (40). A schematic of the experimental apparatus is shown in Figure 1.

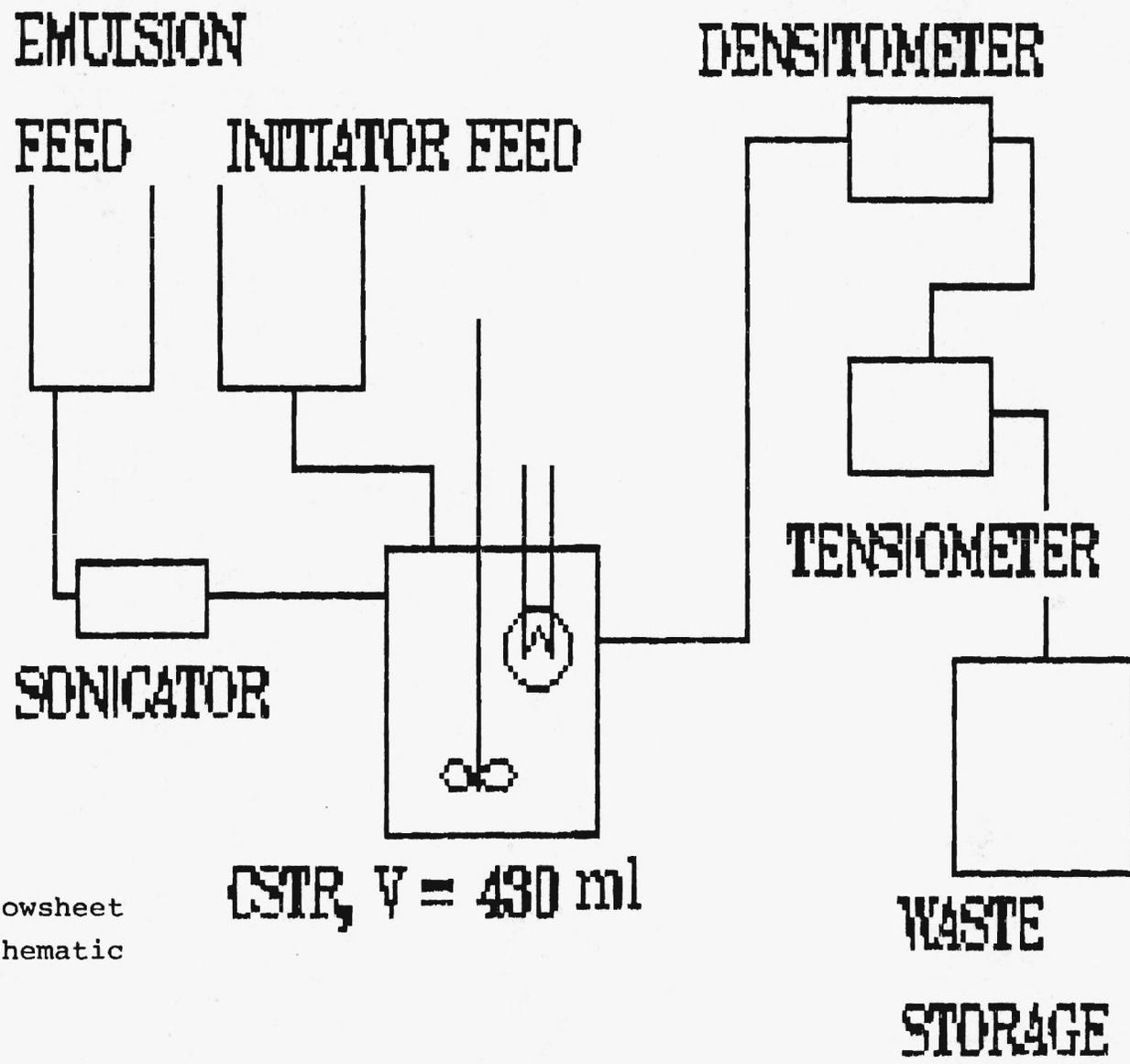


Figure 1: Flowsheet Schematic

## 2. Procedure

In a typical run, the oil-in-water emulsion is prepared by first mixing monomer, water, buffer, and cosurfactant (if any) in the emulsion feed tank. The mixture is then vigorously sparged with nitrogen for 30 minutes to 1 hour in order to remove any oxygen entrained in the various liquid phases. The main surfactant is then added while maintaining a nitrogen blanket over the mixture. The mixture is then emulsified by a high speed stirrer for about 30 minutes. The initiator solution is prepared by mixing water and initiator with gentle stirring in the initiator feed tank. This solution is sparged with nitrogen throughout the run. The reactor is purged of oxygen while these steps are being performed. When the emulsion is ready, it can be pumped to the reactor, which is usually empty at the start.

When the reactor is about two-thirds full, heating of its contents is begun. Shortly after this, the initiator flow is started. The time that initiator flow is begun is established as the start of the reaction. Note however that there is an induction time, as long as an hour, before polymerization is detected by the instruments. The induction period is a result of the feed lines between the tanks and the reactor being full of water at startup.

## V. RESULTS

Early work on the project involved usage of an oil-soluble initiator, lauroyl peroxide. Use of this initiator necessitated dissolving it in an aliquot of monomer in order to introduce it to the reactor. The results of these early experiments were not entirely satisfactory, primarily due to catastrophic coagulation in the system. This problem was severe enough to plug the downstream analysis instruments, hinder heat transfer and stirring in the reactor, and cause variations in the reactor volume. Part of the problem was due to inadequate mixing of the initiator and emulsion streams. The poor mixing produced an overall feed emulsion populated by very large droplets with a ready supply of initiator radicals. The presence of these large droplets seems to promote the onset of coagulation. More critical was the fact that substantial polymerization occurred in the initiator feed tank. This phenomenon was shown to strongly influence the polymerization taking place in the reactor.

Owing to the problems mentioned above, it was decided to concentrate on the use of water-soluble initiators. With these, it would be possible to make comparisons between a typical emulsion polymerization and a miniemulsion polymerization. The beginning of the PIA Fellowship period coincided with the switch of initiator types.

Several runs at varying processing conditions were attempted. The conditions varied included residence time (30 and 20 minutes) and initiator concentration (0.03 and 0.01 mole

ammonium persulfate/l water). The surfactant concentration was fixed at 0.049 mole sodium dodecyl sulfate/l water. A number of sonication policies were attempted in the hope that these would influence the monomer droplet diameter fed to the reactor. Figure 2 summarizes the steady state conversion for these runs. Unfortunately, there was, with a single exception, no observed effect for any of the sonicator settings tested. For the higher initiator concentration, steady state conversion was high, over 80% in most cases. At the lower initiator concentration, steady state conversion was about 20%.

These results led to one of two conclusions, namely that the reduced droplet diameter has no effect on the reaction kinetics or that the droplets are not being significantly affected by the sonicator. To test the latter, a series of experiments were made to quantify the droplet diameter under various sonication conditions. In these experiments, the feed latex was sonicated, examined and then photographed using an optical microscope. A representative photograph is shown in Figure 3. The photographs made it possible to calculate a distribution of droplet diameters.

A plot of these results is shown in Figure 4. Several notes should be made about the data shown in this graph. First, the limit of observable diameters for the microscope-camera system is about 1 micron. Second, in some cases, it was not possible to photograph and count enough particles to form a representative distribution. The recipes studied included a classic emulsion recipe and a cosurfactant miniemulsion recipe. Studies of

MULTIPLICITY PLOT,  $I = .030$

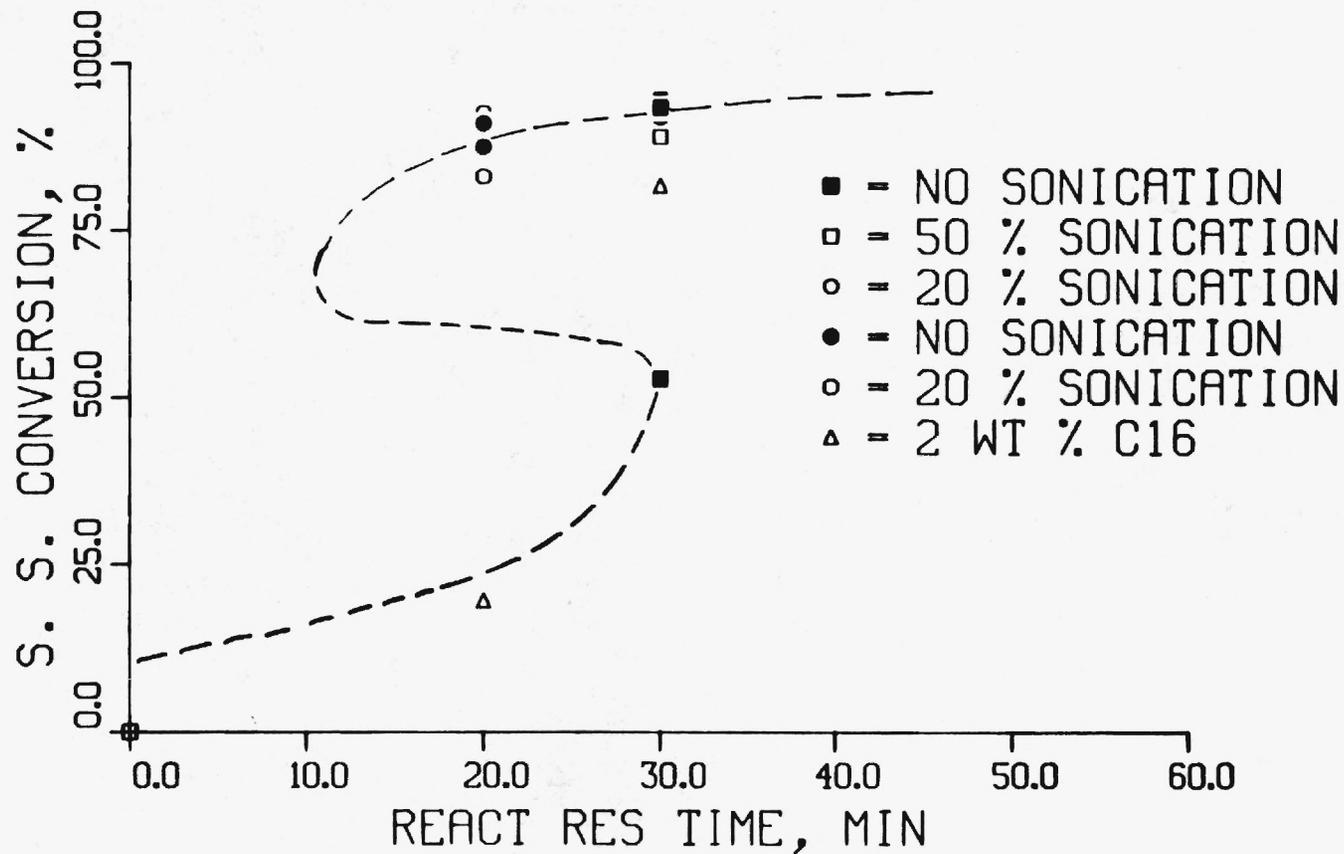
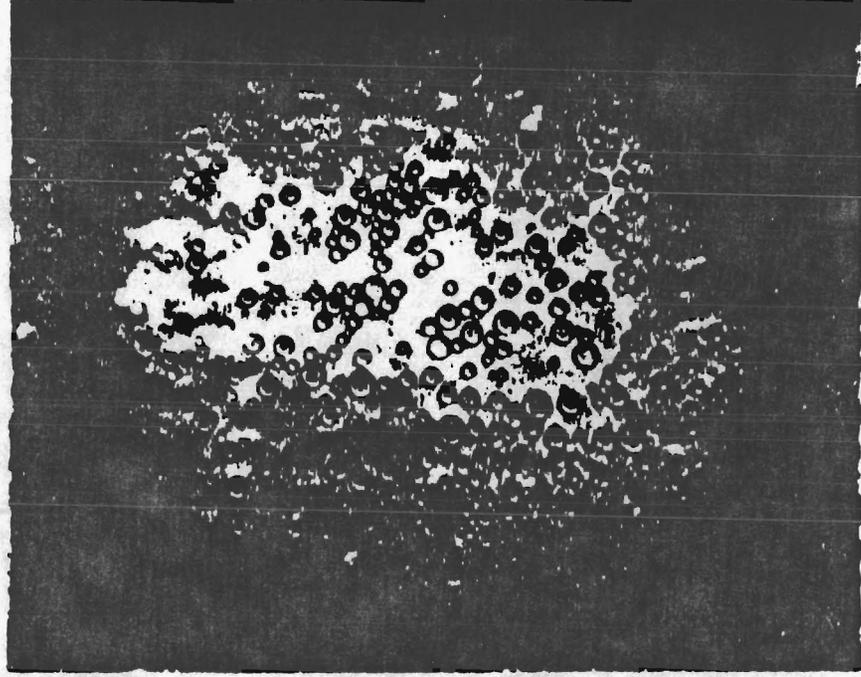


Figure 2. Multiplicity Curve for  
 $I = 0.03$  g mole/liter  
 $S = 0.05$  g mole/liter



||  
10 microns

Figure 3. Representative Photomicrograph of Typical Emulsion

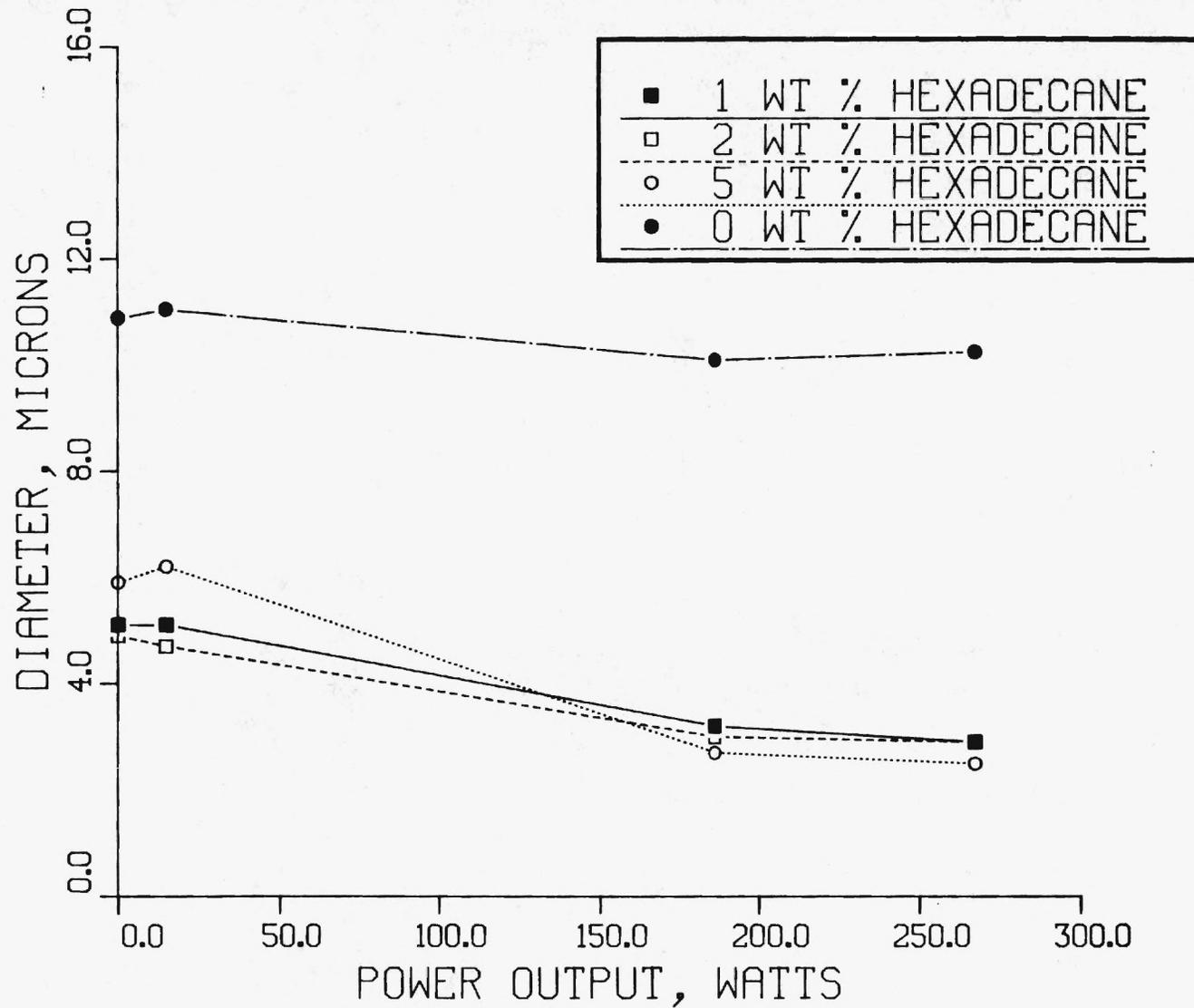


Figure 4: Effect of Shearing (Sonicator Power) and Cosurfactant Level on Average Droplet Diameter

various cosurfactants have been made by Choi (32,33) and Ugelstad (34), with fatty alcohols and long-chain alkanes being among the more favorable. Since it was desired that the cosurfactant be a liquid, hexadecane was chosen.

Several facts are apparent from the data shown in Figure 4. First and foremost is the negligible change in droplet diameter with increasing shear for the classic emulsion recipe. Further, the addition of 1.0 g hexdecane per 100. g methyl methacrylate is sufficient to drop the mean droplet diameter by a factor of two. Increasing shear causes a further reduction to an observed minimum diameter of 2 microns. At low shear and high cosurfactant concentration, an increase in mean droplet diameter is observed. This may be due to having enough cosurfactant present to form pure drops of hexadecane. Because of the strongly hydrophobic nature of hexadecane, these drops may be larger than the stabilized droplets of MMA.

To understand the data discussed above, it is necessary to explain the nature of the process being described. In a normal emulsion, surfactant molecules are found in three distinct places. These are 1) saturating the aqueous phase, 2) stabilizing monomer droplets, and 3) forming micelles. When additional shear is added to the system, droplet fragments are formed which upset the stability of the system by creating monomer surface area which is not covered by surfactant. These fragments can agglomerate to again larger droplets. If the surfactant concentration is above the CMC, a reservoir of surfactant exists to stabilize these fragments. A far more

critical problem is the diffusional stability of these smaller droplets in the presence of larger droplets. Jansson (30) has shown that a logarithmic relationship exists between droplet diameter and average lifetime. To increase the droplet diffusional stability, a hydrophobic cosurfactant such as hexadecane is added.

Also included in Figure 2 is data from a run made using the same basic emulsion recipe modified by the inclusion of 2.0 g hexadecane per 100. g MMA. This concentration appeared to be optimum based on the data shown in Figure 4. It is apparent from Figure 2 that the addition of hexadecane has a significant effect on the reaction kinetics.

To better illustrate the kinetic differences, a new recipe with lower surfactant and initiator levels was chosen. The primary reason for lowering the surfactant concentration is to restrict the number of micelles present in the reactor. Table I summarizes the results of an idealized calculation of particle loading for various surfactant levels. While it would be desirable to eliminate the micelles completely, this would be done at the expense of droplet stability, especially for growing polymer particles swollen by monomer. The initiator concentration is dropped in order to maintain some degree of control over the reaction.

With initiator and surfactant concentrations both set at 0.01 mole/l water, a series of experiments has been run to compare the effect of hexadecane on reaction kinetics. Figures 5 through 10 show the experimental data for these runs. It is

TABLE I

Effect of Surfactant Concentration on Particle Loading  
For a Typical Miniemulsion

<u>Surfactant Concentration</u> (SLS, g mole/liter)	<u>Micelles</u> (number/liter)	<u>Droplets + Micelles*</u> (number/liter)
.05	$2.80 \times 10^{21}$	$2.80 \times 10^{21}$
.04	$2.16 \times 10^{21}$	$2.16 \times 10^{21}$
.03	$1.51 \times 10^{21}$	$1.51 \times 10^{21}$
.02	$8.74 \times 10^{20}$	$8.74 \times 10^{20}$
.01	$2.3 \times 10^{20}$	$2.3 \times 10^{20}$
.005	0	$6.04 \times 10^{14}$
.00645**	0	$6.04 \times 10^{14}$

\* Feed latex contains 2wt% hexadecane (based on MMA). Monomer is assumed to be distributed in 2  $\mu$ m diameter spherical droplets.

\*\* Special case: complete surfactant coverage of droplets with no micelles.

RXN 8F, I=.01, S=.01, C16=0, TR=20

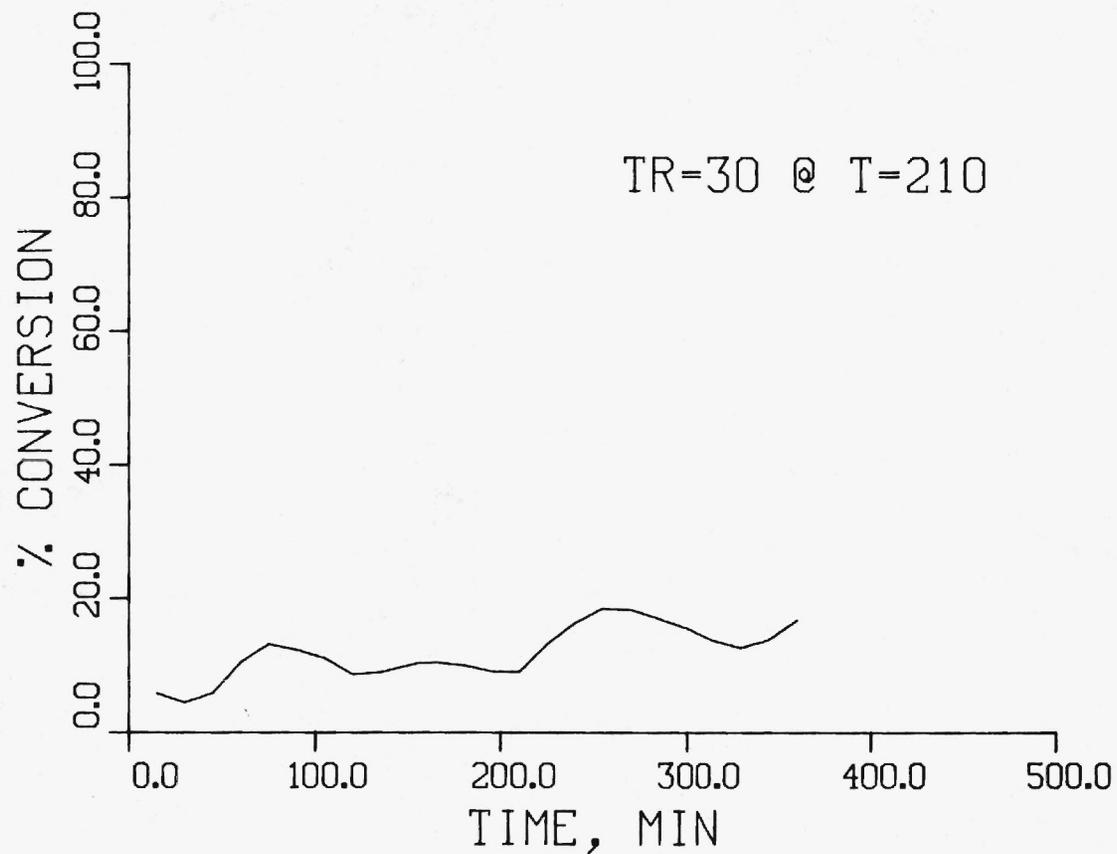


Figure 5: Conversion vs. Time for Run 8F  
I = .01 g mole/liter  
S = .01 g mole/liter  
0.g Hexadecane/100g MMA  
Res. Time = 20 min., 30 min. at T = 210

RXN 8G, I=.01, S=.01, C16=0, TR=30

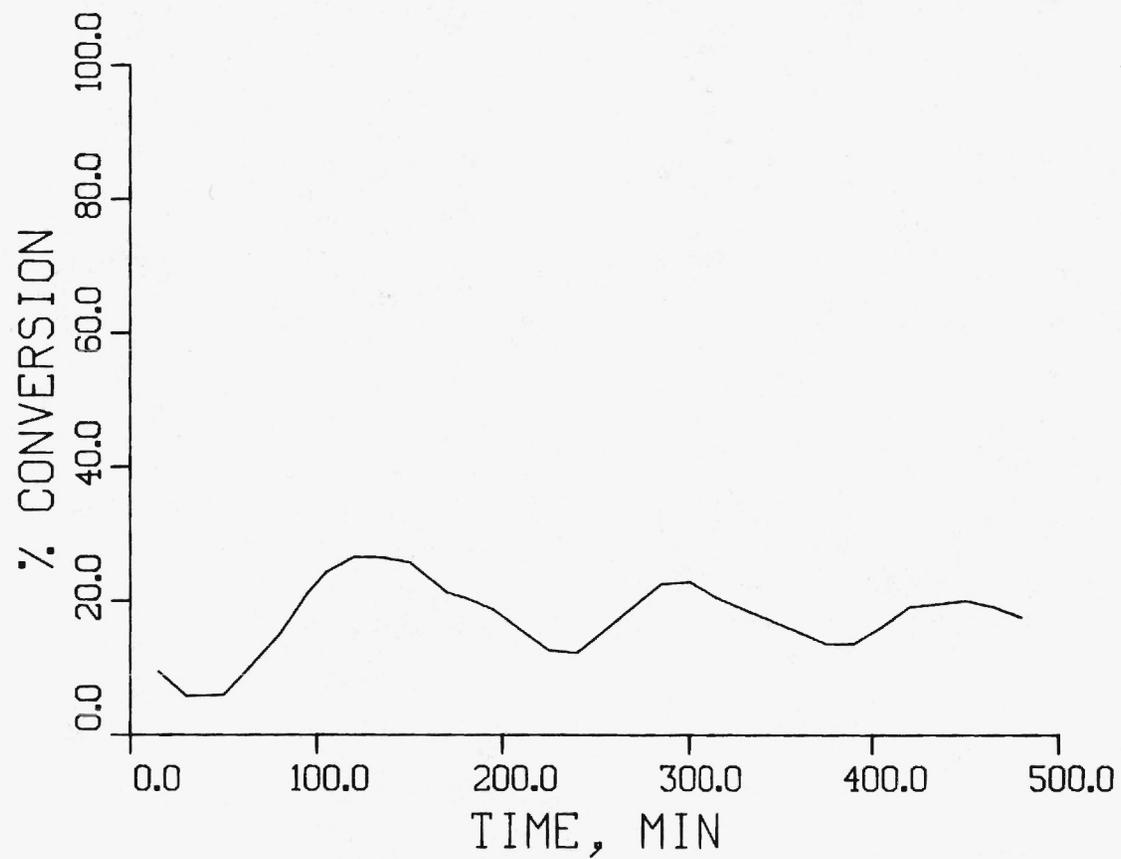


Figure 6: Conversion vs. Time for Run 8G  
I = .01 g mole/liter  
S = .01 g mole/liter  
0.g Hexadecane/100 g MMA  
Res. Time = 30 min.

RXN 8H, I=.01, S=.01, C16=0, TR=50

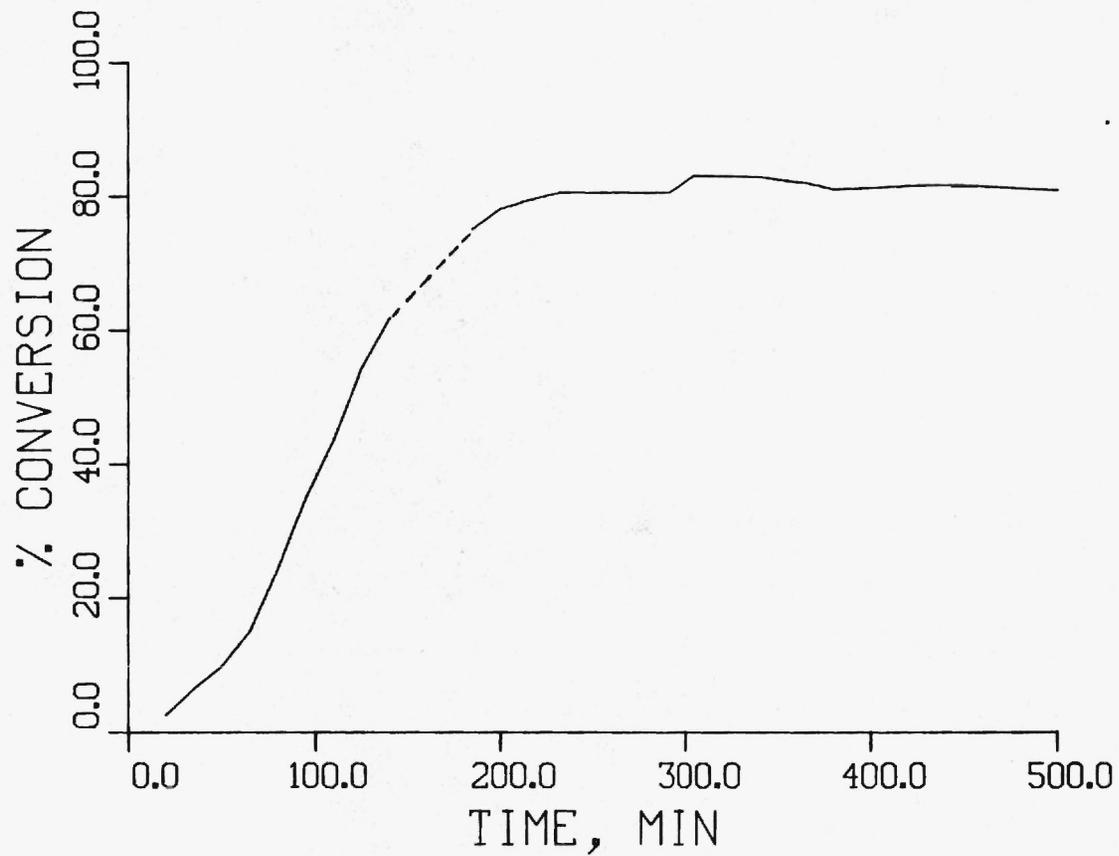


Figure 7: Conversion vs. Time for Run 8H  
I = .01 g mole/liter  
S = .01 g mole/liter  
0.g Hexadecane/100 g MMA  
Res. Time = 50 min.

RXN 8M, I=.01, S=.01, C16=.02, TR=30

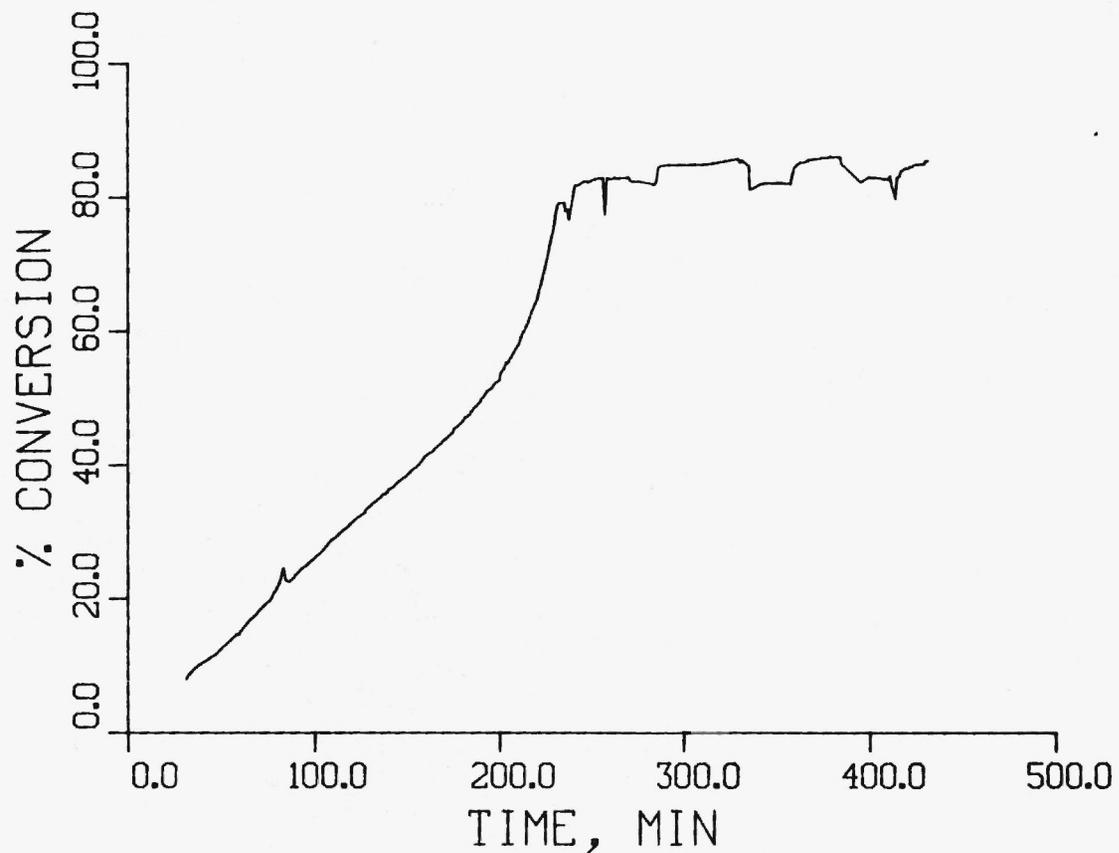


Figure 8: Conversion vs. Time for Run 8M  
I = .01 g mole/liter  
S = .01 g mole/liter  
2g Hexadecane/100 g MMA  
Res. Time = 30 min.

RXN 8J, I=.01, S=.01, C16=.02, TR=50

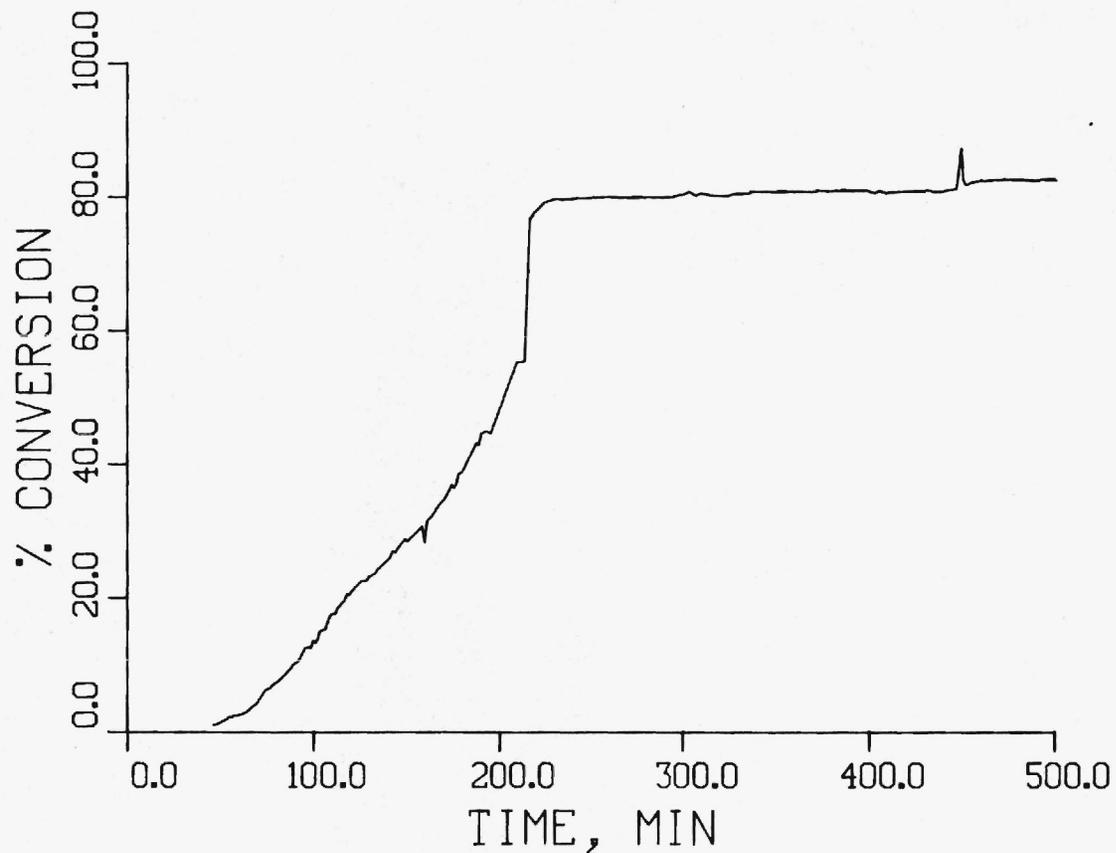


Figure 9: Conversion vs. Time for Run 8J  
I = .01 g mole/liter  
S = .01 g mole/liter  
2g Hexadecane/100 g MMA  
Res. Time = 50 min.

RXN 8K, I=.01, S=.01, C16=.02, TR=20

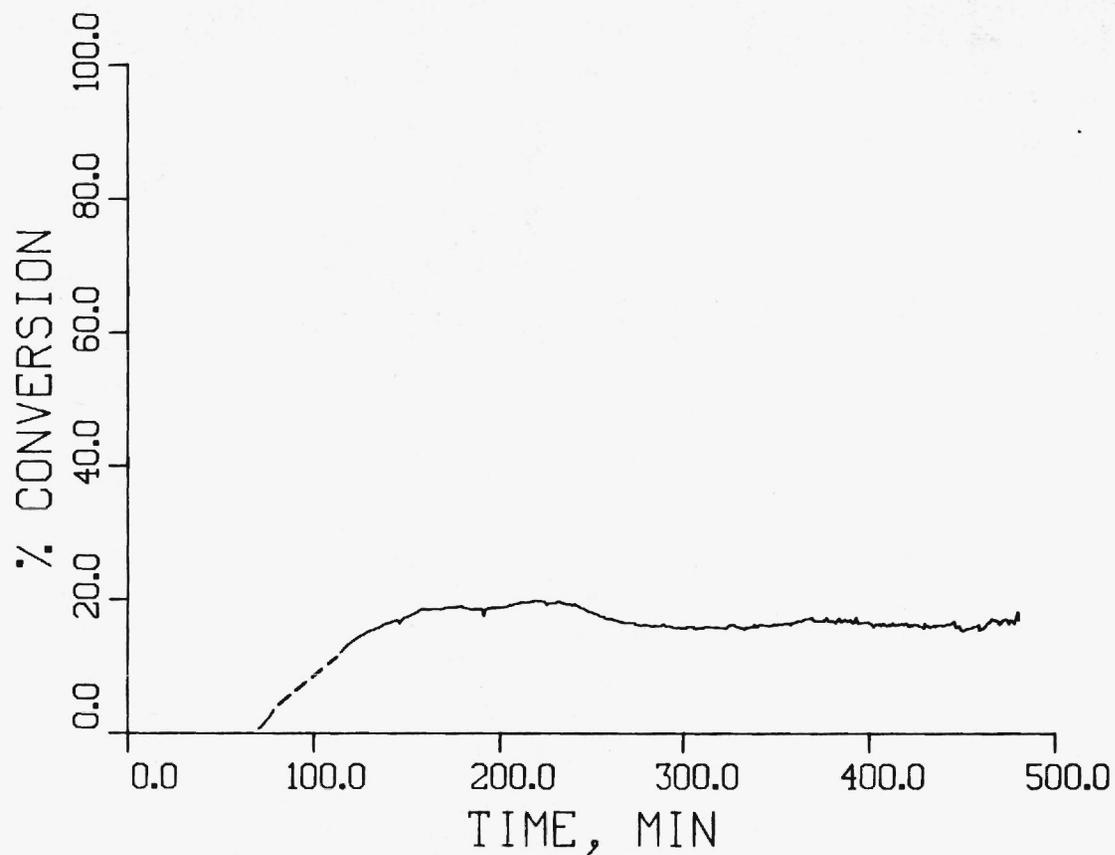


Figure 10: Conversion vs. Time for Run 8k  
I = .01 g mole/liter  
S = .01 g mole/liter  
2g Hexadecane/100 g MMA  
Res. Time = 20 min.

readily observed that those runs at low residence times tend to oscillate in reactor conversion when hexadecane is not present. Hexadecane appears to have the effect of eliminating the oscillatory nature of the system. It also appears that conversion is a bit higher in the presence of hexadecane. At high residence time, there does not seem to be any significant affect due to the presence of hexadecane.

The oscillatory behavior described above is a characteristic of continuous emulsion polymerization. It is due to the alternating presence and absence of micelles in the reactor, which in turn is due the nature of the reaction taking place. As polymer particles grow, the total free surface area rises and creates a demand for surfactant molecules to stabilize this new surface area. As the reaction proceeds, these larger particles are eventually washed out of the reactor, once again leaving free surfactant molecules to form micelles. In the miniemulsion system, the lack of oscillation is a clear sign that the role of micelles in particle nucleation has been severely curtailed. The higher conversion achieved by the miniemulsion system is an effect of limiting the formation of new particles by micellar nucleation and thus allowing nucleated particles to react more completely.

## VI. MATHEMATICAL MODELING

A model of continuous miniemulsion polymerization employing an oil-soluble initiator has been developed. The results have been published (39). A mathematical model for the case of water-soluble initiator is currently being developed. Results are expected soon.

## VII. CONCLUSIONS

The work performed during the grant period has demonstrated several facts. First, sonication of a feed emulsion without cosurfactant is not enough to achieve an appreciable reduction in monomer droplet diameter. Inclusion of a cosurfactant makes it possible to obtain monomer droplets having the desired diameters. The kinetic studies completed to this point indicate several facts. Most apparent is the elimination of conversion oscillations in the miniemulsion system. Further, the conversion appears to be higher in the miniemulsion case than in the emulsion case.

## VIII. FUTURE WORK

Items to be studied in the immediate future include more analysis of the apparent kinetics differences described above. Also, work will be performed to classify the particle size distribution produced by miniemulsion polymerization. Finally, modelling of this system will continue with efforts being made to create a computer simulation of Chen's model and to extend Chen's model to include water-soluble initiators.

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**APPENDIX**

PUBLICATIONS  
(Relating to this work)

"Computer Simulation of Continuous Miniemulsion Polymerization", C. M. Chen, L. Gothjelsen, and F. J. Schork, Polymer Processing, 4, No. 1 (1986).

PRESENTATIONS  
(Relating to this work)

1. "Polymerization in Miniemulsions", Emulsion Polymers Short Course, Davas Switzerland (August 1985, 1986).
2. "Continuous Polymerization in Miniemulsions", D. Barnette and F. J. Schork, 1986 Berlin Workshop on Polymer Reaction Engineering, October, 1986 (Accepted)
3. "Continuous Miniemulsion Polymerization", D. Barnette, G. Wright, and F. J. Schork, AIChE Annual Meeting, Miami Beach, November 1986 (Submitted).

RESEARCH STUDENTS  
(Associated with Miniemulsion Polymerization)

1. Darrell T. Barnette (Ph.D. Candidate) BS, MS, ChE Georgia Institute of Technology, Mr. Barnette is involved in modeling and experimental work for the continuous miniemulsion project.
2. Glenn T. Wright (BS candidate), Mr. Wright is an undergraduate researcher who is currently developing a mathematical model of continuous miniemulsion polymerization employing a water-soluble initiator.

OTHER SUPPORT

1. 3M Company - Support of miniemulsion research
2. Plastics Institute of America - Supplementary Graduate Fellowship

FINANCIAL REPORT

Projected expenditures through June 30, 1986 are indicated in Table A1. No significant deviations from the approved budget are anticipated.

Prepared expenditures for the record year of the grant are shown on the budget. The budget, totaling \$46,419.00 is the same as in the original approved proposal.

TABLE A-1

(Projected Expenditures Through June 30, 1986)

Personal Services	\$21,715
(PI \$3,715; Research Assistants, \$16,400; Support Staff \$1,600)	
Fringe Benefits	1,127
Capital Equipment	3,000
Materials & Supplies	2,000
Travel	1,350
Computer Services	500
Overhead	<u>17,136</u>
TOTAL	\$46,828

E-19-639

**Final Report**

## **Continuous Polymerization in Miniemulsions**

**Principal Investigator By:**

**F. Joseph Schork  
School of Chemical Engineering**

**Prepared for:**

**National Science Foundation**

**Under:**

**Grant Number CBT-8419914**

**February 18, 1988**

**GEORGIA INSTITUTE OF TECHNOLOGY**  
**A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA**  
**SCHOOL OF CHEMICAL ENGINEERING**  
**ATLANTA, GEORGIA 30332**



PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I-PROJECT IDENTIFICATION INFORMATION

1. Institution and Address Georgia Tech Research Corp. Georgia Institute of Technology Atlanta, GA 30332-0420	2. NSF Program Chem. Biochem & Thermal	Sci	3. NSF Award Number CBT 8419914
	4. Award Period From 6/1/85 To 11/30/87		5. Cumulative Award Amount \$91,467

6. Project Title  
"Continuous Polymerization in Miniemulsions"

PART II-SUMMARY OF COMPLETED PROJECT (FOR PUBLIC USE)

Miniemulsion polymerization is differentiated from classical emulsion polymerization by the fact that the monomer droplets are substantially smaller than found in a classic emulsion and can therefore compete effectively with micelles in the nucleation of polymer particles. To achieve the droplet sizes necessary, high shear is used in conjunction with surfactants and cosurfactants. The mechanism of miniemulsion polymerization is different from that of emulsion polymerization because of the role of the droplets as potential polymer particles. In this work, continuous polymerization in the emulsion and miniemulsion systems have been studied and compared experimentally.

Experimental polymerizations in a CSTR have shown that, at low residence times, the classic emulsions oscillate in conversion whereas the miniemulsions do not. The conversion oscillations in classic emulsion polymerization are due to the alternating presence and absence of micelles in the reaction mixture. In the miniemulsions, the lack of oscillations clearly points to the reduced role of micelles. Further, the miniemulsions achieved a polymerization rate twice that of the classic emulsions. The particle size and conversion data indicate that more particles are present in the miniemulsions. The molecular weight data point to a significant degree of radical segregation in both systems.

PART III-TECHNICAL INFORMATION (FOR PROGRAM MANAGEMENT USES)

1. ITEM (Check appropriate blocks)	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses		X			
b. Publication Citations		X			
c. Data on Scientific Collaborators	X				
d. Information on Inventions	X				
e. Technical Description of Project and Results					
f. Other (specify)					
2. Principal Investigator/Project Director Name (Typed) F. Joseph Schork	3. Principal Investigator/Project Director Signature			4. Date	

**PART IV - SUMMARY DATA ON PROJECT PERSONNEL**

NSF Division Chem., Biochem. & Thermal Sci.

The data requested below will be used to develop a statistical profile on the personnel supported through NSF grants. The information on this part is solicited under the authority of the National Science Foundation Act of 1950, as amended. All information provided will be treated as confidential and will be safeguarded in accordance with the provisions of the Privacy Act of 1974. NSF requires that a single copy of this part be submitted with each Final Project Report (NSF Form 98A); however, submission of the requested information is not mandatory and is not a precondition of future awards. If you do not wish to submit this information, please check this box

Please enter the numbers of individuals supported under this NSF grant.  
Do not enter information for individuals working less than 40 hours in any calendar year.

*U.S. Citizens/ Permanent Visa	PI's/PD's		Post-doctorals		Graduate Students		Under-graduates		Precollege Teachers		Others	
	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.
American Indian or Alaskan Native . . . .												
Asian or Pacific Islander . . . . .												
Black, Not of Hispanic Origin . . . . .							1					
Hispanic . . . . .												
White, Not of Hispanic Origin . . . . .	1				1							
Total U.S. Citizens . . . . .	1				1		1					
Non-U.S. Citizens . . . . .	0				0		0					
Total U.S. & Non-U.S. . . . .	1				1		1					
Number of individuals who have a handicap that limits a major life activity.	0				0		0					

\*Use the category that best describes person's ethnic/racial status. (If more than one category applies, use the one category that most closely reflects the person's recognition in the community.)

AMERICAN INDIAN OR ALASKAN NATIVE: A person having origins in any of the original peoples of North America, and who maintains cultural identification through tribal affiliation or community recognition.

ASIAN OR PACIFIC ISLANDER: A person having origins in any of the original peoples of the Far East, Southeast Asia, the Indian subcontinent, or the Pacific Islands. This area includes, for example, China, India, Japan, Korea, the Philippine Islands and Samoa.

BLACK, NOT OF HISPANIC ORIGIN: A person having origins in any of the black racial groups of Africa.

HISPANIC: A person of Mexican, Puerto Rican, Cuban, Central or South American or other Spanish culture or origin, regardless of race.

WHITE, NOT OF HISPANIC ORIGIN: A person having origins in any of the original peoples of Europe, North Africa or the Middle East.

**THIS PART WILL BE PHYSICALLY SEPARATED FROM THE FINAL PROJECT REPORT AND USED AS A COMPUTER SOURCE DOCUMENT. DO NOT DUPLICATE IT ON THE REVERSE OF ANY OTHER PART OF THE FINAL REPORT.**

National Science Foundation

Grant Number CBT-8419914

**Continuous Polymerization in Miniemulsions**

Final Report

Principal Investigator:

F. Joseph Schork

School of Chemical Engineering

Georgia Institute of Technology

Atlanta, Georgia 30332

February 18, 1988

## CONTENTS

	PAGE
I. INTRODUCTION.....	1
II. BACKGROUND.....	2
III. EXPERIMENTAL.....	6
IV. RESULTS.....	12
V. DISCUSSION.....	27
VI. SUMMARY.....	31
NOMENCLATURE.....	32
REFERENCES.....	33
PUBLICATIONS AND PRESENTATION RESULTING FROM THIS WORK.....	34
THESIS ABSTRACT.....	35

## I. INTRODUCTION

Miniemulsion polymerization is a term used to describe heterogeneous polymerization in those systems in which monomer droplets are substantially smaller than found in a typical conventional emulsion polymerization. These polymerizations exhibit some characteristics of the more familiar suspension and emulsion polymerization systems. In each type of polymerization, monomer droplets are dispersed in a continuous aqueous phase in which the monomer is insoluble or only slightly soluble. Surfactants and other colloidal stabilizers are used to stabilize the droplets and prevent particle agglomeration.

While both suspension and emulsion polymerizations are free-radical reactions, each proceeds by a unique mechanism. Initiators for free radical suspension reactions are oil-soluble. The monomer droplets are approximately 1  $\mu\text{m}$  in diameter and each behaves as a small batch reactor, with the monomer reacting to produce polymer. Since the number of free radicals per particle is quite high, the kinetics are those of a bulk free radical polymerization.

Emulsion polymerization, on the other hand, is heavily dependent upon interaction among the various phases. The initial emulsification leads to the formation of a stable emulsion containing 10  $\mu\text{m}$  monomer droplets and surfactant micelles about 0.01  $\mu\text{m}$  in diameter. These micelles are formed from excess surfactant in the continuous phase and have a small amount of monomer at their cores.

Because of their relative size and number, the total surface area of micelles is much greater than the total surface area of the droplets. Thus, free radicals generated by the decomposition of the water-soluble initiator enter micelles much more frequently, resulting in nucleation primarily from micelles. The primary locus of polymerization is the polymer particles thus

formed. As the micelles are nucleated and become polymer particles, monomer molecules diffuse from the monomer droplets, through the continuous phase, and into the polymer particles to supply the polymerization reaction. In the simplest view (Smith-Ewart Case II), termination occurs when a second radical enters the particle. Note that it is possible for the polymerization reaction in any particle to start and stop many times due to absorption of free radicals. The particles eventually grow to a size of about 0.10  $\mu\text{m}$ , forming a final product, referred to as a latex, which is a stable dispersion of polymer particles in the continuous aqueous phase.

In miniemulsion polymerization, high shear is used in combination with surfactants and cosurfactants to produce a fine emulsion of monomer droplets. The monomer droplets are substantially smaller than those found in a typical emulsion polymerization. Reduction of the monomer droplet diameter causes a corresponding increase in the total droplet surface area. This has the effect of making the monomer droplets competitive with the micelles for radical capture since radical absorption is assumed to be competitive on the basis of relative surface area. Also, a reduction in the total number of micelles will occur because the increased surface area of the droplets requires additional surfactant molecules for stabilization purposes.

Given the above considerations, the question arises as to the nature of the kinetics of miniemulsion polymerization. The overall reaction mechanism is thought to contain elements of both the suspension and emulsion mechanisms. However, the extent to which one is prevalent over the other is not known. For example, when using a water-soluble initiator, the relative surface area of droplets to micelles may be such that significant nucleation in the droplets can occur in addition to normal micellar nucleation. This research will address these issues as well as the effects of droplet

nucleation on the well-known oscillatory transients in continuous emulsion polymerization. These questions have been investigated via the bench-scale, continuous miniemulsion polymerization of methyl methacrylate (MMA) with a water-soluble initiator (ammonium persulfate). Comparisons are made between the miniemulsion and conventional continuous emulsion polymerization of MMA in terms of reaction kinetics, particle sizes, and polymer molecular weights.

## II. BACKGROUND

### Cosurfactant Characterization

As discussed above, the small monomer droplet diameters needed to carry out a miniemulsion polymerization are achieved by a combination of high shear, surfactants, and cosurfactants. A good deal of work has been done to identify the best cosurfactants and to quantify the stabilization effects of the cosurfactants. The stability of monomer droplets can be divided into two areas, shear stability and diffusional stability. Shear stability is a measure of the droplets' ability to resist coalescence in the presence of shear forces. Diffusional stability refers to the droplets' ability to resist degradation via diffusion to the continuous phase or other droplets.

Jansson (1) demonstrated that small droplets are diffusionally unstable in the presence of larger droplets. Lack et. al. (2) examined the interfacial aspects of miniemulsion stability and concluded that the overall droplet stability is not comprised solely of diffusional stability. Liquid crystals forming at the oil-water interface apparently increase the droplets' shear stability.

Choi et al. (3,4) and Ugelstad et. al. (5) studied various cosurfactants, recipes and methods of preparation. Cosurfactants are usually water-insoluble, monomer soluble and operate on the principle of eliminating the thermodynamic driving force for diffusion of monomer out of the small

droplets. The studies of Choi and Ugelstad indicate that long chain hydrocarbons and alcohols are favored as cosurfactants. Further, the order of mixing appears to be an important factor in the stability of the miniemulsion. For example, use of a long-chain alcohol dictates that the alcohol, water, and surfactant be thoroughly mixed prior to the addition of the monomer. If, however, sufficient shear is applied, the order of mixing becomes unimportant.

El-Aasser (6) has reported on the formation and stability of miniemulsions. The process of forming a miniemulsion is dependent upon the efficiency of obtaining the initial distribution of monomer droplets and on the effectiveness of maintaining the distribution during the reaction. The most important factors in meeting these criteria are the ratio between the surfactant and cosurfactant and the means by which these substances are mixed together. In addition, the chain length of the hydrocarbon cosurfactant plays a role. Longer-chain molecules tend to increase the long-term stability of the miniemulsion latex.

#### Batch Miniemulsion Polymerizations

Several authors (4,7,8) have studied the use of water-soluble initiators in batch miniemulsion polymerizations of styrene. In these studies, it was reported the bimodal polymer particle size distributions were obtained for various surfactant-cosurfactant ratios. The large particles were about the same size as the initial droplets and were attributed to droplet nucleation. The small particles that were observed were thought to arise from aqueous-phase nucleation phenomena.

The availability of kinetic data for batch miniemulsion polymerization reactions is limited. In an early work, Ugelstad and Hansen (7) reported changes in reaction kinetics for various droplet sizes. They reported

reaction kinetics varying from bulk, to Smith-Ewart Case III and then to Case II kinetics as the droplet size is reduced.

Gilbert et al. (9) have also studied the kinetics of the batch miniemulsion polymerization reaction. Shifts between aqueous phase nucleation and droplet nucleation were observed for various recipes and processing conditions. Their kinetic data show a rate of polymerization that is lower for the case of droplet nucleation. This fact is attributed to a reduced rate of radical entry into the particles.

Both Gilbert (9) and Choi (10) have attempted to define models that describes the polymerization reaction that is taking place. Their models are similar to the Smith-Ewart description of emulsion polymerization. They postulate four kinetic regions. In Region i, monomer droplets are nucleated to become polymer particles. This region is marked by an increasing rate of polymerization as the population of nucleated droplets rises. Region ii is marked by a constant rate of polymerization and appears to have many of the characteristics of Smith-Ewart Case II, including constant monomer concentration at the reaction sites and a constant average number of free radicals per particle. Region iii begins when all of the monomer droplets have been nucleated. In Region iii, the polymerization rate falls due to the consumption of monomer and subsequent drop in the monomer concentration at the reaction sites. Region iv is marked by the onset of the gel effect and continues as the remaining monomer is consumed.

In each of the batch miniemulsion studies discussed above, the monomer used was styrene. In this work, the monomer used will be MMA. Several important differences exist between these monomers. First, MMA is more water-soluble than styrene. Thus, the importance of aqueous-phase nucleation should be more pronounced in the miniemulsion polymerization of MMA. Also, MMA

exhibits a much stronger gel effect than styrene. This fact means that the gel effect may start at lower conversions in MMA polymerizations and could greatly affect the observed kinetics of the reaction taking place in the droplets. Also, note that a continuous reactor system will be used in this work. This reactor configuration permits analysis of reaction kinetics under steady-state rather than dynamic operating conditions.

### III. EXPERIMENTAL APPROACH

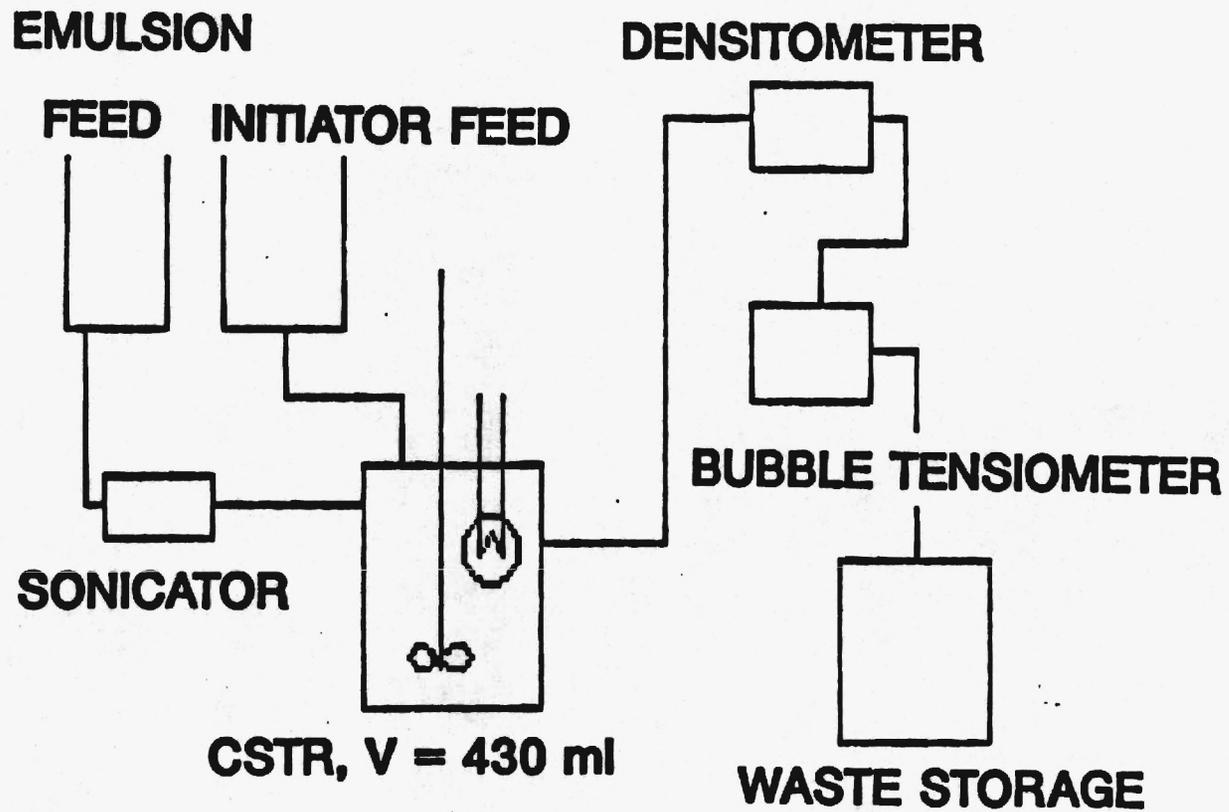
As discussed above, this work involves the use of a continuous reactor system to study the miniemulsion polymerization of MMA. The equipment and experimental procedures used to generate the data are described below.

#### Equipment

A schematic of the experimental system used in this work is shown in Figure 1. The reactor is a two-piece, glass resin kettle with a reaction volume of 430 ml and is operated as a CSTR. Closed-loop control of reactor temperature is achieved by manipulating the temperature of water flowing through a stainless steel coil placed inside the reactor. Other equipment in the reactor includes a two-blade turbine agitator to maintain a constant level of agitation in the reactor and a nitrogen purge which maintains an oxygen-free environment inside the reactor.

Shear is applied to the miniemulsion feed mixture by the sonicator. This device, a Sonic Dismembrator (Model 300) manufactured by Fisher Scientific, consists of a control unit, the sonicator tip, and a continuous flow chamber. The shear field generated by the sonicator within the flow chamber causes, in the presence of a cosurfactant, the reduction of droplet diameter necessary to form a miniemulsion. The maximum power output of the sonicator tip is 300 Watts. The flow chamber clamps over the sonicator tip by means of

Figure 1 Flowsheet of Experimental Apparatus.



an O-ring. The residence time of material inside the flow chamber is small (less than 0.5 min) since its volume is less than 5 ml. Tap water is fed through a jacket on the flow chamber to remove heat generated by the action of the sonicator tip.

Upon exiting from the reactor, the polymer latex is pumped to two on-line analysis instruments. The first of the is an Anton Paar densitometer and provides a means for measuring monomer conversion as described by Schork (11). The unit consists of a flow cell (Model DPR Ye 402) and a serial computer interface (Model DPR-S). The flow cell has a thermostatted U-shaped tube through which the miniemulsion mixture flows. The tube in the cell is excited electronically. As the density of fluid in the tube changes, the frequency of vibration also changes. The relationship between the instrument output,  $\tau$  (proportional to the period of oscillation) and sample density is given by

$$\rho = A [\tau^2 - b] \quad (1)$$

A two-point calibration, using water and air for example, can be performed to determine the constants A and b. The value of  $\tau$  and the cell temperature are displayed on the computer interface.

As a mixture is polymerized, it undergoes an increase in density. The degree of conversion of monomer to polymer is given by (11)

$$x = \frac{v_0 - v_x}{v_0 - v_{100}} \quad (2)$$

The quantity  $v_x$  is calculated from the densitometer data as

$$v_x = \frac{1}{\rho_x} \quad (3)$$

Expressions for  $v_0$  and  $v_{100}$  are defined as

$$v_0 = \frac{V_{H_2O} + V_{MMA} + \frac{NPS}{1.37}}{V_{H_2O} \rho_{H_2O} + V_{MMA} \rho_{MMA} + NPS} \quad (4)$$

$$v_{100} = \frac{V_{H_2O} + V_{pMMA} + \frac{NPS}{1.37}}{V_{H_2O} \rho_{H_2O} + V_{pMMA} \rho_{pMMA} + NPS} \quad (5)$$

Note that these quantities must be calculated for the specific recipe that is used. The term NPS represents non-polymer solids in the recipe, and includes initiator, buffer, surfactant, and any cosurfactant.

The 1.37 factor appearing in equations (4) and (5) is the non-polymer solids density factor. Initially treated as an adjustable parameter, the present value of the factor, 1.37, has been found to give conversion measurements from the densitometer that are accurate to within one percent for a number of polymerizations.

The other on-line analysis instrument used in this work is the surface tensiometer or bubble tensiometer. The theory of this device is given by Schork (12). The unit consists of a jacketed flow cell, a pressure transducer, a signal filter, and a digital display meter. The mixture being analyzed is fed into the bottom of the flow cell. A side arm allows material to drain from the cell and maintains constant cell volume at about 20 ml. Two tubes are immersed just under the liquid surface in the cell. The immersed tip of one tube is very large while the immersed tip of the other is very small. Nitrogen gas is fed through the tubes at low pressure causing bubbles to be formed at the tips. The back pressure of the bubble formation in each tube varies with surface tension, more so in the case of the small tip. Side arms on each tube are connected to opposite ports of a differential pressure transducer (Sentra Systems Model 239) which measures this pressure difference. The pressure transducer generates a voltage signal which is

passed through a low-pass filter (Frequency Devices 744/745 Series), which extracts the DC component of the wave-form. The filtered signal is displayed on a digital volt meter. By manipulating the zero and span, the digital volt meter can be made to display the value of surface tension directly, in dyne/cm. The filtered signal may be sent to a strip-chart recorder or a digital data acquisition system. Surface tension measurements with this device are accurate to within 2 to 5 percent.

#### Procedures

The basic chemical recipe used in this work is shown in Table I. The MMA monomer, supplied by Rohm and Haas and inhibited with 25 ppm hydroquinone (HDQ) was purified by vacuum distillation at 35°C and 65 mmHg vacuum. The surfactant used was BDH Chemicals Specially Pure sodium lauryl sulfate (SLS). The remaining chemicals were Fisher A.C.S. certified reagent grade. Note that only the miniemulsion experiments included the cosurfactant. Hexadecane was chosen because it was desired to have a liquid cosurfactant at ambient temperature.

The emulsion feed mixture was prepared by mixing the monomer, water, buffer, and cosurfactant, if any. The mixture was sparged with nitrogen for 30 minutes and then emulsified for 30 minutes with a high-speed agitator after the surfactant was added. After the initial sparging, a nitrogen blanket was maintained in the emulsion tank. The initiator feed mixture was prepared while the sparging of the emulsion tank was taking place. The contents of the initiator tank were sparged with nitrogen for the duration of the experiment.

The emulsion feed mixture was then pumped to the reactor. As it was being filled, the contents of the reactor were raised to the reaction temperature of 40°C. When the reactor was filled to capacity with the emulsion feed, the flow of the initiator mixture to the reactor was started.

Table I

Basic Miniemulsion Recipe

<u>Monomer</u>	<u>Mass, g</u>	<u>Vol., ml</u>	$\frac{\text{mol}}{2\text{H}_2\text{O}}$	<u>PPHM</u> (parts per hundred (monomer))
Methyl-methacrylate (MMA)	2378	2530	---	100
<u>Emulsion</u>				
H <sub>2</sub> O	3620	3620	---	152.2
Sodium Lauryl Sulfate (SLS)	15.46	---	.010	.65
Hexadecane (C16)	47.56	---	.039	2.00
Sodium bicarbonate (SBC)	4.50	---	.010	.19
<u>Initiator</u>				
H <sub>2</sub> O	1740	1740	---	73.2
Ammonium Persulfate (A <sub>m</sub> Ps)	12.23	---	.010	.51

This action constituted the start of the reaction. Shortly after the reaction start, the pump which delivered the polymer latex to the analysis instruments was activated.

#### IV. RESULTS

Two different series of experiments were performed. In the first, the effects of reactor residence time on reaction kinetics in the emulsion and miniemulsion systems were studied. In the second series of experiments, the effects of varying the molar monomer-to-water ratio at fixed residence time were investigated.

##### Reactor Residence Time Studies

The conversion-versus-time profiles for an emulsion and a miniemulsion at residence time of 25 minutes are shown in Figure 2. The oscillatory behavior of the emulsion profile has been explained by Omi et al. (13). Initially, there is a burst of particles formed as micelles are nucleated to become polymer particles. As the conversion rises, the particles grow in size and require increasingly larger amounts of surfactant to stabilize the particle surface area. Thus, the population of micelles is eventually driven to zero and no new particles can form. At this point, the conversion is a maximum. The polymer particles continue to grow but are slowly washed out of the reactor. This action causes the conversion to decrease toward a minimum while the surfactant concentration increases. At the point of minimum conversion, micelles can again be present, meaning that a new generation of particles can be formed. Thus, the cycle can be repeated either as sustained or damped oscillations. Similar arguments can be made if homogeneous, rather than micellar nucleation is thought to be dominant. In the miniemulsion, the lack

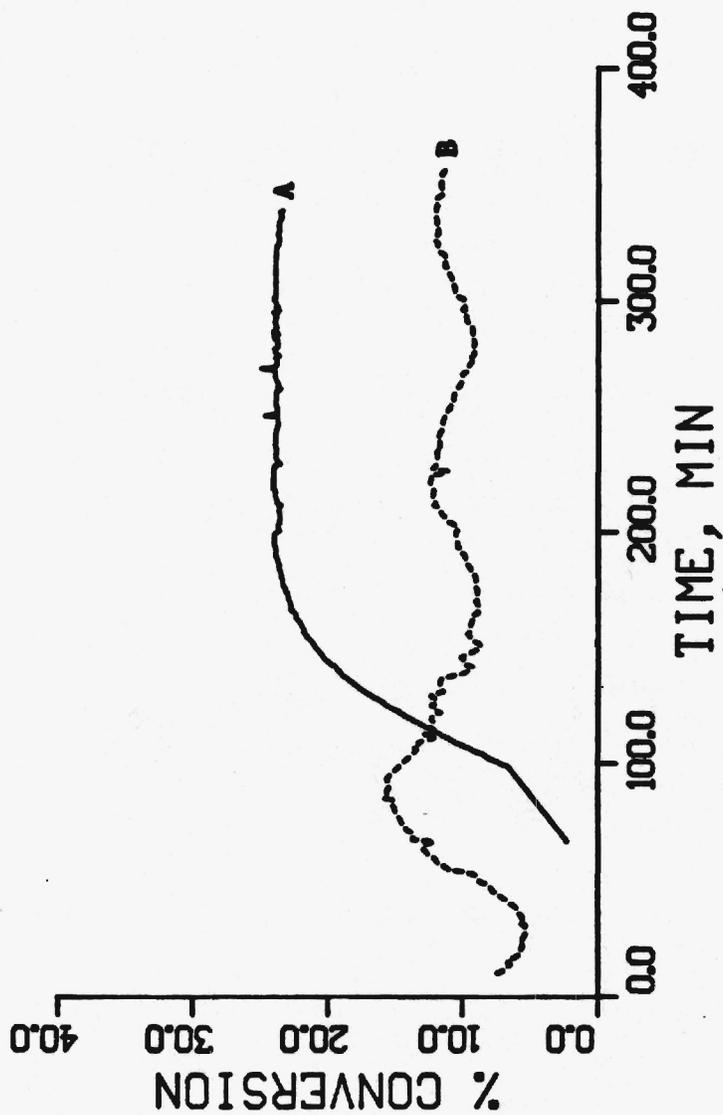


Figure 2 Comparison of Conversion-versus-Time Profiles for Miniemulsion, (A) and Conventional Emulsion, (B).

of oscillation points to the greatly diminished role of micellar or homogeneous nucleation.

Figures 3, 4, and 5 present other data obtained for the experiments shown in Figure 2. The surface tension profiles, Figure 3, show a higher surface tension and a decreased tendency to oscillate for the miniemulsion than for the conventional emulsion. Since surface tension is a measure of free surfactant concentration, it provides a direct indication of the relative saturation of the aqueous phase. In the case of the conventional emulsion, the oscillations reflect the alternating periods of particle nucleation and particle growth and washout. The higher surface tension in the miniemulsion reflects the increased droplet surface area and subsequent decrease in free surfactant.

The molecular weight data, Figure 4, show little difference between the two systems. The fact that such high molecular weights were attained suggested a significant degree of radical segregation exists in both polymerization systems. The absence of a small molecular weight peak in the miniemulsion distribution indicate the absence of any suspension-like (bulk) polymerization kinetics. Thus, if any droplets were nucleated, they exhibited the same radical segregation behavior as the nucleated micelles.

The particle size distributions (by transmission electron microscopy) for the respective product latexes are shown in Figure 5. The particle size distribution of the miniemulsion product has a higher mean and is somewhat broader than its conventional emulsion counterpart. The broader distribution in the miniemulsion suggests a shear-induced particle formation mechanism compatible with droplet nucleation.

The steady-state conversion data for a number of conventional and miniemulsion polymerizations using the recipe in Table I are summarized in

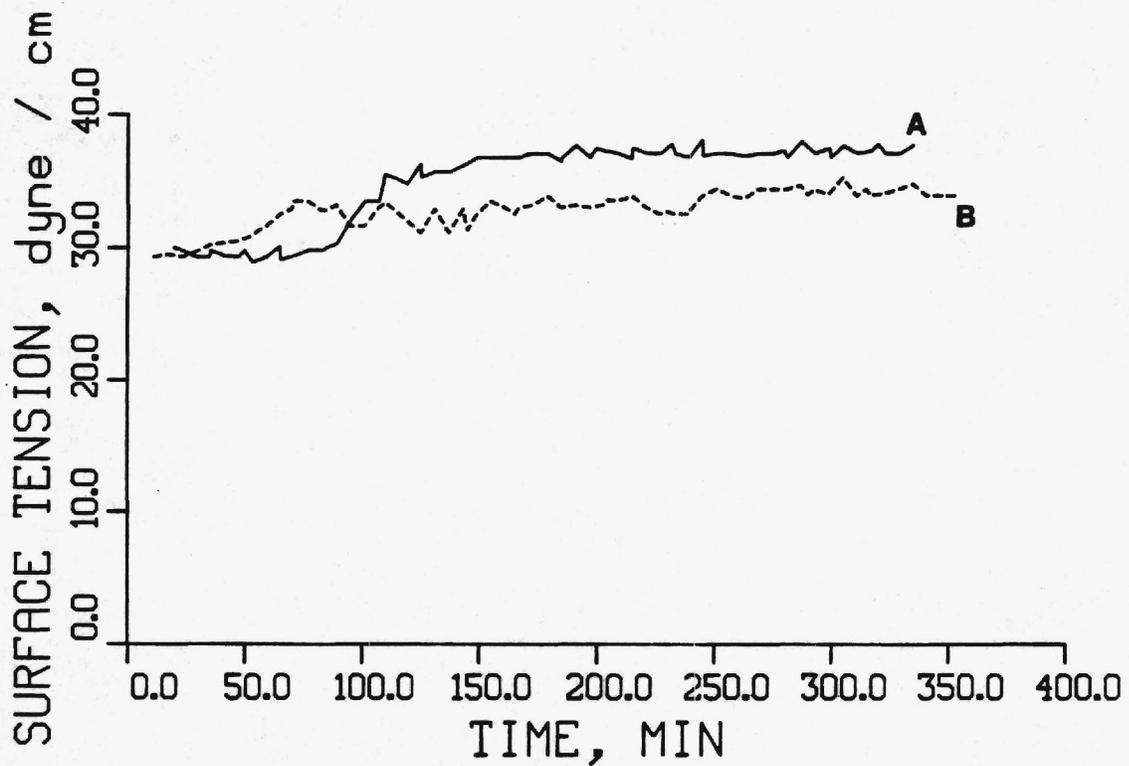


Figure 3 Surface Tension-versus-Time Profiles for Miniemulsion, (A) and Conventional Emulsion, (B).

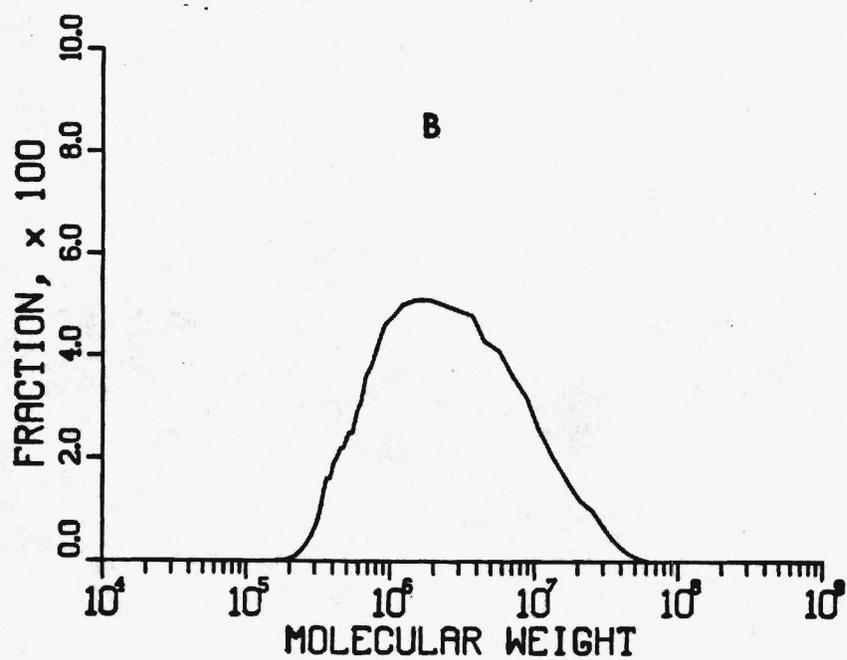
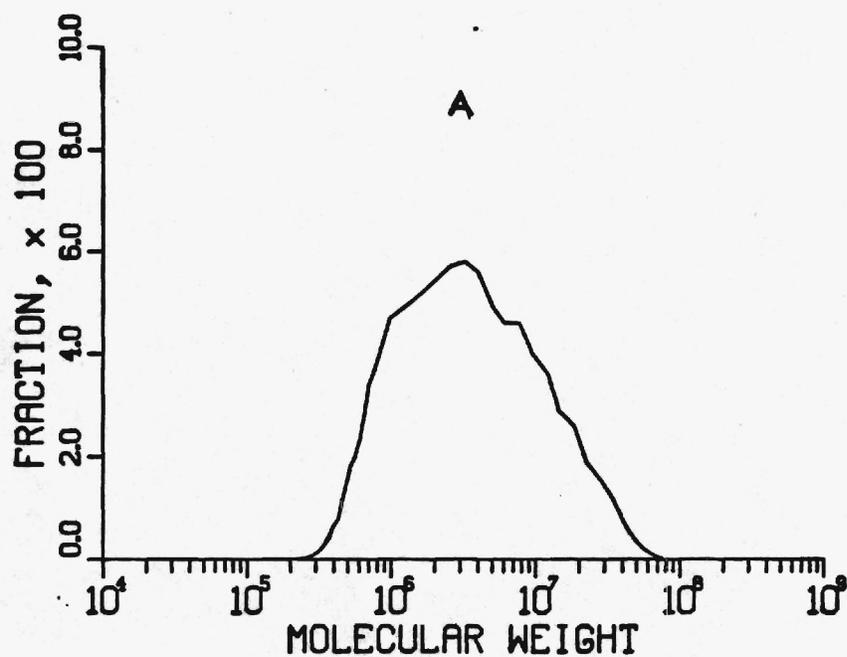


Figure 4 Molecular Weight Distributions for Polymer Samples from Miniemulsion, (A) and Classic Emulsion, (B).

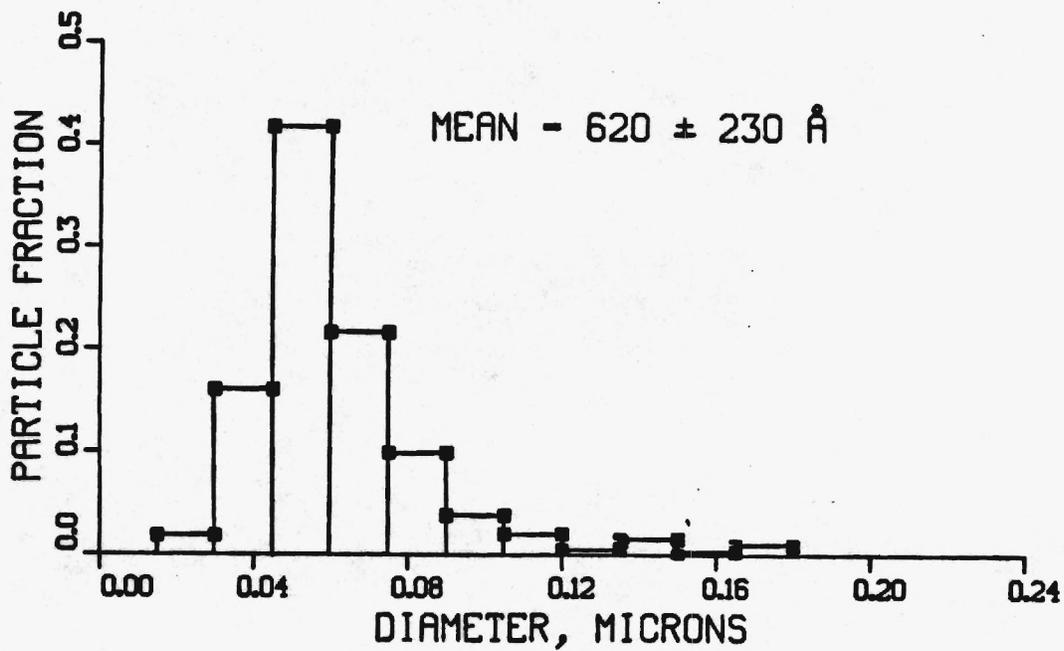
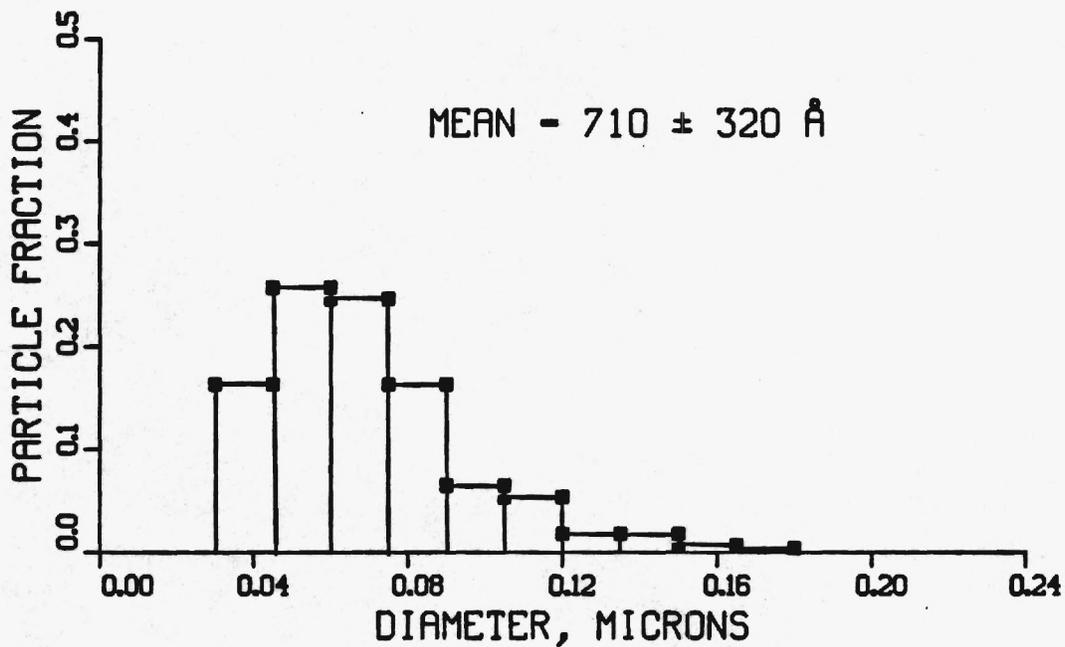


Figure 5 Particle Size Distributions for Polymer Samples from Miniemulsion, (A) and Conventional Emulsion, (B).

Figure 6. For the oscillatory conventional emulsion polymerizations, the steady-state conversion was estimated as the average of the maxima and minima of the oscillations. At high residence times, no difference between the two reaction systems is observed. This is due to the fact that the gel effect predominates at high conversion, thus obscuring any observable particle nucleation phenomena. At low residence times, the conventional emulsion runs oscillated in conversion while the miniemulsions achieved higher conversion levels and exhibited no oscillations in conversion.

The various data shown in Figures 2 through 5 lead to several conclusions concerning miniemulsion polymerization as carried out in this work. The conversion and surface tension profiles indicate that the role of the micelles has been greatly diminished in the miniemulsion system. However, the lack of any significant differences in the molecular weight and particle size distributions would seem to indicate that either micellar nucleation is the dominant mechanism of particle formation or that the nucleated droplets are small enough to exhibit a significant degree of radical segregation:

#### Effect of Monomer-to-Water Ratio

Additional polymerization were carried out to study of the effects of lowering the monomer-to-water ratio in both conventional emulsion and miniemulsion polymerizations. By decreasing the total amount of monomer in the reaction mixture, a reduction in the total number of monomer droplets was to be achieved. If the droplets serve as the primary reaction locus, the reaction rate is expected to fall as the number of droplets in the reaction mixture is reduced. The recipes for lower monomer to water ratio were developed by reducing the monomer in the recipe then scaling the entire recipe to get the desired volume. In the case of the conventional emulsions, the recipes were designed to give the same total number of micelles as the emulsion recipe

MULTIPLICITY PLOT, I-.01, S-.01

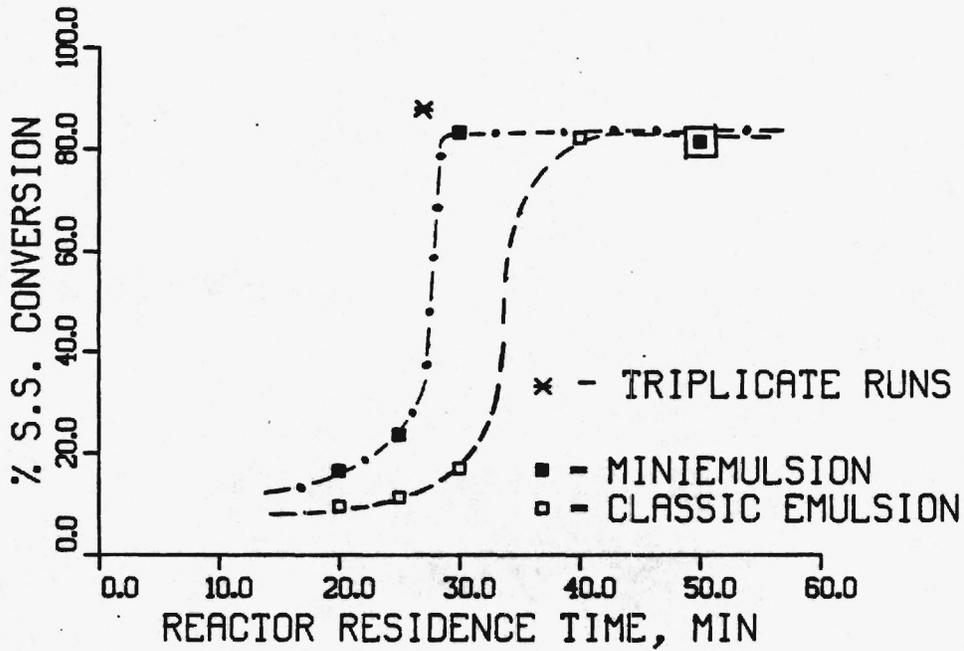


Figure 6 Multiplicity Plot Showing Steady State Conversion Levels for Miniemulsion and Classic Emulsion as a Function of Reactor Residence Time.

listed in Table I. Note that the recipe listed in Table I was used as a basis for these reduced monomer experiments and that a reactor residence time of 25 minutes was chosen. Comparisons between the various reduced monomer recipes were made by calculating the volumetric steady-state reaction rates and then plotting the rates as a function of the molar monomer-to-water ratio.

An expression for the reaction rate is given by Equation (6).

$$R_p = \frac{X_F M_{MMA}}{V T_R} \quad (6)$$

Note that the reaction volume can be expressed either as the total volume of the reactor or as the aqueous fraction of the total reactor volume. The latter method is appropriate for particle nucleation occurring in the aqueous phase and is representative of conventional emulsion polymerization. The former method reflects changes in the number of particles per unit volume of reaction mixture and is appropriate to a system involving nucleation in monomer droplets.

The reaction rate data for a series of conventional emulsions and mini-emulsions at various reduced monomer levels are summarized in Figures 7 and 8. In Figure 7, the rate is expressed as a function of the total reaction volume while in Figure 8 the rate is calculated on the basis of the aqueous fraction of the reaction volume. In Figure 8, the conventional emulsion data show a decreasing rate of polymerization as the molar monomer-to-water ratio is decreased. As noted above, these emulsion polymerization experiments were designed to produce the same total number of micelles as the recipe listed in Table I. As will be shown, the aqueous-phase concentration of micelles decreased due to the change in water content of the recipes. This concentration decrease is in spite of the fact that the total number of micelles actually increased slightly as the monomer-water ratio was reduced. The polymeriza-

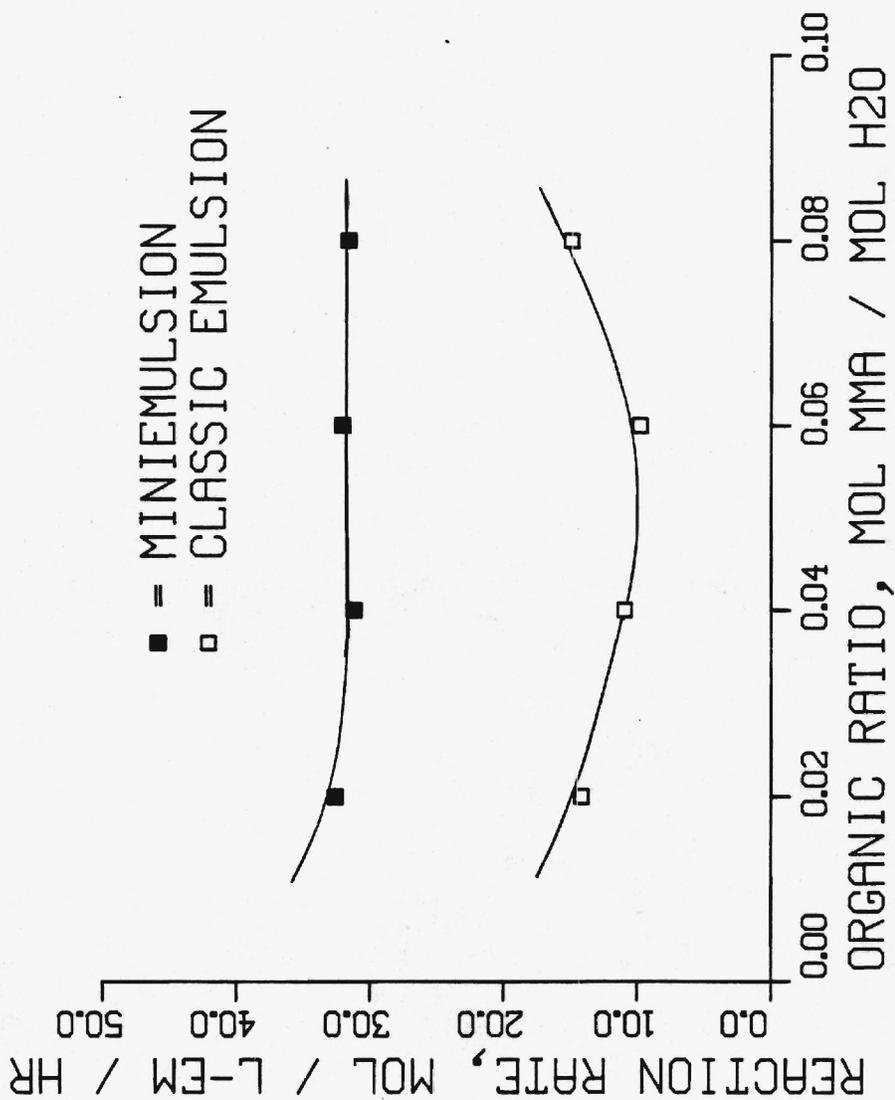


Figure 7 Reaction Rate versus Molar Monomer-to-Water Ratio where Rate is on the Basis of Total Reaction Volume.

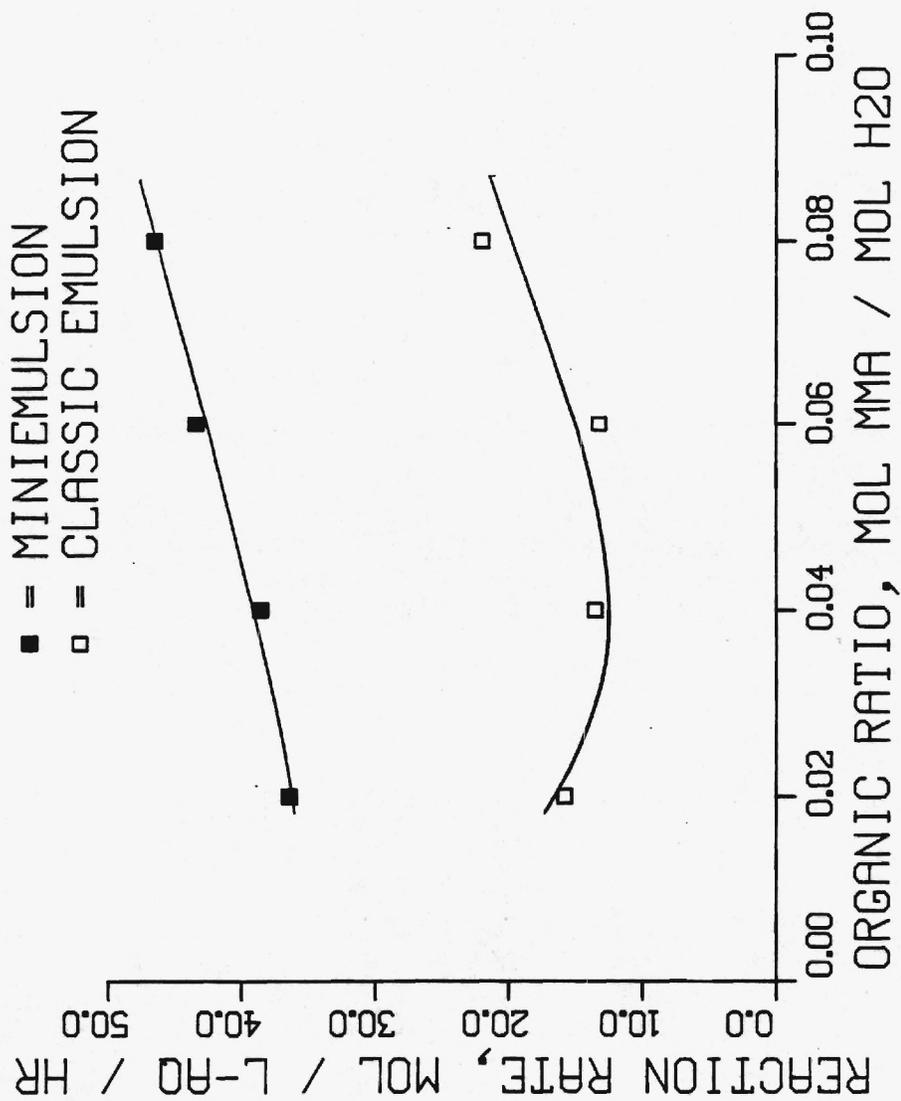


Figure 8 Reaction Rate versus Molar Monomer-to-Water Ratio where Rate is on the Basis of Aqueous Reaction Volume.

tion rate in conventional emulsion system has been shown to be proportional to the number of polymer particles. Since micellar nucleation in the aqueous phase is assumed to be the primary mechanism of particle formation, a decreasing rate implies a decrease in the number of micelles per unit volume of aqueous phase. As indicated above, these conventional emulsion recipes show a drop in the number of micelles and, hence, the number of particles, thus producing a subsequent decline in the polymerization rate. At a monomer to water ratio of 0.02 the rate of polymerization rises again. This is due to the early onset of the gel effect at low monomer levels.

The reaction rate data for the miniemulsion polymerizations show strikingly different behavior. In Figure 7, the rate is shown to be essentially constant with decrease in the monomer-to-water ratio. These observations imply that the number of particles, and hence the number of droplets remain constant with respect to the total volume of the reaction mixture. The large difference in the reaction rates between the conventional emulsion and miniemulsion systems make it clear that the mechanism of polymerization is different in the miniemulsion system.

To investigate the essentially constant rate of polymerization for the miniemulsions (Figure 8), calculations were made to determine the number of monomer droplets and micelles for the recipes used in these runs. Assuming a value of 0.57 g SLS/  $2 \text{ H}_2\text{O}$ , the fractional saturation of the available droplet surface area was determined for a miniemulsion with a molar monomer-to-water ratio of 0.08 in which spherical droplets of diameter  $0.2 \text{ }\mu\text{m}$  were assumed. The droplet diameter was chosen on the basis of measurements made on the unpolymerized miniemulsion with the Malvern Autosizer IIc. Using the assumed CMC and the fractional saturation determined above, the number and diameter of monomer droplets were calculated for miniemulsions with monomer-water ratios of 0.06, 0.04 and 0.02. The results of this calculation

are summarized in Table II. The fractional saturation was found to be 0.17. This result indicates that the cosurfactant provides a large measure of stability to the droplets. For monomer-to-water ratios of 0.08, 0.06, and 0.04, these calculations indicate a constant number of monomer droplets (potential polymer particles). This is due to fortuitous adjustments in the surfactant concentration for various values of monomer-to-water ratio. A rise in the number of droplets for a monomer-to-water ratio in Table II is reflected in a slightly higher rate of polymerization in Figure 7. A range of values for the CMC have been reported in the literature and range from 0.15 to 2.0 g per % H<sub>2</sub>O. The value used here is well within this range. The interpretation of the rate data is, however, dependent on the value of CMC used.

Using the CMC value determined above, (0.57 g / % H<sub>2</sub>O), the concentration of micelles for each of the conventional emulsion polymerization recipes was calculated. Ten micron spherical droplets and complete coverage of the droplet surface area by surfactant were assumed. Table III lists the results of these calculations. The conclusion drawn from Figure 8 that a decrease in the aqueous phase concentration of micelles occurred as the monomer-water ratio was reduced is verified by the data shown in Table III. The high rate of reaction at a monomer-to-water ratio of 0.02 (Figure 8) is not in agreement with these calculations and is attributable to the early onset of the gel effect at low monomer loading.

Another feature of the data presented in Figures 7 and 8 that must be explained is the difference in the polymerization rates for the two systems. As can be seen, the rate for the miniemulsion system is about twice the rate of the conventional emulsion system. This result is in direct opposition to the reported results of Gilbert (9), Ugelstad (8), and Choi (10). Ugelstad

Table II

Summary of CMC and Droplet Diameter  
Calculations for Miniemulsion Recipes

$\frac{o}{w}, \frac{\text{mol MMA}}{\text{mol H}_2\text{O}}$	$N_{D-em}^1$	$N_{D-aq}^2$	$D, \mu\text{m}$
.08	$7.66 \times 10^{16}$	$1.13 \times 10^{17}$	.200
.06	$7.48 \times 10^{16}$	$1.01 \times 10^{17}$	.188
.04	$7.65 \times 10^{16}$	$0.95 \times 10^{17}$	.168
.02	$9.71 \times 10^{16}$	$1.08 \times 10^{17}$	.127

1 - number of droplets per liter miniemulsion mixture

2 - number of droplets per liter of aqueous fraction of miniemulsion mixture

$$\text{CMC} = 0.57 \frac{\text{g SLS}}{\text{g H}_2\text{O}}$$

Table III

Summary of Calculation of Number of  
Micelles for Conventional Emulsion Recipes

$\frac{o}{w} \frac{\text{mol MMA}}{\text{mol H}_2\text{O}}$	$N_{m - em}^1$	$N_{m - aq}^2$
.08	$4.69 \times 10^{19}$	$6.90 \times 10^{19}$
.06	$4.77 \times 10^{19}$	$6.45 \times 10^{19}$
.04	$4.87 \times 10^{19}$	$6.02 \times 10^{19}$
.02	$5.01 \times 10^{19}$	$5.60 \times 10^{19}$

1 - number of micelles per liter emulsion mixture

2 - number of micelles per liter of aqueous fraction of emulsion mixture

$$\text{CMC} = 0.57 \frac{\text{g SLS}}{\text{l H}_2\text{O}}$$

(7), however, has reported rates of polymerization for styrene-hexadecane miniemulsions exposed to high shear rates which are substantially higher than those of the equivalent conventional emulsions. One possible explanation lies in the number of polymer particles being generated in the two systems. To achieve the faster rate, polymerization in the miniemulsion system would have to generate more particles than the conventional emulsion system. Calculations to verify this can be made using the particle size distribution and conversion data for the runs shown in Figure 2. Table IV summarizes the results of these calculations assuming all particles are spherical and have a diameter equal to the mean of the distribution. As can be seen, approximately twice as many particles are generated in the miniemulsion as in the conventional emulsion. Recall that the molecular weight data (Figure 4) implied similar polymerization kinetics within the particles in both systems. Based on the particle number calculations shown in Table IV, the reaction rates per particle for the miniemulsion and conventional emulsion are  $7.71 \times 10^{-17}$  mol/hr/particle and  $7.07 \times 10^{-17}$  mol/hr/particle respectively. Therefore, the molecular weight, particle size and reaction rate data show that, while a different mechanism of particle formation exists in the miniemulsion system, the mechanism of polymerization after particle formation is similar to that occurring in the conventional emulsion system.

## V. DISCUSSION

The various experiments that have been performed have demonstrated a number of interesting points. First, the conventional emulsion polymerizations were seen to oscillate in conversion whereas the miniemulsions did not. This observation indicates that the role of micelles in the miniemulsion reaction has been greatly reduced. In the experiments in which the monomer-water

Table IV

Calculation of Number of Polymer Particles  
for Conventional Emulsion and Miniemulsion Systems

<u>RXN</u>	<u>Type</u>	<u>SS Conv, %</u>	<u>PSD Mean, Å</u>	<u>N<sub>p</sub> particle &amp; mixture</u>
80	Mini	23.9	710	$4.09 \times 10^{17}$
8P	Conventional	11.2	620	$2.09 \times 10^{17}$

ratio was varied, the mechanism of particle formation in the conventional emulsion system appears to be micellar. In the miniemulsion system, the monomer droplets were shown to be the source of polymer particles.

The molecular weight data have shown that a high degree of radical segregation exists in both systems. This fact suggests that the polymer particles in each system polymerize and grow in a similar fashion.

Ugelstad et. al. (7) have reported similar results for batch miniemulsion of polymerizations of styrene in which hexadecane was used as a cosurfactant. Table V summarizes these results. Note that a homogenizer was used to provide the necessary high shear in Ugelstad's work. By varying the intensity of the homogenization, Ugelstad was able to change the droplet size and thus change the free-emulsifier concentration. The free-emulsifier concentration is a measure of the amount of surfactant that is not saturating the surface of the droplets and reflects the droplet size and the concentration of micelles. Thus, small values of the free-emulsifier correspond to small concentrations of micelles. Note the interdependence of conversion, particle number, and free-emulsifier concentration in Table V. Ugelstad's results also show that conversion is directly related to the particle number, as was postulated above for the present work. Thus, the similarity between the experimental results in the present work and Ugelstad's results serve to confirm the polymerizations involving the use of a cosurfactant in the present work were of the miniemulsion type.

The differences and similarities between the conventional emulsion and miniemulsion polymerization systems in the present work can be explained by considering the mechanisms of particle formation and growth in each system. In conventional emulsion polymerization, new polymer particles arise from the nucleation of micelles. However, since surfactant molecules must also

Table V

Experimental Results of Ugelstad

<u>Experiment</u>	<u>Free-Emulsifier Concentration, g/dm<sup>3</sup></u>	<u>Particle Number, No./dm<sup>3</sup></u>	<u>Conversion<sup>2</sup></u>
A	2.01	$1.9 \times 10^{17}$	115
B	1.20	$1.2 \times 10^{16}$	20
C	0.16	$5.4 \times 10^{16}$	50
D	0.14	$7.7 \times 10^{16}$	75
E	0.12	$2.9 \times 10^{17}$	190

1 -- No Homogenization

2 -- Estimated monomer conversion, in g/dm<sup>3</sup>, at 100 minutes after reaction start

saturate the surface areas of the monomer droplets and the growing polymer particles, micelles may not always be present in the reactor. During those periods in which micelles are not present, no new particles are formed and those present at the time micelles disappear are eventually washed out of the reactor. In miniemulsion polymerization, on the other hand, the mechanism of particle formation involves the nucleation of monomer droplets. At low to moderate conversion levels, droplets will always be present and thus the nucleation of monomer droplets can keep pace with the washout of existing polymer particles and eliminate the possibility of oscillation. Since it has been shown that polymer particles in both systems exhibit similar radical segregation and thus similar particle growth characteristics, the miniemulsion system is able to maintain a greater number of particles (due to the large number of monomer droplets) and a greater degree of conversion than the conventional emulsion system.

## VI. SUMMARY

Under this great dynamic data for the continuous miniemulsion polymerization of methyl methacrylate have been developed. The data clearly show that the monomer droplets serve as the source of polymer particles in the miniemulsion system. However, due to the extremely small size of the monomer droplets (induced by sonication) the polymer particles in the miniemulsion system exhibit growth characteristics which are similar to those for particles in a conventional continuous emulsion polymerization system.

## NOMENCLATURE

- A = densitometer constant, g/ml  
b = densitometer constant, dimensionless  
 $M_{MMA}$  = moles of monomer in the recipe, mol  
NPS = non-polymer solids; includes initiator, buffer cosurfactant, g  
 $R_p$  = reaction rate, mol/l/hr  
 $T_R$  = reactor residence time, hr  
V = reactor volume, l  
 $V_{H_2O}$  = volume of water in recipe, ml  
 $V_{MMA}$  = volume of monomer in recipe, ml  
 $X_F$  = fractional conversion of monomer at steady state, dimensionless  
x = fractional conversion of monomer to polymer, dimensionless

### Greek Symbols

- $v_x$  = specific volume at x fractional conversion, ml/g  
 $v_0$  = specific volume at 0 % conversion, ml/g  
 $v_{100}$  = specific volume at 100 % conversion, ml/g  
 $\rho$  = density, g/ml  
 $\rho_x$  = density of polymer solution at x fractional conversion, g/ml  
 $\tau$  = densitometer output, dimensionless

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PUBLICATIONS AND PRESENTATIONS

RESULTING FROM THIS WORK

PUBLICATIONS

Chen, C. M., L. Gothjelsen, and F. J. Schork, "Computer Simulation of Continuous Miniemulsion Polymerization," Polymer Process Eng., 4 (1) (1986).

Barnette, D. T., and F. J. Schork, "Continuous Miniemulsion Polymerization," Chem. Eng. Progress, 83, No. 6, 25-30, (1987).

Barnette, D. T., and F. J. Schork, "Continuous Miniemulsion Polymerization," Encyclopedia of Chemical Processing and Design, John J. McKetta, (ed.), Marcel Dekker, New York (in press).

Barnette, D. T., and F. J. Schork, "Continuous Miniemulsion Polymerization: Kinetic Investigations," J. Appl. Polymer Sci., (in review).

PRESENTATIONS

Schork, F. J., "Polymerization in Miniemulsions," Emulsion Polymers Short Course, Davos, Switzerland (August 1985, 1986).

Barnette, D. T., and F. J. Schork, "Continuous Polymerization in Miniemulsions," 1986 Berlin Workshop on Polymer Reaction Engineering, Berlin, FRG, October, 1986.

Barnette, D. T., and F. J. Schork, "Continuous Miniemulsion Polymerization," AIChE Annual Meeting, Miami Beach, November, 1986.

CONTINUOUS MINIEMULSION POLYMERIZATION

A THESIS

Presented to

The Faculty of the Division of Graduate Students

By

Darrell Thomas Barnette

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy in Chemical Engineering

Georgia Institute of Technology

December, 1987

## SUMMARY

Miniemulsion polymerization is differentiated from classical emulsion polymerization by the fact that the monomer droplets are substantially smaller than found in a classic emulsion and can therefore compete effectively with micelles in the nucleation of polymer particles. To achieve the droplet sizes necessary, high shear is used in conjunction with surfactants and cosurfactants. The term cosurfactant is standard terminology in this field and refers to organic additives which are not surface active but which enhance the stabilization properties of the surfactant. The mechanism of miniemulsion polymerization is different from that of emulsion polymerization because of the role of the droplets as potential polymer particles. In this work, continuous polymerization in the emulsion and miniemulsion systems have been studied and compared both experimentally and through computer simulation.

Conclusions from previous studies concerning the importance of the cosurfactant to obtaining stable distributions of small monomer droplets have been confirmed. Experimental polymerizations in a CSTR have shown that, at low residence times, the classic emulsions oscillate in conversion whereas the miniemulsions do not. The conversion oscillations in classic emulsion polymerization are due to the alternating presence and absence of micelles in the reaction mixture. In the miniemulsions, the lack of oscillations clearly points to the reduced role of micelles. Further, the miniemulsions achieved a polymerization rate twice that of the classic emulsions. The particle size and conversion

data indicate that more particles are present in the miniemulsions. The molecular weight data point to a significant degree of radical segregation in both systems.

Other experimental data show that the polymerization rate in the miniemulsion system is a function of the concentration of monomer droplets in the emulsion. In the classic emulsion system, the polymerization rate is a function of the concentration of micelles. The source of particle formation in the two systems is different. In the miniemulsion system, the monomer droplets are the primary source of polymer particles while micelles are the main source of polymer particles in the classic emulsion system.

Mathematical models have been developed which describe the classic emulsion and miniemulsion systems. The models are based upon a series of differential material balances and are solved numerically. While predictions of the dynamic behavior of the systems are beyond the scope of these models, good agreement between simulation and experimental results have been obtained at steady state reactor conditions. In addition, it is also shown that the models predict more polymer particles in the miniemulsion system than in the classic emulsion, as was observed in the experiments.