10:16:34 OCA PAD INITIATION - PROJECT HEADER INFORMATION 12/16/87

Active

Project #: [redacted]-599 Cost share #: E-19-346 Rev #: 0
Center # : R6430-0A0 Center shr #: F6430-0A0 OCA file #:
Work type : RES
Contract#: CBT-8717926 Mod #: Document : GRANT
Prime #: Contract entity: GTRC

Subprojects ? : N
Main project #:

Project unit: CHE Unit code: 02.010.114
Project director(s):
[redacted]

Sponsor/division names: NATL SCIENCE FOUNDATION / [redacted]
Sponsor/division codes: 107 / 000

Award period: 871201 to 890531 (performance) 890831 (reports)

Sponsor amount	New this change	Total to date
Contract value	66,734.00	66,734.00
Funded	66,734.00	66,734.00
Cost sharing amount		667.00

Does subcontracting plan apply ?: N

Title: EMULSION POLYMERIZATION KINETICS

PROJECT ADMINISTRATION DATA

OCA contact: [redacted] 894-4820

Sponsor technical contact

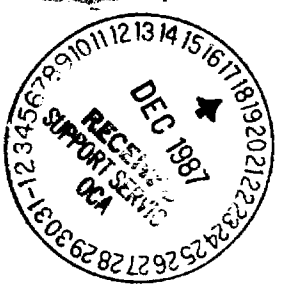
MARIA BURKA
(202)357-9606
NATIONAL SCIENCE FOUNDATION
ENG/CBT
WASHINGTON, DC 20550

Sponsor issuing office

CHARLES ZEIGLER
(202)357-9602
NATIONAL SCIENCE FOUNDATUION
DGC/ENG
WASHINGTON, DC 20550

Security class (U,C,S,TS) :
Defense priority rating :
Equipment title vests with: Sponsor GIT

ONR resident rep. is ACO (Y[redacted])
NSF supplemental sheet



Administrative comments -
PROJECT INITIATION

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 05/23/91

Project No. E-19-699 Center No. R6430-0A0

Project Director POEHLEIN G W School/Lab CHEM ENGR

Sponsor NATL SCIENCE FOUNDATION/GENERAL

Contract/Grant No. CTS-8717926 Contract Entity GTRC

Prime Contract No.

Title EMULSION POLYMERIZATION KINETICS

Effective Completion Date 910630 (Performance) 910930 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	N	
Final Report of Inventions and/or Subcontracts	Y	910522
Government Property Inventory & Related Certificate	Y	
Classified Material Certificate	N	
Release and Assignment	N	
Other	N	

Comments BILLING VIA NSF LINE-OF-CREDIT. 98A SUBMITTED WITH FINAL REPORT SATISFIES REQUIREMENT FOR PATENT REPORTING.

Subproject Under Main Project No.

Continues Project No.

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Managment	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other	N
	N

~~NOTE: Final Patent Questionnaire sent to PDPI~~

8-19-699
Pat

Georgia Institute of Technology
A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA
ATLANTA, GEORGIA 30332-0370
OFFICE OF VICE PRESIDENT
FOR RESEARCH

July 22, 1988

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

Dear Dr. Burka:

I have enclosed a brief report that covers the first eight months of my grant. Things are busy since I have recently had two Ph.D.'s finish and two new students starting. I should have more information on future research details by the end of the year as the new students become more focused.

Please let me know if you need any further information.

Sincerely,

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

GWP:sd

Enclosures

ANNUAL REPORT
EMULSION POLYMERIZATION KINETICS

NATIONAL SCIENCE FOUNDATION

Grant Number: CBT-8717926

Period Covered: 12/1/87 - 7/31/88

Title: Emulsion Polymerization Kinetics

Georgia Tech Project Number: E-19-699

submitted to:

Dr. Maria K. Burka, Program Director

Process and Reaction Engineering

Division of Chemical, Biochemical,

of Thermal Engineering

submitted by:

Dr. Gary W. Poehlein

Professor of Chemical Engineering

Georgia Institute of Technology

July 22, 1988

EMULSION POLYMERIZATION KINETICS

PERSONNEL:

Dr. Gary W. Poehlein; Principal Investigator

Richard N. Mead: GRA, Post Doc. (ChE)

Dr. Mead completed requirements for the Ph.D. in December, 1987, Dissertation title, "Emulsion Copolymerization in Continuous Reactors." He remained as a Post Doc through March, 1988. He is now employed by Champion International in Florida.

Zhiqiang Song: GRA, Post Doc. (ChE)

Dr. Song completed requirements for the Ph.D. in June, 1988, Dissertation title, "Kinetics of Emulsion Polymerization." He will remain as a Post Doc through August when he will leave to join a research group at Queen's University in Canada.

Glenn A. Shoaf: Ph.D. Candidate (ChE)

Primary financial support from Dow Chemical, USA. Research project title, "Emulsion Copolymerization with Vinyl Acid Monomers." Mr. Shoaf received NSF and NATO support to attend the 1988 Advanced Study Institute on Polymer Colloids.

David Lange: Ph.D. Candidate (ChE)

Research project title, "Emulsion Copolymerization with Functional Monomers in Continuous Reactors."

Paul Thurner: Ph.D. Candidate (ChE)

Started in March, 1988. Will probably work on a problem related to grafting kinetics.

Cheryl Matthews Gilmore: Ph.D. Candidate (ChE)

Co-directed by Professor F. J. Schork. Primary financial support from Air Products and Chemicals, Inc. Research project title, "Modeling and Control of Particle Nucleation and Growth in Sterically Stabilized Vinyl Acetate Emulsion Polymerization."

Yasuhiko Sasagawa: Visiting Scholar

Employee of and supported by Japan Synthetic Rubber Company. Working in a variety of emulsion polymerization areas.

PUBLICATIONS:

1. "Particle Formation in Emulsion Polymerization: Transient Particle Concentration," Z. Song and G. W. Poehlein, J. Macromol. Sci. - Chem., A25(4), 403-443 (1988).

2. "Batch and Continuous Emulsion Copolymerization of Ethyl Acrylate and Methacrylic Acid," G. L. Shoaf and G. W. Poehlein, Polym. Process Engr., 6(1), 61 - 89 (1988).

3. "Free Radical Transport from Latex Particles," R. N. Mead and G. W. Poehlein, accepted by J. Appl. Polym. Sci., (1988).

4. "Particle Formation in Emulsion Polymerization: Particle Number at Steady State," Z. Song and G. W. Poehlein, accepted by J. Macromol. Sci. - Chem. (1988).

5. "Emulsion Copolymerization of Styrene-Methyl Acrylate and Styrene - Acrylonitrile in Continuous Stirred-Tank Reactors (I)," R. N. Mead and G. W. Poehlein, accepted by I & EC Research (1988).

6. "Emulsion Copolymerization of Styrene-Methyl Acrylate and Styrene - Acrylonitrile in Continuous Stirred-Tank Reactors (II): Aqueous-Phase Polymerization and Radical Capture," R. N. Mead and G. W. Poehlein, accepted by I & EC Research (1988).

7. "Particle Nucleation in Emulsifier-Free Aqueous-Phase Polymerization: State 1," Z. Song and G. W. Poehlein, accepted by J. Coll. Interface Sci. (1988).

8. "Particle Formation in Emulsifier-Free Aqueous-Phase Polymerization of Styrene," Z. Song and G. W. Poehlein, accepted by J. Coll. Interface Sci. (1988).

RESEARCH PROGRESS SUMMARY

Considerable effort has been devoted to the understanding and modeling of particle nucleation in emulsion polymerization. Work has involved systems with classical anionic surfactants and emulsifier-free recipes (Song). Work is now underway with vinyl-acetate emulsion polymerization in the presence of stearic stabilizers (Matthew-Gilmore).

Copolymerization studies have involved several monomer systems and a variety of continuous and batch reactors (Shoaf and Mead). Current copolymerization research is focused on water-soluble functional monomers such as vinyl acids. Batch, semi-batch and continuous reactors will be used (Shoaf, Lange, and Sasagawa).

New work to be initiated in 1988 will involve studies of grafting reactions and, in some cases, the influence of such reactions on particle morphology.

Georgia Tech

Georgia Institute of Technology
Graduate Studies and Research
Atlanta, Georgia 30332-0265
(404) 894-3090

November 9, 1988

Dr. Maria K. Burka
Program Director, Process and Reaction Engineering
National Science Foundation
Washington, DC 20550

REFERENCE: NSF Grant No. CBT-8717926 "Emulsion Polymerization Kinetics"

Dear Dr. Burka:

I have enclosed the first annual report on my NSF Grant. The research is going well and we look forward to a high level of continued activity.

The highlights of the first year were as follows:

(1) Two doctoral students, Richard Mead and Zhigiang Song, completed PhD dissertations.

(2) Two other doctoral students joined the program; David Lange and Paul Thurner.

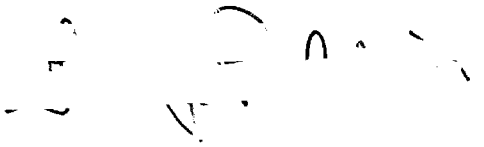
(3) Eleven papers were published or accepted.

Further details are provided in the annual report.

The second purpose of this letter is to request continuation funding for the second year at the level of $70,563 which was previously approved. I understand that it is not necessary to submit a new budget.

Thank you for the consideration of this request. Please let me know if you need any other information.

Sincerely,



Gary W. Poehlein
Associate Vice President and
Dean of Graduate Studies

Enclosure

Lynn Boyd
Contracting Officer

ANNUAL REPORT

NATIONAL SCIENCE FOUNDATION

Grant Number: CBT-8717926

Period Covered: 12/1/87 - 11/30/88

Title: Emulsion Polymerization Kinetics

Georgia Tech Project Number: E-19-699

submitted to:

Dr. Maria K. Burka, Program Director

Process and Reaction Engineering

Division of Chemical, Biochemical,

of Thermal Engineering

submitted by:

Dr. Gary W. Poehlein

Professor of Chemical Engineering

Georgia Institute of Technology

November 30, 1988

EMULSION POLYMERIZATION KINETICS

PERSONNEL:

Dr. Gary W. Poehlein; Principal Investigator

Richard N. Mead: GRA, Post Doc. (ChE)
Dr. Mead completed requirements for the PhD in December, 1987, Dissertation title, "Emulsion Copolymerization in Continuous Reactors," He remained as a Post Doc through March, 1988. He is now employed by Champion International in Florida.

Zhiqiang Song: GRA, Post Doc. (ChE)
Dr. Song completed requirements for the PhD in June, 1988, Dissertation title, "Kinetics of Emulsion Polymerization." He remained as a Post Doc through August when he left to accept a Post Doctoral position with a research group at Queen's University in Canada.

Glenn A. Shoaf: PhD Candidate (ChE)
Primary financial support from Dow Chemical, USA. Research project title, "Emulsion Copolymerization with Vinyl Acid Monomers," Mr. Shoaf received NSF and NATO support to attend the 1988 Advanced Study Institute on Polymer Colloids in France.

David Lange: PhD Candidate (ChE)
Research project title, "Emulsion Copolymerization with Functional Monomers in Continuous Reactors."

Paul Thurner: PhD Candidate (ChE)
Started in March 1988. Will probably work on a problem related to grafting kinetics in solution and emulsion polymerization.

Cheryl Matthews Gilmore: PhD Candidate (ChE)
Co-directed by Professor F. J. Schork. Primary financial support from Air Products and Chemicals, Inc. Research project title, "Modeling and Control of Particle Nucleation and Growth in Sterically Stabilized Vinyl Acetate Emulsion Polymerization."

Yasuhiko Sasagawa: Visiting Scholar
Employee of and supported by Japan Synthetic Rubber Company. Working in a variety of emulsion polymerization areas.

Knut Möller: Visiting Scholar

Dr. Möller is an employee of Metallgesellschaft (West Germany). He will be spending about 10 weeks at Georgia Tech working on emulsion copolymerization.

PUBLICATIONS:

1. "Particle Formation in Emulsion Polymerization: Transient Particle Concentration ," Z. Song and G. W. Poehlein, J. Macromol. Sci. - Chem.,A25(4) , 403-443 (1988).

2. "Batch and Continuous Emulsion Copolymerization of Ethyl Acrylate and Methacrylic Acid," G. L. Shoaf and G. W. Poehlein, Polym. Process Engr., 6(1), 61-89 (1988).

3. "Free Radical Transport from Latex Particles," R. N. Mead and G. W. Poehlein, accepted by J. Appl. Polym. Sci., (1988).

4. "Particle Formation in Emulsion Polymerization: Particle Number at Steady State," Z. Song and G. W. Poehlein, J. Macromol. Sci.-Chem., A25(12) , 1587-1632 (1988).

5. "Emulsion Copolymerization of Styrene-Methyl Acrylate and Styrene-Acrylonitrile in Continuous Stirred-Tank Reactors (I)," R. N. Mead and G. W. Poehlein, in press, I & EC Research (1988).

6. "Emulsion Copolymerization of Styrene-Methyl Acrylate and Styrene - Acrylonitrile in Continuous Stirred-Tank Reactors (II): Aqueous-Phase Polymerization and Radical Capture," R. N. Mead and G. W. Poehlein, in press, I & EC Research (1988).

7. "Particle Nucleation in Emulsifier-Free Aqueous-Phase Polymerization: State 1," Z. Song and G. W. Poehlein, accepted by J. Coll. Interface Sci. (1988).

8. "Particle Formation in Emulsifier-Free Aqueous-Phase Polymerization of Styrene," Z. Song and G. W. Poehlein, accepted by J. Coll. Interface Sci. (1988).

9. "Polymerization in Non-Uniform Latex Particles II: Kinetics of Two-Phase Emulsion Polymerization," C. S. Chern and G. W. Poehlein, accepted by J. Polym. Sci., Part A. Poly. Chem. (1988).

10. "Polymerization in Non-Uniform Latex Particles III: Kinetics of Grafting in Emulsion Polymerization," C. S. Chern and G. W. Poehlein, accepted by J. Polym. Sci., Part A, Poly. Chem. (1988).

11. "Emulsion Polymers/Emulsion Polymerization, G. W. Poehlein and F. J. Schork, Polymer News, 13, 231-240 (1988).

RESEARCH PROGRESS SUMMARY

Considerable effort has been devoted to the understanding and modeling of particle nucleation in emulsion polymerization. Work has involved systems with classical anionic surfactants and emulsifier-free recipes (Song). Work is now underway with vinyl-acetate emulsion polymerization in the presence of stearic stabilizers (Matthews-Gilmore).

Particle nucleation is one of the more important aspects of emulsion polymerization. The complex interrelated phenomena that are involved are known in a qualitative sense. The work of Song has been successful in developing good, and in some cases rather simple, models for nucleation in the presence and absence of classical ionic emulsifiers. Song's models have been used to simulate a rather broad range of experimental data. The concept of a variable critical oligomeric chain length in emulsifier-free emulsion polymerization is new and the models developed from this concept fit styrene emulsion polymerization data.

Particle nucleation in the presence of polymeric stabilizers is not nearly as well understood. Important issues such as water solubility, adsorption, grafting, molecular weight, molecular blockiness, etc. can all be important in such systems. Cheryl Matthews-Gilmore is studying the emulsion polymerization of vinyl acetate in the presence of polyvinylalcohol; an important commercial system. We hope the results of this work will include a better understanding of the important nucleation pheonomena when dissolved and/or adsorbed polymers are present.

Copolymerization studies have involved several monomer systems and a variety of continuous and batch reactors (Shoaf and Mead). Current copolymerization research is focused on water-soluble functional monomers such as vinyl acids. Batch, semi-batch and continuous reactors will be used (Shoaf, Lange, and Sasagawa).

New work to be initiated in 1989 will involve studies of grafting reactions and in some cases, the influence of such reactions on particle

morphology. Grafting can take place in the continuous phase or in the monomer-swollen latex particles. In some cases added polymeric materials are involved: e.g., polybutodiene seeds, water-soluble polyvinylalcohol, etc. Grafting reactions can influence polymerization kinetics, molecular architecture and particle morphology.

Most commercial emulsion polymerization processes involve two or more monomers. Mead's work has been focussed on copolymerization in continuous reactor systems. His models for steady-state CSTR's can be used to predict reaction rates, copolymer composition and latex particle size distributions. The models account for difference in monomer water solubility and for reactions in both aqueous and organic phases. The experimental results have also been used to study the important phenomena of free radical transport out of the polymerizing monomer-swollen latex particles. This component of the work also includes an evaluation of cross monomer chain transfer reactions for copolymerization.

Mead studied systems in which one monomer had modest water solubility (Methyl acrylate and Acrylonitrile). This work is being continued by Glenn Shoaf and David Lange with completely water soluble monomers such as the vinyl acids. The reactions in the aqueous phase are more important in such systems.

Georgia Tech

Georgia Institute of Technology
Graduate Studies and Research
Atlanta, Georgia 30332-0265
(404) 894-3090

October 26, 1989

Dr. Maria K. Burka
Program Director
Process and Reaction Engineering
National Science Foundation
Washington, DC 20550

REFERENCE: NSF Grant No. CBT-8717926 "Emulsion Polymerization Kinetics"

Dear Dr. Burka:

I have enclosed the second annual report on my NSF Grant. The research continues to go well and we look forward to a high level of activity next year.

The highlights of the first two years are as follows:

(1) Two doctoral students, Richard Mead and Zhigiang Song, completed PhD dissertations; a third, Glenn Shoaf, will complete his PhD in December 1989.

(2) Three other doctoral students, Cheryl Matthews-Gilmore, David Lange and Paul Thurner, are making significant progress on their research problems.

(3) One undergraduate student, Chris Durden, was supported with an REU Supplement.

(4) Sixteen papers were published, accepted or submitted.

Of course, not all of these students were supported on my NSF grant, but it is the keystone. Further details on the students, publications and research results are provided in the attached annual report.

Thank you for the consideration of this request. Please let me know if you need any other information.

Sincerely,

Gary W. Poehlein
Associate Vice President and
Dean of Graduate Studies

Lynn Boyd
Contracting Officer

Enclosure

cc: OCA Reporting Office

ANNUAL REPORT

NATIONAL SCIENCE FOUNDATION

Grant Number: CBT-8717926

Period Covered: 12/1/88 - 11/30/89

Title: Emulsion Polymerization Kinetics

Georgia Tech Project Number: E-19-699

submitted to:

Dr. Maria K. Burka, Program Director

Process and Reaction Engineering

Division of Chemical, Biochemical,

of Thermal Engineering

submitted by:

Dr. Gary W. Poehlein

Professor of Chemical Engineering

Georgia Institute of Technology

October 26, 1989

EMULSION POLYMERIZATION KINETICS

PERSONNEL:

Dr. Gary W. Poehlein; Principal Investigator

Richard N. Mead: GRA, Post Doc. (ChE)
Dr. Mead completed requirements for the PhD in December, 1987, Dissertation title, "Emulsion Copolymerization in Continuous Reactors," He remained as a Post Doc through March, 1988. He is now employed by Champion International in Florida.

Zhiqiang Song: GRA, Post Doc. (ChE)
Dr. Song completed requirements for the PhD in June, 1988, Dissertation title, "Kinetics of Emulsion Polymerization." He remained as a Post Doc through August when he left to accept a Post Doctoral position with a research group at Queen's University in Canada.

Glenn A. Shoaf: PhD Candidate (ChE)
Primary financial support from Dow Chemical, USA. Research project title, "Emulsion Copolymerization with Vinyl Acid Monomers," Mr. Shoaf received NSF and NATO support to attend the 1988 Advanced Study Institute on Polymer Colloids in France. He will complete his PhD in late 1989 or early 1990.

David Lange: PhD Candidate (ChE)
Research project title, "Emulsion Copolymerization with Functional Monomers in Continuous Reactors," with additional studies related to polymerization in large particles. Expected PhD completion in mid 1991.

Paul Thurner: PhD Candidate (ChE)
Research project involves kinetics of dispersion polymerization.

Cheryl Matthews Gilmore: PhD Candidate (ChE)
Co-directed by Professor F. J. Schork. Partial financial support from Air Products and Chemicals, Inc. Research project title, "Modeling and Control of Particle Nucleation and Growth in Sterically Stabilized Vinyl Acetate Emulsion Polymerization."

Yasuhiko Sasagawa: Visiting Scholar
Employee of and supported by Japan Synthetic Rubber Company. Worked in a variety of emulsion polymerization areas. Returned to Japan in December 1988.

Knut Möller: Visiting Scholar
Dr. Möller, an employee of Metallgesellschaft (West Germany), spent about 10 weeks at Georgia Tech working on emulsion copolymerization and other areas in 1988.

Xizhen Qian: Visiting Scholar
Professor Qian from Tianjin Institute of Technology (P.R. China) spent the period December 1988 - December 1989 at Georgia Tech. She studied grafting in emulsion polymerization.

E. Christopher Durden: Undergraduate Research Student
Mr. Durden was funded with an REU Supplement. He worked with Glenn Shoaf and David Lange on various projects related to Emulsion Polymerization with Carboxylic Monomers during the Summer of 1989

PUBLICATIONS:

1. "Particle Formation in Emulsion Polymerization: Transient Particle Concentration," Z. Song and G. W. Poehlein, *J. Macromol. Sci.-Chem.*,. **A25(4)**, 403-443 (1988).

2. "Batch and Continuous Emulsion Copolymerization of Ethyl Acrylate and Methacrylic Acid," G. L. Shoaf and G. W. Poehlein, *Polymer-Plastics Tech. & Engr.*, **28(3)**, 289-317 (1989).

3. "Free Radical Transport from Latex Particles," R. N. Mead and G. W. Poehlein, accepted by *J. Appl. Polym. Sci.*, (1988).

4. "Particle Formation in Emulsion Polymerization: Particle Number at Steady State," Z. Song and G. W. Poehlein, *J. Macromol. Sci.-Chem.*, **A25(12)**, 1587-1632 (1988).

5. "Emulsion Copolymerization of Styrene-Methyl Acrylate and Styrene-Acrylonitrile in Continuous Stirred-Tank Reactors (I)," R. N. Mead and G. W. Poehlein, *I & EC Research*, **27(12)**, 2283-93 (1988).

6. "Emulsion Copolymerization of Styrene-Methyl Acrylate and Styrene - Acrylonitrile in Continuous Stirred-Tank Reactors (II): Aqueous-Phase Polymerization and Radical Capture," R. N. Mead and G. W. Poehlein, *I & E C Research*, **28(1)**, 51-57 (1988).

7. "Particle Nucleation in Emulsifier-Free Aqueous-Phase Polymerization: Stage 1," Z. Song and G. W. Poehlein, *J. Coll. Interface Sci.*, **128(2)**, 486-500 (1989).

8. "Particle Formation in Emulsifier-Free Aqueous-Phase Polymerization of Styrene," Z. Song and G. W. Poehlein, *J. Coll. Interface Sci.*, **128(2)**, 501-510 (1989).

9. "Polymerization in Non-Uniform Latex Particle II: Kinetics of Two-Phase Emulsion Polymerization," C. S. Chern and G. W. Poehlein, accepted by *J. Polym. Sci., Part A. Poly. Chem.* (1988).

10. "Polymerization in Non-Uniform Latex Particles III: Kinetics of Grafting in Emulsion Polymerization," C. S. Chern and G. W. Poehlein, accepted by *J. Polym. Sci.. Part A. Poly. Chem.* (1989).

11. "Emulsion Polymers/Emulsion Polymerization, G. W. Poehlein and F. J. Schork, *Polymer News*, **13**, 231-240 (1988).

12. "Free Radical Transport from Latex Particles," Richard Mead and Gary Poehlein, *J. Appl. Polym. Sci.*, **38**, 105-122 (1989).

13. "Kinetics of Emulsifier-Free Emulsion Polymerization of Styrene in the Presence of Chain Transfer Agents," Z. Song and G. W. Poehlein, accepted by *Polymer-Plastics Techn. & Engr. J.*, (1989).

14. "Kinetics of Emulsifier-Free Emulsion Polymerization of Styrene," Z Song and G. W. Poehlein, submitted to *J. Polym. Sci., Part A, Poly. Chem.* (1989).

15. "Partition of Carbozylic Acids in an Emulsion Copolymerization System," G. Shoaf and G. W. Poehlein, submitted to *Ind. & Engr. Chem. Research* (1989).

16. "Kinetic Analysis of Seeded Emulsion Polymerization of Vinyl Acetate," D. M. Lange, G. W. Poehlein, S. Hayashi, A. Komatsu and T. Hirai, paper under final review by Japanese collaborators.

GRANT PROGRESS SUMMARY

The most important contribution during the first two years of this grant has been the education of students. Two students have received PhD's and a third will complete all doctoral degree requirements in late

1989. Three doctoral students are in earlier stages of their graduate education and dissertation research. Five of these six students are U.S. citizens. The research group has also included three visiting scholars and one undergraduate student. Obviously not all of these students and scholars have been supported by funds in the Grant No. CBT-8717926. The NSF grant, however, represents the centerpiece of my research support structure. It is the glue that holds the pieces in place.

Research progress during the first year of the grant was focussed on the following major issues in emulsion polymerization technology.

- Particle nucleation
- Copolymerization in continuous reactor systems.

More details concerning this work was a part of the progress report submitted in November 1988 and in some of the publications listed in this report.

The research during the current year has involved emulsion copolymerization with functional, water-soluble, monomers and vinyl acetate emulsion polymerization in the presence of polyvinylalcohol. Glenn Shoaf is in the final stages of his doctoral dissertation which is concerned with the copolymerization of carboxylic acids and styrene. The acid monomers are completely water soluble and hence behave very different from the hydropholic monomers which are normally used in emulsion polymerization reactions. Mr. Shoaf's work included:

- Fundamental studies of the solution polymerization of acid monomers in water.

- Thermodynamic experiments and modeling concerning the partitioning of the reaction ingredients among the various phases present in emulsion polymerization systems.

- Experiments and modeling of the copolymerization reactions.

The results of this work have significantly increased our knowledge of the important details of emulsion copolymerization with water-soluble monomers. The work of David Lange with continuous reactor systems has also contributed to the understanding of these systems.

The second area of research involves the emulsion polymerization of vinyl acetate in the presence of polyvinylalcohol stabilizer. This system is

important commercially and represents a good system for fundamental kinetics studies. The use of polyvinylalcohol (water-soluble) stabilizer results in chain transfer branching reactions which alters the mechanisms and kinetics of the reaction.

Particle nucleation undoubtably involves chain transfer branching and adsorption of the PVOH stabilizer. These phenomena are understood in a qualitative sense but a sound base has not been established for quantitative modeling. The present work includes significant modeling efforts as well as experimental work.

Future work, during the next year, will continue the above projects and increase efforts in other areas such as dispersion polymerization in non-aqueous media and the kinetics of branching and grafting reactions. The development of more fundamental understanding of these phenomena will help to enhance present polymerization processes and to develop new systems.

OMB Number 345-0058

NATIONAL SCIENCE FOUNDATION
1800 G STREET, NW
WASHINGTON, DC 20550

BULK RATE
POSTAGE & FEES PAID
National Science Foundation
Permit No. G-69

PI/PD Name and Address

Dr. Gary W. Poehlein
School of Chemical Engineering and
Office of Interdisciplinary Programs
Georgia Institute of Technology
Atlanta, GA 30332-0370

NATIONAL SCIENCE FOUNDATION
FINAL PROJECT REPORT

PART I - PROJECT IDENTIFICATION INFORMATION

1. Program Official/Org. Dr. Maria Burka

2. Program Name Chemical Reaction Processes Program

3. Award Dates (MM/YY) **From:** 12-4-87 **To:** 6-30-91

4. Institution and Address

GEORGIA TECH RESEARCH CORPORATION
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GA 30332-0420

5. Award Number CBT - 8717926

6. Project Title

Emulsion Polymerization Kinetics

This Packet Contains
NSF Form 98A
And 1 Return Envelope

Attachment 1

PART II

SUMMARY OF COMPLETED PROJECT / AWARD # CBT-8717926

P.I.: Gary Poehlein, Georgia Institute of Technology

Project Title: Emulsion Polymerization Kinetics

Emulsion polymerization is a major industrial process used for the production of synthetic rubbers, plastics and environmentally desirable water-based coatings and adhesives. The primary objective of this project was to develop a more complete understanding of the fundamental reaction mechanisms and kinetics of emulsion copolymerization when one monomer has significant water solubility. The research involved theoretical modeling of batch, semi-batch and continuous reactors. The utility of these models has been demonstrated with experimental studies involving five copolymer systems with styrene and comonomers of differing water solubilities such as methyl acrylate and acrylic acid.

The combination of mathematical modeling and carefully designed experiments has led to a better quantitative understanding of: (1) the distribution of various ingredients among the various phases and interfaces in the reaction system, (2) the transfer of active free radicals between the aqueous and organic phases, and (3) the rates of polymerization in the continuous and disperse phases. This increased knowledge base has placed in the hands of other researchers and industrial workers an enhanced ability to define future research and to develop commercial products and processes.

Attachment 2

PART III

TECHNICAL INFORMATION / AWARD # CBT-8717926

P.I.: Gary Poehlein, Georgia Institute of Technology

Project Title: Emulsion Polymerization Kinetics

The results of the research conducted under CBT-8717926 have been made available to the external community via a number of accepted mechanisms: (1) publications in the archival literature; (2) symposium presentations; (3) seminars; (4) professional consulting and, last but not least, (5) generation of educated professionals in an important field. Documentation of contributions in these area are provided in the remainder of this section.

(1) Publications during Grant Period:

1. "Particle Formation in Emulsion Polymerization: Transient Particle Concentration," with Z. Song, *J. Macromol. Sci.-Chem.*, A25(4), 403-443 (1988).

2. "Particle Formation in Emulsion Polymerization: Particle Number at Steady State," with Z. Song, *J. Macromol. Sci-Chem.*, A25(12), 1587-1632 (1988).

3. "Emulsion Copolymerization of Styrene-Methyl Acrylate and Styrene-Acrylonitrile in Continuous Stirred-Tank Reactors (I)," with Richard Mead, *I&EC Research*, 27(12), 2283-93 (1988).

4. "Emulsion Copolymerization of Styrene-Methyl Acrylate and Styrene-Acrylonitrile in Continuous Stirred-Tank Reactors (II), Aqueous-Phase Polymerization and Radical Capture," with Richard Mead, *I&EC Research*, 28(1), 51-57 (1988).

5. "Emulsion Polymers/Emulsion Polymerization," with F. J. Schork, *Polymer News*, 13, 231-40 (1988).

6. "Batch and Continuous Emulsion Copolymerization of Ethyl Acylate and Methacrylic Acid," with Glenn Shoaf, *Polym.-Plast. Technol. Eng.*, 28, No. 3, 289-327 (1989).

7. "Free Radical Transport from Latex Particles," with Richard Mead, *J. Appl. Polym. Sci.*, 38, 105-122 (1989).

8. "Particle Nucleation in Emulsifier-Free Aqueous-Phase Polymerization: Stage 1," with Z. Song, *J. Coll. Interface Sci.*, 128, No. 2, 486-500 (1989).

9. "Particle Formation in Emulsifier-Free Aqueous-Phase Polymerization of Styrene," with Z. Song, *J. Coll. Interface Sci.*, 128, No. 2, 501-510 (1989).

10. "Emulsion Copolymerization in Continuous Reactors," with D. M. Lange, G. Shoaf and R. N. Mead, Proceedings of International Conference, *Polymer Latex III*, London (June 1989).

11. "Kinetics of Emulsifier-Free Emulsion Polymerization of Styrene in the Presence of Chain Transfer Agents," with Z. Song, *Polym.-Plast. Technol. Eng.*, 29(4), 377-405 (1990).

12. "Polymerization in Non-Uniform Latex Particles II: Kinetics of Two-Phase Emulsion Polymerization," with C.-S. Chern, *J. Polym. Sci., Part A, Polym. Chem.*, 28, 3055-3071 (1990).

13. "Polymerization in Non-Uniform Latex Particles III: Kinetics of Grafting in Emulsion Polymerization," with C.-S. Chern, *J. Polym. Sci., Part A, Polym. Chem.*, 28, 3073-3099 (1990).

14. "Partition of Carboxylic Acids in an Emulsion Copolymerization System," with G. L. Shoaf, *I&EC Research* 29, 1701-1709 (1990).

15. "Kinetics of Crosslinking Vinyl Polymerization," with C.-S. Chern, *Polym.-Plast. Technol. Eng.*, 29(5&6), 575-589 (1990).

16. "Kinetics of Emulsifier-Free Emulsion Polymerization of Styrene," with Z. Song, *J. Polym. Sci., Part A, Polym. Chem.*, 28, 2359-2392 (1990).

17. "Kinetics of Emulsion Copolymerization with Acrylic Acids," with G. L. Shoaf, *J. Appl. Polym. Sci.*, 42:5, 1213-1238 (1991).

18. "Solution and Emulsion Polymerization with Partially Neutralized Methacrylic Acid," with G. L. Shoaf, *J. Appl. Polym. Sci.*, 42:5, 1239-1258 (1991).

19. "Kinetic Analysis of Seeded Emulsion Polymerization of Vinyl Acetate," with David M. Lange, Sadao Hayashi, Akihiko Komatsu and Toshihiro Hirai, *J. Polym. Sci., Part A, Polym. Chem.*, 29, 785-792 (1991).

(2) & (3) Seminars and Presentations (Selected List):

1. Lectures (2) on "Emulsion Polymerization Mechanisms and Kinetics" and "Reaction Engineering for Emulsion Polymerization" have been presented every year at short courses at Lehigh University and in Davos, Switzerland.

2. Seminars have been presented at universities and industrial laboratories including:

   - Dow Chemical Co.
   - EniChem Corp.
   - Rohm & Haas Co.
   - University of South Florida
   - Japanese Synthetic Rubber Co.
   - B.P. Research
   - University of Alabama
   - GenCorp

3. Papers have been presented by G. W. Poehlein and by graduate students at:

   - AIChE Meetings (G.W.P. and Z. Song)
   - NATO Advanced Study Institute (G. Shoaf)
   - U.K. Polymer Colloids Symposium (D. Lange)
   - ACS Meetings

(4) Consulting:

Consulting on emulsion polymerization has included Dow Chemical, Rohm & Haas, B.P., GenCorp and Flexible Products.

(5) Students:

Students listed below have received some support from Grant CBT-8716926:

(1) Richard Mead (PhD 1987) - Currently with American Cyanamid.

(2) Z. Song (PhD in 1989) - Currently with Guertin Bros. Coating and Sealant Ltd. (Canada).

(3) Glenn Shoaf (PhD 1989) - Currently with Tennessee Eastman Co.

(4) David Lange (PhD 1991) - Accepted position with Ameripol Synpol (Uniroyal-Goodrich)

(5) Xizhen Qian (Visiting Scholar) - Currently on Faculty of Tianjin Institute of Technology, PRC.

(6) - (12) Kevin Fontenot (PhD Cand.), Paul Thurner (PhD Cand.), Cheryl Matthews-Gilmore (PhD Cand.) Pei Yang (PhD Cand.), O. Badmus (PhD Cand.), Ganti Sriniwas (MS Cand.), and Chris Durden (UG) - Currently students at Georgia Tech.

FINAL TECHNICAL REPORT / AWARD CBT-8717926

P.I.: Gary W. Poehlein / Georgia Institute of Technology

Project Title: Emulsion Polymerization Kinetics

INTRODUCTION

The major goals of the Polymerization Engineering Research Program directed by Gary Poehlein are:

(1) Generation of human capital in the form of educated professionals.

(2) Expand the fundamental knowledge base in the general area of heterogeneous free-radical polymerization reactions.

(3) Achieve technology transfer of important research results to other organizations.

The remainder of this report includes a summary of progress achieved during the period of Grant CBT-8717926 in each of these "goal" areas.

STUDENTS

The students involved in polymerization research who have received financial support of some form from the subject grant are listed below along with degrees received and current status.

Students listed below have received some support from Grant CBT-8716926:

(1) Richard Mead (PhD 1987) - Currently with American Cyanamid.

(2) Z. Song (PhD in 1989) - Currently with Guertin Bros. Coating and Sealant Ltd. (Canada).

(3) Glenn Shoaf (PhD 1989) - Currently with Tennessee Eastman Co.

(4) David Lange (PhD 1991) - Accepted position with Ameripol Synpol (Uniroyal-Goodrich)

(5) Xizhen Qian (Visiting Scholar) - Currently on Faculty of Tianjin Institute of Technology, PRC.

(6) - (12) Kevin Fontenot (PhD Cand.), Paul Thurner (PhD Cand.), Cheryl Mathews-Gilmore (PhD Cand.) Pei Yang (PhD Cand.), O. Badmus (PhD Cand.), Ganti Sriniwas (MS Cand.), and Chris Durden (UG) - Currently students at Georgia Tech.

RESEARCH RESULTS

Brief descriptions of research results are provided in the remainder of this section.

1. Kinetics in Continuous Reactors:

The study of emulsion polymerization in continuous reactors has been an active interest of the Principal Investigator for a period of years. These studies have resulted in a better understanding of fundamental mechanisms and kinetics and have helped industrial scientists and engineers design more effective processes to produce commodity and innovative specialty latexes. Recent efforts have involved copolymerization with water-soluble monomers in a reactor system comprising a tubular prereactor followed by a series of two CSTRs. The focus of the work involves measurement of reaction rate, particle size distribution, composition of the copolymer formed in each reactor, and molecular weights. These measurements permit evaluation of kinetic parameters such as radical desorption coefficients and monomer cross-transfer reaction rate constants.

The reactor system is designed to permit variation of feed introduction location. Hence, portions of recipe components can be added downstream of the tubular prereactor to control copolymer composition, solids concentration, particle size distribution and particle morphology. Past copolymerization work involved styrene-methyl acrylate and styrene-acrylonitrile systems. Present research involves copolymerization with water-soluble monomers such as acrylic and methacrylic acid. The results of this research will permit a more rational design of commercial reactors and help to increase our understanding of the important relationships between reactor design and operation and product quality parameters.

Future work with continuous reactors will involve studies of grafting reaction kinetics, morphology of the latex particles and molecular microstructure from copolymerization reactions, the use of functional monomers that are water soluble, and dispersion copolymerization. A more detailed knowledge of these phenomena is important for the operation and modification of present processes and especially for the development of new products and processes.

2. Nonuniform Latex Particles:

Reaction kinetic theories for emulsion polymerization have almost all been based on the assumption that the various reagent species are uniformly distributed (except for stochastic variations) within the monomer-swollen polymer particles. Grancio and Williams (*J. Polym. Sci.:A-1, 8,* 2617 (1970)) suggested a nonuniform monomer distribution with a monomer-rich shell but their model has been challenged by other workers. In addition, the experimental results of Grancio and Williams can be explained without resorting to arguments based on a monomer-rich shell.

Our work has been concerned with the distribution of free radicals in latex particles. Most emulsion polymerization systems employ water-soluble initiator which generate oligomers in the aqueous phase. These oligomers have hydrophilic and often ionic end groups. When such free radicals penetrate the monomer-swollen latex particles, the end groups would have a very strong tendency to remain at or near the surface, at least during the short active life of the radical. The free radical end of the oligomer could move into the particle by diffusion or monomer propagation.

We have made calculations of free radical distributions in a lattice model of a latex particle. These calculations predict a significant nonuniformity in the radial distribution of free radicals. This phenomena is quite important because it can effect polymerization kinetics, grafting reactions and particle morphology.

We have used this concept of a nonuniform radical distribution to model grafting reactions. Initial results are very promising and this work will continue. Future efforts will also be aimed at studying the development of particle morphology. Being able to predict and control particle structure is a key factor in developing new and innovative latex products.

3. Particle Nucleation:

Particle concentration and size distribution are very important latex characteristics. They influence rheology and, in many cases, application performance. The ability to control particle number and size characteristics is, therefore, essential for the development and manufacture of most latex products. Work in the areas of nucleation theory and particle number control was the subject of Dr. Song's Ph.D. dissertation and is being considered in Ms. Gilmore's work on VAc polymerization in the presence of PVOH stabilizer.

Song's work included nucleation theory and experiments with and without added emulsifier. The results of his work have enhanced our knowledge of particle nucleation with conventional emulsion polymerization recipes and in emulsifier-free systems.

Future work will include studies of particle number control efforts for semi-batch systems. Cheryl Matthews-Gilmore (Ph.D. candidate) is involved with this project which includes collaboration with Air Products and Chemicals, Inc. Systems employing steric stabilizers are being studied. Grafting reactions with the stabilizer can contribute to particle formation in such systems.

4. Acid Monomers:

Functional monomers such as those with carboxyl groups are often used as minor ingredients in emulsion polymerization. Such monomers can help stabilize the particles and improve application performance. We have completed a process development research study with ethyl acrylate-methacrylic acid comonomers in which up to 78 mole % of the water-soluble monomer, MAA, was used. The fact that typical, nonviscous latexes with very little water-soluble polymer were formed was somewhat surprising.

The extension of this work to styrene recipes with smaller amounts of acid monomer was the subject of G. Shoaf's and D. Lange's Ph.D. dissertations. Their work has helped to show how reactions in the continuous phase can contribute to the overall process. Experimental work and reaction modeling considered the distribution of reagents in the various phases and the corresponding reactions. The relative rates of reaction of the different monomers was studied as was the influence of partial neutralization of the acid monomer. Future work on the nature of the copolymer molecules formed (i.e., blockiness) represents an important extension of Shoaf's and Lange's work. A greater understanding of what is happening in the continuous phase is needed.

TECHNOLOGY TRANSFER

Communication of the research results of others has involved the standard mechanisms of published papers, oral presentations, consulting and the employment of graduates by industries and universities. Documentation of these activities are included in the standard NSF Final Project Report -- Form 98A.

PART IV — FINAL PROJECT REPORT — SUMMARY DATA ON PROJECT PERSONNEL

(To be submitted to cognizant Program Officer upon completion of project)

The data requested below are important for the development of a statistical profile on the personnel supported by Federal grants. The information on this part is solicited in response to Public Law 99-383 and 42 USC 1885C. All information provided will be treated as confidential and will be safeguarded in accordance with the provisions of the Privacy Act of 1974. You should submit a single copy of this part with each final project report. However, submission of the requested information is not mandatory and is not a precondition of future award(s). Check the "Decline to Provide Information" box below if you do not wish to provide the information.

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

	Senior Staff		Post-Doctorals		Graduate Students		Under-Graduates		Other Participants[1]	
	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.
A. Total, U.S. Citizens	1				4	1	1			
B. Total, Permanent Residents										
U.S. Citizens or Permanent Residents[2]:										
American Indian or Alaskan Native										
Asian										
Black, Not of Hispanic Origin						1				
Hispanic										
Pacific Islander										
White, Not of Hispanic Origin	1				4		1			
C. Total, Other Non-U.S. Citizens										
Specify Country NIGERIA					1					
1. CHINA (P.R.)					1					1
2. INDIA					1					
3. NATIONALIST CHINA					1					
D. Total, All participants (A + B + C)	1				8	1	1			1
Disabled[3]										

☐ Decline to Provide Information: Check box if you do not wish to provide this information (you are still required to return this page along with Parts I-III).

[1]Category includes, for example, college and precollege teachers, conference and workshop participants.

[2]Use the category that best describes the ethnic/racial status for all U.S. Citizens and Non-citizens with Permanent Residency. *(If more than one category applies, use the one category that most closely reflects the person's recognition in the community.)*

[3]A person having a physical or mental impairment that substantially limits one or more major life activities; who has a record of such impairment; or who is regarded as having such impairment. *(Disabled individuals also should be counted under the appropriate ethnic/racial group unless they are classified as "Other Non-U.S. Citizens.")*

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

ASIAN: A person having origins in any of the original peoples of East Asia, Southeast Asia and the Indian subcontinent. This area includes, for example, China, India, Indonesia, Japan, Korea and Vietnam.

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.

PACIFIC ISLANDER: A person having origins in any of the original peoples of Hawaii; the U.S. Pacific Territories of Guam, American Samoa, or the Northern Marianas; the U.S. Trust Territory of Palau; the islands of Micronesia or Melanesia; or the Philippines.

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.