

## PROJECT ADMINISTRATION DATA SHEET



ORIGINAL



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

Project No. E-19-637 (R5960-0A0)GTRC/GIT ~~XXX~~DATE 6 / 20 / 85Project Director: G. W. PoehleinSchool/~~Lab~~ ~~XXX~~

ChE

Sponsor: National Science FoundationType Agreement: Grant CBT-8413987Award Period: From 7/1/85 To 12/31/86\* (Performance) 3/31/87 (Reports)

Sponsor Amount:

This ChangeTotal to Date

Estimated: \$ \_\_\_\_\_

\$ 114,533

Funded: \$ \_\_\_\_\_

\$ 56,020Cost Sharing Amount: \$ 4,500Cost Sharing No: E-19-330Title: Emulsion Polymerization Kinetics and Continuous Reactor Processes

## ADMINISTRATIVE DATA

OCA Contact

John Schonk x4820

1) Sponsor Technical Contact:

2) Sponsor Admin/Contractual Matters:

Attn: Maria K. Burka, ENG/CPEWinston S. ShermanNational Science FoundationNational Science Foundation~~ENG/CPE~~ 1800 G ST. N.W.DGC/ENGWashington, DC 20550Washington, DC 20550202/357-9606202/357-9626Defense Priority Rating: N/AMilitary Security Classification: N/A(or) Company/Industrial Proprietary: N/A

## RESTRICTIONS

See Attached NSF Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of \$500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT

## COMMENTS:

\*Includes a six month unfunded flexibility period.No Funds may be expended after 12/31/86

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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 4/8/88

Project No. E-19-637 School/~~Lab~~ CHE

Includes Subproject No.(s) N/A

Project Director(s) G. W. Poehlein GTRC/~~GIT~~

Sponsor National Science Foundation

Title Emulsion Polymerization Kinetics and Continuous Reactor Processes

Effective Completion Date: 12/31/87 (Performance) 3/31/88 (Reports)

Grant/Contract Closeout Actions Remaining:

- ☒ None
- ☐ Final Invoice or Copy of Last Invoice Serving as Final
- ☐ Release and Assignment
- ☐ Final Report of Inventions and/or Subcontract:  
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Georgia Institute of Technology

School of Chemical Engineering

Atlanta, Georgia 30332-0100

(404) 894-2867

October 17, 1986

Ms. Maria K. Burka  
Program Director, Process and  
Reaction Engineering  
Division of Chemical, Biochemical and  
Thermal Engineering  
National Science Foundations  
1800 G Street, NW  
Washington, DC 20550

REFERENCE: NSF Grant No. CBT-8413987

Dear Dr. Burka:

I have attached a brief progress report on our work with emulsion polymerization. The work is going well since I am fortunate to have several very good students.

We were pleased that you were able to spend a day with us at Georgia Tech.

Best regards,

Gary W. Poehlein  
Director, School of  
Chemical Engineering

Enclosure

cc: OCA

TITLE: Emulsion Polymerization Kinetics and Continuous Reactor Processes

PRINCIPAL INVESTIGATOR: Gary W. Poehlein

PERIOD COVERED: July 1, 1985 - October 31, 1986

RESEARCH STUDENTS:

Chorn-Shyan Chern (PhD Candidate)

Richard Mead (PhD Candidate)

Z. Song (PhD Candidate)

Glenn Shoaf (MS Candidate)

Kyle Atkinson (Undergraduate/ChE)

(Partial support provided for students by three industrial organizations and a Petroleum Research Fund grant. Funding from NSF was instrumental in obtaining funding from other sources.)

Research Summary:

Research progress can be divided into two general areas: (1) the utilization of continuous reactor systems to study the fundamental kinetics of emulsion polymerization reactions and (2) examination of phenomena in individual monomer-swollen polymer particles where most of the polymerization occurs in emulsion systems.

The continuous reactor studies have been carried out in a reactor system comprised of a plug-flow tubular reactor (PFT) followed by one or more continuous stirred-tank reactors (CSTR). The purpose of the PFT was to generate a particle seed for the CSTR's that follow. This reactor system, which was developed by Poehlein and students, offers significant advantages for commercial practice and fundamental kinetic studies.

Generation of the latex seed in PFT completely eliminates the unstable oscillations often observed in unseeded CSTR's. In addition a higher concentration of particles can be produced. The stable operation of the downstream CSTR can serve as the basis for kinetic studies. CSTR feed and effluent streams can be analyzed for monomer conversion, particle concentration and particle size distribution. These data can be utilized, with reactor models, to study specific reaction mechanisms such as radical transfer and desorption from the particles.

Steady-state experiments have been carried out with several important monomers both with and without added chain transfer agents. The data were utilized to obtain values for the so-called radical desorption coefficient; and important parameter in emulsion polymerization models.

Preliminary continuous reactor experiments have also been carried out with copolymerization systems. The monomer pairs studied include: styrene-methyl acrylate, styrene-acrylonitrile and ethyl acrylate-acrylic acid. Research has focused on incorporation of copolymer concepts into the CSTR steady-state model. Experimental results will be used for model testing.

A second area of work involves the study of non-uniform latex particles. A new concept concerning the non-uniform distribution of free radicals in the polymer particles has been developed. This work will be important for grafting reactions, radical transport phenomena and development of an understanding of producing structured particles.

Several side studies have resulted from the major thrusts mentioned above. A more comprehensive theory has been developed for vinyl acetate emulsion polymerization and compared with published experimental results. The gel-effect concept from free radical polymerization has also been applied to an epoxy curing reaction. These studies are both in areas of widespread commercial interest.

Papers and presentations resulting from our work are listed below. Copies of the papers are attached as a part of this progress report.

1. "Polymerization in Non-Uniform Latex Particles: Distribution of Free Radicals," C.-S. Chern and G. W. Poehlein, accepted for publication by J. Polym. Sci., A-1.
2. "Continuous Tube-CSTR Reactor System for Emulsion Polymerization Studies," H. E. Lee and Gary W. Poehlein, Chem. Eng. Sci., 41:4, 1023-1030 (1986).
3. "Free Radical Transport and Reactions in Emulsion Polymerization," G. W. Poehlein, H.-C. Lee and C.-S. Chern, Presented and published in the proceedings of the 2nd Berlin International Workshop on Polymer Reaction Engineering (October 1986).
4. "Kinetics of Grafting in Semi-Batch Emulsion Polymerization," C.-S. Chern and G. W. Poehlein, Presented at ACS Rubber Division Meeting, Atlanta, GA (October 1986).

5. "A Kinetic Model for Curing Reactions of Epoxides with Amines," C.-S. Chern and G. W. Poehlein, accepted for publication by Polym. Eng. & Sci.
6. Reaction Kinetics of Vinyl Acetate Emulsion Polymerization," C.-S. Chern and G. W. Poehlein, Accepted by J. Apply. Polym. Sci.

Papers and seminars have also been presented at:

Chicago AIChE Meeting 1985  
Dow Chemical Company (Midland, MI)  
United Merchants Company (Augusta, GA)  
Short courses at Lehigh University at Davos Switzerland  
Louisiana State University  
University of Houston  
California Institute of Technology  
Union Oil Company  
University of California, San Diego  
Purdue University (Nov 1986)  
Miami AIChE Meeting (Nov 1986)  
DSM Company (Holland)  
Chemical Specialities Manufacture Assoc. Conference

NSF GRANT NO. CBT-8413987

Principal Investigator: Gary W. Poehlein

Funding was initiated under Grant No. CBT-8413987 on July 1, 1985, however, some work outlined in the proposal had already been completed. A brief summary of prior work is presented in this report along with an outline of work completed during the first six months of the present grant. Plans for the duration of the grant period are also presented. These sections are followed by a list of publications, presentations, the names of students working in the area covered by the grant, a list of other related support and financial projections. Copies of some papers are also attached.

RESEARCH PROGRESS

A steady-state model had been developed for emulsion polymerization in a seed-fed continuous stirred-tank reactor (CSTR). This model was used to simulate performance of such reactors. An experimental reactor system comprised of a plug-flow tubular reactor (PFT) followed by a single CSTR was constructed and used to study the influence of chain transfer agents on reactor performance and product characteristics such as particle concentration, particle size distribution and polymer molecular weights. The results of this work were reported in a

PhD dissertation entitled, "Emulsion Polymerization in a Seed-Fed Continuous Stirred-Tank Reactor" by H. C. Lee (March 1985).

Work since June 1985 has involved modeling and experimental work in two different areas. The experimental work has involved modification of the continuous reactor system by the addition of a second, larger CSTR, downstream of the present PFT-CSTR combination. The new three-reactor system will allow higher conversion experiments which are common to industrial practice.

The new reactor system has separate temperature controls for each reactor and capability for separate feed streams into each reactor. Thus copolymerization experiments with intermediate feed streams will be possible.

Reactor modeling work, since June 1985, has been focused on modifying the previous model to add the second CSTR and to include multiple monomers. This second modification is a major change since it involves rather complex thermodynamic relationships for monomer concentrations in three phases. Significant progress has been made in completing this new model.

A second thrust of the research work has been to develop a new kinetic model for emulsion polymerization which accounts for non-uniform distribution of free radicals in the monomer-swollen polymer particles. This phenomena has an impact on reaction kinetics as well as particle morphology of the latex produced and on molecular architecture.

Work has been partially completed on a preliminary model for the free-radical distribution in the particles and the effect of this distribution on radical desorption and grafting reactions. This latter area is of particular importance for a number of commercial products. The preliminary model has been successfully used to analyze and explain some published data on grafting reactions.

A third area of research, which is just starting, involves emulsion polymerization of monomer mixtures which include one monomer with significant water solubility. This effort will involve use of the continuous reactor system described above.

#### FUTURE WORK

Efforts during the next 1-3 years will include a continuation of the work described above. The copolymerization model will be completed and used to analyze data from the PFT-CSTR-CSTR reactor system. The experimental design will involve emulsion copolymerization with the monomers divided in different proportions between the three reactors. Thus we will be able to study the influence of reactor operating policies on reactor performance and product characteristics.

The work on non-uniform latex particle will be focused on grafting reactions. Model developments will continue and published data will be evaluated. In addition, experiments will

be carried out, in our laboratories, to study polystyrene grafting on polybutadiene seed latexes. The Dow Chemical Company has agreed to provide the seed latexes.

The continuous reactor work with water-soluble monomers will be primarily experimental. Commercial formulations will be used to study reaction kinetics and the resultant product properties. This work will involve substantial interactions with an industrial organization, Milliken & Company. Some of the work will be done in their laboratories.

#### PUBLICATIONS

1. "Emulsion Polymerization in a Seed-Fed Continuous Stirred-Tank Reactor," Hsueh-Chi Lee and Gary W. Poehlein, J. Dispersion Sci. & Technol., 5(3&4), 247-265 (1984).--Based on previous work: copy attached.
2. "Latex Particle Size Distributions from Steady-State Continuous Stirred-Tank Reactor-Systems," Gary W. Poehlein, H. C. Lee and Nada Stubicar, J. Polym. Sci., Polym. Symp. 72, 207-220 (1985).--Based on previous work: copy attached.
3. "Emulsion Polymerization," Gary W. Poehlein, Ch 6 in Applied Polymer Science, 2nd Ed., G. W. Poehlein and R. W. TESS (Editors), ACS Symposium Series 285, ACS, Washington, DC (1985).--Review paper: copy attached.
4. "Mechanisms and Kinetics of Emulsion Polymerization," Gary W. Poehlein, Ch. 2 in Polymer Colloids, R. Buscall, T. Corner and J. F. Stageman (Editors), Elsevier Appl. Sci. Pub., London (1985).--Review Paper: copy attached.
5. "Emulsion Polymerization," Gary W. Poehlein, Encyclopedia of Polymer Science and Engineering, 2nd Ed. (In press)--An extensive state-of-the-art paper.

6. "Emulsion Polymerization in a Seed-Fed Continuous Stirred-Tank Reactor-Influence of Transfer Reactors," H. C. Lee and G. W. Poehlein,--In Preparation, to be submitted to Polymer Process Engineering in January 1986.
7. "Polymerization in Non-Uniform Latex Particles I; Non-Uniform Distribution of Free-Radicals in Latex Particles," C-S Chern and G. W. Poehlein,--First draft completed; revised paper to be submitted in early 1986.
8. "Polymerization in Non-Uniform Latex Particles II; Two-Phase and Grafting Emulsion Polymerization," C.-S. Chern and G. W. Poehlein,--First draft completed; revised paper to be submitted in early 1986.

#### PRESENTATIONS

1. "Emulsion Polymerization in Continuous Reactors," Emulsion Polymers Short Course, Davos, Switzerland (August 1985).
2. "Emulsion Polymerization in a Seed-Fed CSTR: Chain Transfer Effects," H. C. Lee and G. W. Poehlein, Paper 113a, 1985 Annual AIChE Meeting, Chicago (Nov. 10-15, 1985).
3. "Use of Continuous Reactors for Emulsion Polymerization Kinetic Studies," Chemical Engineering Department, University of Houston (September 1985).
4. "Emulsion Polymerization in Continuous Reactors," Eastman Kodak Co., Rochester, NY (October 1985).
5. "Emulsion Polymerization in a Seed-Fed CSTR," Chemical Engineering Department, Lehigh University (October 1985).
6. "Use of Continuous Reactors for Emulsion Polymerization Kinetic Studies," Chemical Engineering Department, Louisiana State University (October 1985).
7. "Reactor Options for Continuous Emulsion Polymerization," The Dow Chemical Co., Midland, Michigan (November 1985).

#### RESEARCH STUDENTS

1. Richard Mead (PhD Candidate)  
BS, ChE North Carolina State University  
MS, ChE University of Florida  
Mr. Mead is involved with modeling and experimental work for emulsion copolymerization in continuous reactors.

2. Chorng-Shyan Chern (PhD Candidate)  
BS, ChE National Tawain University  
MS, ChE University of New Hampshire  
Mr. Chern is developing the concept of non-uniform distribution of free-radicals in latex particles. This idea and model will be used to study grafting reactions in emulsion polymerization.
3. Glenn Shoaf (MS Candidate)  
BS, CHE North Carolina State University  
Mr. Shoaf is working on continuous emulsion copolymerization with functional monomers that are water soluble.
4. Zhigland Song  
Visiting Scholar: Peoples Republic of China  
Mr. Song is currently evaluating several potential research topics. One would involve the kinetics of particle nucleation and the other inverse emulsion polymerization of acrylamide.

#### OTHER SUPPORT

1. S. C. Johnson Foundation--Graduate Fellowship
2. Milliken & Co.--Graduate Research Support via Georgia Tech's Graduate Cooperative Program.
3. Peoples Republic of China--Support for visiting scholar.

#### FINANCIAL REPORT

Projected expenditures through June 30, 1986, are indicated on Table 1 which is attached. These expenditures follow closely the budget which was originally approved by NSF. A small change has involved shifting some funds from computer services to equipment. In addition support for students has been developed from The S. C. Johnson Foundation (\$8000), Milliken & Company (\$22,000/1.5 years) and the Peoples Republic of China (support of Visiting Engineer).

Proposed expenditures for the second year of the grant total \$58,513. The proposed division of expenditures are given on the

attached budget sheet. This 2nd-year budget is the same as the original approved proposal.



# Georgia Institute of Technology

A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA

ATLANTA, GEORGIA 30332-0370

OFFICE OF VICE PRESIDENT  
FOR RESEARCH

March 9, 1988

National Science Foundation  
ATTN: Maria Burka  
Division of Chemical, Biochemical  
and Thermal Engineering  
1800 G Street, NW  
Washington, DC 20550

SUBJECT: Final Project Report/NS Award # CBT-8413987

Dear Dr. Burka:

I have attached the Final Project Report for my recently completed grant # CBT-8413987 on NSF Form 98. I believe that the results have been quite good and my students and I are continuing to work in the general area of emulsion polymerization, thanks to your decision to approve a new award. The new work, however, will move into some very different problem areas involving water soluble monomers and grafting reactions.

I am fortunate to have some good students and I believe the research results during the next three years will be quite solid. Thanks again for your continued support.

Sincerely,

Gary W. Poehlein  
Associate Vice President for  
Graduate Studies and Research

Enclosure

cc: LOCA: The final project reports--technical and NSF Form 98A  
have been transmitted with this letter.

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I—PROJECT IDENTIFICATION INFORMATION

1. Institution and Address Georgia Tech Research Corporation Georgia Institute of Technology Atlanta, GA 30332-0420	2. NSF Program Process and Reaction Engineering	3. NSF Award Number CRT-8413988
	4. Award Period From 7/85 To 12/30/87	5. Cumulative Award Amount \$114,533
5. Project Title Emulsion Polymerization in Continuous Reactors		

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


Emulsion polymerization is a widely used process for the production of polymer colloids; more commonly called latexes. The major thrust of this work was a study of reaction kinetics of emulsion polymerization and copolymerization in continuous reactor systems. Steady-state models were developed and used to analyze experimental results obtained with various reactor configurations and recipe formulations.

The initial work was focused on the influence of chain transfer agents on polymerization in a seed-fed continuous stirred tank reactor (CSTR). Experimental results included reaction rates, particle concentrations, particle size distributions and molecular weight. These measurements were utilized with the mathematical model, to study the important phenomena of free radical transport out of the polymerizing latex particles. Chain transfer agents were shown to have a significant influence on polymerization rate and particle size distribution as well as molecular weights.

The second part of the study involved copolymerization reactions with the monomer pairs; styrene-methyl acrylate, styrene-acronitrile and ethyl acrylate-methacrylic acid. Various continuous reactor configurations were employed and the results were used to study important components of the polymerization mechanisms.

The results of the work have led to a better quantitative understanding of the complex mechanisms of emulsion polymerization reactions and the performance of continuous reactor systems. This work will help industrial producers design better processes for the production of elastomers, coatings, adhesives, paper additives, medical colloids and many other important latex products.

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	X		
b. Publication Citations			X		
c. Data on Scientific Collaborators	X				
d. Information on Inventions	X				
e. Technical Description of Project and Results		X			
f. Other (specify)					
2. Principal Investigator/Project Director Name (Typed) Gary W. Poehlein	3. Principal Investigator/Project Director Signature 			4. Date 3/10/88	

## TECHNICAL DESCRIPTION/PROJECT RESULTS

Publications resulting from work on NSF Award #CBT-8413987, as well as those from closely related research are listed in Table 1 which is attached. The major thrust of the work carried out under NSF support was the study of the fundamental kinetics of emulsion polymerization reactions in continuous reactor systems. The results of this work serve two significant purposes. First, the combination of reactor modeling and experimental programs has provided a better quantitative understanding of polymerization and copolymerization in emulsion reactions. Second, the results demonstrate the utility, strengths and short-falls of various continuous reactor configurations.

In the first area, the major focus was on the transport of free radicals between phases, transfer reactions and monomer reactions in copolymer systems. Homopolymerizations, with and without added chain transfer agents, were used to study the phenomenon of free radical transport out of the monomer-swollen latex particles. This radical transport phenomena can have a significant influence on polymerization rate, particle formation and particle size distribution in a continuous stirred-tank reactor (Papers 1-4). The radical transport mechanism involves the formation of a small free radical via a transfer reaction with monomer or a chain transfer agent followed by diffusion across the particle-water interface. This was the motivation for experiments with different kinds and amounts of chain transfer agent.

Radical transport out of particles can also be important in copolymerization reactions; especially if monomer chain transfer reactions are important. Hence our studies have also involved reactor modeling and copolymerization experiments. Magnitudes of radical transport can be measured and these measurements used to estimate the magnitudes of rate constants for monomer cross-transfer reactions; an area that has received very little attention in the literature. This area was the subject of Richard Mead's PhD dissertation. Two papers on this thesis have been submitted for publication and one more is being prepared.

Copolymerization reactions with ethyl acrylate and a significant fraction of the water-soluble monomer methacrylic acid are very fast with reaction completion being achieved in 8-15 minutes. A variety of continuous reactor configurations were used to study this system; tubular reactors, CSTRs and tube-CSTR combinations (Paper 5). The results are focused at the second purpose of the research; continuous reactor development. Research in this area is continuing with several vinyl acid monomers. The objective of this research is to develop a more fundamental understanding of the kinetics of such systems; especially the reaction phenomena in the water phase.

Most of the continuous reactor work has involved the use of pretubular reactors followed by one or two CSTRs. The tubular reactor serves to form a latex seed for the CSTRs that are downstream. Again this reactor configuration has proven to be quite stable when contrasted to unseeded CSTRs which tend to oscillate.

Other papers listed in Table 1 include review articles (Papers 6 & 7); an examination of the calculation of the average number of free radicals per particle,  $\bar{n}$ , (Paper 8); an extension of the "gel effect" concepts of free radical polymerization to the important area of epoxy curing (Paper 9); and the development of a new concept concerning the distribution of free radicals in polymerizing latex particles (Paper 10). Additional papers have been submitted in some of these areas.

The results of our research will be useful to others involved in the study of mechanisms and kinetics of such heterogeneous polymerization systems. The results have been and will continue to be valuable to industrial organizations who are engaged in the production of latex products.

TABLE 1

NSF Award # CBT-8413987/Polymerization Reaction Engineering

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Continuous Reactor System:

1. "Latex Particle Size Distributions from Steady State Continuous Stirred-Tank Reactor Systems," with H. C. Lee and N. Stubicar, J. Polym. Sci., Part C, 72, 207-220 (1985).
2. "Free Radical Transport and Reactions in Emulsion Polymerization," Polym. Reaction Engineering, 59-70 (1986) with H.-C. Lee and C.-S. Chern. (Book edited by K.-H. Reichert and W. Geiseler, Huthig & Wepf, Heidelberg).
3. "Continuous Tube-CSTR Reactor System for Emulsion Polymerization Kinetic Studies," with H.-C. Lee, Chem. Eng. Sci., 41, 1023-30 (1986).
4. "Emulsion Polymerization in a Seed-Fed Continuous Stirred Tank Reactor: Influence of Transfer Reactions," with H.-C. Lee, Polym. Process. Engr., 5(1), 37-74 (1987).
5. "Batch and Continuous Emulsion Copolymerization of Ethyl Acrylate and Methacrylic Acid," with Glenn Shoaf, accepted by Polym. Process Eng. (1987).

General Emulsion Polymerization Kinetics:

6. "Emulsion Polymerization," Chapter in Applied Polymer Science, 2nd Edition, R. Tess and G. Poehlein, ACS, Washington, DC (1985).
7. "Emulsion Polymerization," Encyclopedia of Polymer Science and Engineering, Vol. 6, 2nd Ed., J. Wiley & Sons, New York (1986).
8. "Reaction Kinetics of Vinyl Acetate Emulsion Polymerization," with Chorng-Shyan Chern, J. Applied Poly. Sci., 33, 2117-2136 (1987).

Other Related Polymerization Papers:

9. "A Kinetic Model for Curing Reactions of Epoxides with Amines," with C.-S. Chern, Polym. Eng. Sci., 27:11, 788-795 (1987).
10. "Polymerization in Nonuniform Latex Particles: Distribution of Free Radicals" with C.-S. Chern, J. of Polymer Sci.: Part A Polymer Chemistry, 25, 617-635 (1987).

FEASIBILITY STUDY FOR CONTINUOUS EMULSION  
COPOLYMERIZATION OF ETHYL ACRYLATE AND  
METHACRYLIC ACID

xi

Glenn Lewis Shoaf

M.S. Thesis

December 1986

SUMMARY

Work reported in this thesis involved the study of the emulsion copolymerization of methacrylic acid and ethyl acrylate. Both monomers have significant water solubility which results in behavior that greatly differs from the behavior of conventional emulsion polymerization systems with relatively water-insoluble monomers. A series of batch and continuous copolymerizations were performed.

The monomer system was characterized primarily through batch studies. Conversion and temperature data were obtained as a function of time and used to determine reaction rates. Relative to conventional emulsion polymer systems, the adiabatic batch reaction occurred very quickly with the attainment of complete conversion in 10 to 12 minutes when initiated at 49°C. Conversion was determined by gravimetric analysis and checked for accuracy with gas chromatography. The copolymer composition was calculated with the copolymer composition equation and compared to experimental data obtained with the gas chromatograph. Results showed that the methacrylic acid reacted rapidly over a large extent of the initial fractional conversion. Then, the ethyl acrylate reacted almost exclusively with itself as the acid was depleted.

Studies on particle size and particle formation revealed that stabilized particles formed in the batch reaction had an average diameter of 120 nm. A significant amount of methacrylic acid polymerized in the aqueous phase and either physically adsorbed or chemically bonded to polymer particles dispersed in the continuous phase. A large portion of the acid also copolymerized inside the

polymer particles. The acid served to help stabilize the particles. At low conversions when less methacrylic acid polymer had formed and become incorporated with the particles, coagulation increased dramatically. Mixing intensity had little effect on particle size. Isothermal reactions at high temperatures, 60°C to 70°C, led to increased particle diameters, 200 to 300 nm. Isothermal reactions at 50°C to 55°C, and adiabatic reactions initiated at 49°C (peaking at 72°C) produced small particles with diameters of 120 to 130 nm.

A series of continuous runs were made with continuous stirred-tank reactors (CSTR's) and several plug-flow reactors (PFR's) operated under various conditions. Unseeded reactions with the CSTR produced conversion oscillations. PFR runs at high temperatures, (60°C to 70°C) and/or low conversions (<60%) resulted in large particles. At a lower temperature, 55°C, small particles were formed when the PFR effluent exited with a conversion of 60% or greater. Conversions between 60% and 100% required residence times between 14 and 20 minutes at 55°C. In a PFR-CSTR combination, small stable particles were not formed if the PFR effluent had a conversion lower than 60%.

Scale-up calculations were made using an arbitrary production rate. An actual plant-scale design was also made based on the scale-up calculations.

POLYMERIZATION IN NON-UNIFORM LATEX PARTICLES  
Chorng-Shyan Chern  
PhD Thesis  
June 1987

SUMMARY

The kinetics of polymerization in non-uniform latex particles is the major focus of this dissertation. The goal was to develop a new and quite different model for the monomer-swollen polymer particles during polymerization.

Free radicals which diffuse into latex particles from the aqueous phase normally have hydrophilic end-groups. The preferential location of these end-groups on or near the particle surface would lead to non-uniform distribution of free radicals in the particles. Monte Carlo simulations of a growing polymer chain in a particle have been used to develop a relationship for free radical density as a function of radial position within the particles. A novel cubic lattice model which represents a styrene-swollen polybutadiene latex particle has been employed to calculate instantaneous grafting efficiency via random walk calculations.

Published theories for transport of free radicals out of the polymerizing latex particles have been reexamined based on the concept of non-uniform distribution of free radicals. A modified expression for the desorption rate constant has been presented.

The concept of non-uniform radical distribution has also been used to develop a new theory for the kinetics of two-phase emulsion polymerization. The kinetic model allows prediction of polymerization rate and the distribution of free radicals in the two polymer phases as a function of reaction conditions.

The new theory includes model components for grafting emulsion reactions. This theory permits prediction of grafting efficiency as a function of reaction conditions. It can also be used for evaluation of grafting reaction rate constants.

A mechanistic kinetic model has also been developed for the kinetics of grafting in solution polymerization. This model allows prediction of the rate of polymerization and grafting efficiency under various reaction conditions. It permits evaluation of grafting reaction rate constants. Different methods of polymerization (such as bulk, solution or emulsion) have been shown to result in different grafting behavior with respect to individual reaction parameters.

Recent research efforts on morphological studies of non-uniform latex particles have been reviewed and important physical parameters and polymerization conditions identified. A general discussion has been included to highlight the important mechanistic aspects in the formation of various morphological structures of

latex particles. Particular attention has been placed on the effect of interfacial tension on the particle morphology.

The experimental program involved the polymerization of styrene in the presence of polybutadiene or composite polystyrene/polybutadiene (shell/core) seeds. All reactions were conducted in a batch reactor. A transmission electron microscope was used to characterize the particle size distributions. Solvent extraction was employed to determine the degree of grafting. Gel permeation chromatography was used to determine the molecular weight distribution of the extracted polymers. Differential scanning calorimetry was used to determine the glass transition temperatures of the composite latexes.

Experimental data for two-phase and grafting emulsion polymerization reactions available in the literature and obtained in this work were used to assess the hypothesis of non-uniform distribution of free radicals in the particles. The results support this hypothesis.

EMULSION POLYMERIZATION IN A SEED-FED CONTINUOUS  
STIRRED-TANK REACTOR

Hsueh-Chi Lee

PhD Thesis

March 1985

ACKNOWLEDGMENTS

I wish to express my sincere appreciation to the following:

Dr. Gary W. Poehlein, Director of School of Chemical Engineering, for his professional guidance, valuable advice and constructive criticisms throughout the progress of this study.

The members of my doctoral committee, Dr. Agaram S. Abhiraman, Dr. William R. Ernst, Dr. John D. Muzzy and Dr. Robert A. Pierotti.

Dr. F. Joseph Schork, Dr. A. H. Peter Skelland and Dr. Ervin E. Underwood for their helpful discussion and suggestions.

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## EMULSION COPOLYMERIZATION IN CONTINUOUS REACTORS

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## SUMMARY

The kinetics and mass transfer phenomena associated with emulsion copolymerization in a seed-fed continuous stirred-tank reactor (CSTR) operating at steady state were examined in this work. The goal was to develop a mathematical model to predict the particle size distribution, copolymer composition, and conversion of the effluent latex from a seed-fed CSTR operating at steady state.

Published theories for the prediction of the number of free radicals per particle for emulsion copolymerization in a batch reactor were modified for the broad particle size distribution of a latex produced in a CSTR. An age distribution analysis was used to relate particle size and growth rate to the time spent by the particle in the CSTR. The model accounts for the absorption of aqueous-phase free radicals by particles. The diffusion of monomer free radicals from the particles is also accounted for by the model.

Monomer partitioning between the particles, aqueous phase, and monomer droplets (when present) was calculated using published thermodynamic theories. The thermodynamic interaction parameters required for these calculations were determined by fitting the thermodynamic relations to

An analytical solution was derived for the concentration of monomer free radicals as a function of radial position in the latex particle. A monomer radical desorption rate constant was derived based on the nonuniform distribution of monomer free radicals within the latex particle. The desorption rate constant for styrene emulsion homopolymerization was calculated with the desorption rate constant expression derived in this work and with desorption rate constants which do not consider nonuniform monomer radical distribution within the particles. The monomer radical transport theory was extended to emulsion copolymerization and desorption rate constants were derived.

A kinetic model for aqueous-phase polymerization during seeded emulsion copolymerization was derived. An expression for the concentration of radicals in the aqueous phase was derived from a balance on radicals in the aqueous phase. The rate of aqueous-phase polymerization and copolymer composition can be calculated with the model.

Simulations of aqueous-phase polymerization during the seeded emulsion copolymerization of styrene-methyl acrylate and styrene-acrylonitrile reveal that the aqueous-phase termination rate constant and radical capture coefficient control the aqueous-phase radical concentration and rate of polymerization. An iterative method was used to calculate the particle-size-independent radical capture constant for these experiments. The capture constants determined in this

work are similar in magnitude to a capture constant determined for styrene emulsion homopolymerization by an independent researcher. The analysis indicates that the capture constant cannot be predicted by collision theory alone. Repulsive interactions between aqueous-phase radicals and latex particles must be accounted for.