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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.