GEORGIA INSTITUTE OF TECHNOLOGY — OFFICE OF CONTRACT ADMINISTRATION

# PROJECT ADMINISTRATION DATA SHEET

[X] ORIGINAL [ ] REVISION NO. ____

Project No. E-19-653 (R-6088-0A0) GTRC/~~EES~~ DATE 2 /12 /86

Project Director: G. Poehlein School/~~Dept~~ ChE

Sponsor: American Chemical Society (Petroleum Research Fund)

1155 Sixteenth Street Washington, D.C. 20036

Type Agreement: Grant # PRF 17638-AC 7

Award Period: From 1/1/86 To 8/31/88 (Performance) 8/31/88 (Reports)

| Sponsor Amount: | This Change | Total to Date |
|---|---|---|
| Estimated: | $ | $ |
| Funded: | $ 34,750 | $ 34,750 |

Cost Sharing Amount: $ 22,000 Cost Sharing No: None Assigned *

Title: Kinetic Model for Non-Uniform Emulsion Polymer Particles

**ADMINISTRATIVE DATA** OCA Contact Ralph Grede X 4820

1) Sponsor Technical Contact:

Mr. Joseph E. Rogers, Jr.
Program Administrator
American Chemical Society
1155 Sixteenth Street, N.W.
Washington, D.C. 20036

2) Sponsor Admin/Contractual Matters:

Mr. Joseph E. Rogers, Jr.
Program Administrator
American Chemical Society
1155 Sixteenth Street, N.W.
Washington, D.C. 20036

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

(or) Company/Industrial Proprietary: ____

**RESTRICTIONS**

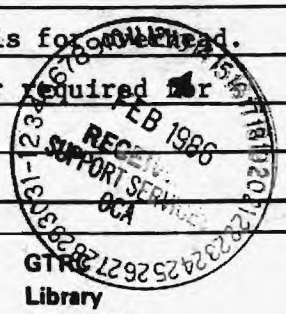
See Attached N/A Supplemental Information Sheet for Additional Requirements.

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 Sponsor - However no equipment is proposed.

**COMMENTS:**

* Institute is cost sharing that portion of project budget which is for overhead. Grants and Contracts Accounting has indicated there is no number required for overhead cost sharing.




SPONSOR'S I. D. NO. ____

**COPIES TO:**

Project Director
Research Administrative Network
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Research Communications (2)
GTRC
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Other A.Jones; LEGAL

FORM OCA 65:285

12 / 88

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Date 12/21/88

Project No. E-19-653 Center No. R6088-0A0

Project Director G.W. Poehlein School/Lab ChE

Sponsor American Chemical Society (Petroleum Research Fund)

Contract/Grant No. PRF 17638-AC7 GTRC XX GIT ____

Prime Contract No. N/A

Title Kinetic Model for Non-Uniform Emulsion Polymer Particles

Effective Completion Date 8/31/88 (Performance) 8/31/88 (Reports)

Closeout Actions Required:

____ None
_X_ Final Invoice or Copy of Last Invoice
_X_ Final Report of Inventions and/or Subcontracts - Patent Questionnaire sent to PI.
____ Government Property Inventory & Related Certificate
____ Classified Material Certificate
____ Release and Assignment
____ Other

Includes Subproject No(s).

Subproject Under Main Project No.

Continues Project No. Continued by Project No.

Distribution:

_X_ Project Director
_X_ Administrative Network
_X_ Accounting
_X_ Procurement/GTRI Supply Services
_X_ Research Property Management
___ Research Security Services

_X_ Reports Coordinator (OCA)
_X_ GTRC
_X_ Project File
_X_ Contract Support Division (OCA)
___ Other

E-19-653

GEORGIA TECH 1885-1985

DESIGNING TOMORROW TODAY

**Georgia Institute of Technology**
School of Chemical Engineering
Atlanta, Georgia 30332-0100
(404) 894-2867

October 17, 1986

Mr. Joseph E. Rogers, Jr.
Program Administrator/PRF
American CHemical Society
1155 Sixteenth Street, NW
Washington, DC 20036

Dear Mr. Rogers:

I have enclosed a progress report covering research related to Grant # PRF 17638-AC 7. Support for the Petroleum Research Fund is sincerely appreciated and we look forward to continuation of our efforts during the second year of the grant.

Please let me know if you would like any additional information on this work.

Best regards,

Gary W. Poehlein
Director, School of
Chemical Engineering

Enclosure

cc: OCA

PROGRESS REPORT

PETROLEUM RESEARCH FUND GRANT 17638-AC-7

PERIOD COVERED: Jan 1986- November 1986

TITLE: Kinetic Model for Non-Uniform Emulsion Polymer Particles

PROJECT DIRECTOR: Gary W. Poehlein

RESEARCH STUDENTS: C.-S. Chern (PhD Candidate/ChE)
Z. Song (PhD Candidate /ChE)
Richard Mead (PhD Candidate/ChE)
Glenn Shoaf (MS Candidate/ChE)

(Part of the funding for the graduate students was provided by three industrial organizations and a grant from NSF.)

SUMMARY:

Kinetic theories for emulsion polymerization reactions have all been based on the assumption that most reagents, including the active free radicals, have been uniformly distributed (in a stocastic sense) in the monomer-swollen polymer particles. Water-soluble initiators are almost always used in emulsion polymerization systems. The hydrophilic end groups associated with such initiators are almost certain to remain on the surface of the polymer particles during the life of the attached free radical.

We have used Monte Carlo techniques to follow free radicals as they penetrate polymer particles via the propagation reaction. Such calculations clearly demonstrate (1) that free radicals are not uniformly distributed in latex particles during emulsion polymerization. Non-uniform distribution of free radicals, as proposed in the new model, can be significant in a number of emulsion polymerization problems such as:

Development of polymer particle morphology.

Grafting reactions.

Transport of free radicals out of particles following transfer reactions.

Polymerization rate.

The results of preliminary Monte Carlo calculations (1) have been applied to theoretical problems of "radical desorption" (2,3) and to the problem of calculating grafting efficiencies in two-phase particles (4).

Our kinetic modeling has involved the study of concepts which are important in other polymerization systems. Expansion of the work into these areas has resulted in papers related to the curing of epoxy resins (5) and the kinetics of vinyl acetate emulsion polymerization (6).

Copies of all six (6) papers are attached as a part of this 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.

Georgia Tech

E-17-653

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

September 8, 1987

The Petroleum Research Fund
American Chemical Society
1155 Sixteenth Street, NW
Washington, DC 20036

REFERENCE: PRF Grant No. 17638-AC7

Gentlemen:

I have enclosed the following components of the annual report on my PRF grant.

1. Research Progress Report
2. Bibliographic Citations (4)
3. Personnel Statement

The financial statement will be mailed shortly.

Sincerely,

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

cc: OCA

THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 17638-AC7

Page 1 of 2 pages.

PREPARED BY

Gary W. Poehlein

Date September 8, 1987

Please refer to instructions.

Fill in information requested above for each page.

The report heading, narrative, and all drawings must be prepared within the box.

Please submit one sharp, clear "original" and a copy (Xerox, carbon, etc.) for each page.

PRF 8/78 - 1

17638-7 Kinetic Model for Non-Uniform Emulsion Polymer Particles

Gary Poehlein, Georgia Institute of Technology

Kinetic theories for emulsion polymerization reactions have all been based on the assumption that most reagents, including the active free radicals, have been uniformly distributed (in a stochastic sense) in the monomer-swollen polymer particles. Water-soluble initiators are almost always used in emulsion polymerization systems. The hydrophilic end groups associated with such initiators are almost certain to remain on the surface of the polymer particles during the life of the attached free radical.

We have used Monte Carlo techniques to follow free radicals as they penetrate polymer particles via the propagation reaction. Such calculations clearly demonstrate that free radicals are not uniformly distributed in latex particles during emulsion polymerization (1). Non-uniform distribution of free radicals, as proposed in the new model, can be significant in a number of emulsion polymerization problems such as:

Development of polymer particle morphology.
Grafting reactions.
Transport of free radicals out of particles following ransfer reactions.
Polymerization rate.

The results of preliminary Monto Carlo calculations (1) have been applied to theoretical problems of "radical desorption" (2) and to the problem of calculating grafting efficiencies in two-phase particles (3).

Our kinetic modeling has involved the study of concepts which are important in other polymerization systems. Expansion of the work into these areas has resulted

THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

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in papers related to the curing of epoxy resins (5).

(1) Chern, C.-S., Poehlein, G. W., J. Polym. Sci., Part A, (1987) 25 617.

(2) Poehlein, G. W., Lee, H.-C., Chern, C.-S., Polymer Reaction Engineering, Huthig & Wepf Pub. (1986) 59.

(3) Chern, C.-S., "Polymerization in Non-Uniform Latex Particles," PhD Dissertation, School of Chemical Engineering Georgia Inst. of Tech. (6/87).

(4) Chern, C.-S., Poehlein, G. W., J. Appl. Polym. Sci., (1987) 33, 2117.

(5) Chern, C.-S., Poehlein, G. W., Polym. Engr. & Sci., (1987) 27:11, 788.

BIBLIOGRAPHIC INFORMATION PRF# 17638-AC7

**Please refer to instructions. Fill in information requested on each card. Type (double space) complete reference for one article in space below.**

PRINCIPAL INVESTIGATOR(S) Gary W. Poehlein

Chern, C.-S., POEHLEIN, G. W.

"Polymerization in Non-Uniform Latex Particles: Distribution of Free Radicals," J. Polym. Sci., Part A. (1987) 25, 617.

PRF 6/76 - 6

BIBLIOGRAPHIC INFORMATION PRF# 17638-AC 7

**Please refer to instructions. Fill in information requested on each card. Type (double space) complete reference for one article in space below.**

PRINCIPAL INVESTIGATOR(S) Gary W. Poehlein

POEHLEIN, G. W., Lee, H. C., Chern, C.-S.,
"Free Radical Transport and Reactions in Emulsion Polymerization,"
Polymer Reaction Engineering, Reichert & Geiseler (Eds.)
Hutlhig & Wepf Pub. (1986) 59.

PRF 6/76 - 6

BIBLIOGRAPHIC INFORMATION

PRF# 17638-AC7

**Please refer to instructions. Fill in information requested on each card. Type (double space) complete reference for one article in space below.**

**PRINCIPAL INVESTIGATOR(S)** Gary W. Poehlein

Chern, C.-S., POEHLEIN, G. W.
"Reaction Kinetics of Vinyl Acetate Emulsion Polymerization,"
J. Appl. Polym. Sci. (1987) 33, 217.



BIBLIOGRAPHIC INFORMATION

PRF# 17638-AC7

**Please refer to instructions. Fill in information requested on each card. Type (double space) complete reference for one article in space below.**

**PRINCIPAL INVESTIGATOR(S)** Gary W. Poehlein

Chern, C.-S., POEHLEIN, G. W.

"A Kinetic Model for Curing Reactions of Epoxides with Amines,"
Polymer Engineering and Science, June 1987, 27, 788.

# PERSONNEL STATEMENT

PRF# 17638-AC7 REPORTING PERIOD Sept. 1, 1986 TO August 31, 1987

GRANTEE INSTITUTION Georgia Institute of Technology DEPARTMENT Chemical Engineering

PRINCIPAL INVESTIGATOR(S) Gary W. Poehlein

GRANT PROJECT TITLE Kinetic Model for Non-Uniform Emulsion Polymer Particles

**List undergraduate, graduate, and postdoctoral co-workers receiving stipends under the above named grant:**

| NAME | TITLE OR ACADEMIC APPOINTMENT | PREVIOUS EDUCATION & DEGREES* | COUNTRY OF PERMANENT RESIDENCE | PERIOD OF SUPPORT (MONTHS) | PERCENT OF SUPPORT FROM PRF ** | DEGREES RECEIVED (IF ANY) DURING REPORTING PERIOD |
|---|---|---|---|---|---|---|
| Christopher Smith | Student Assistant | | USA | Summer 87 | 100% | |
| Zhigiang Song | GRA | BS & MS from | China | 12 mos | 40% | |
| | | Zhetiang University | | | | |
| | | China | | | | |

**List other co-workers on grant project not directly supported with ACS - PRF funds:**

| NAME | SOURCE OF SUPPORT | DATES ASSOCIATED WITH GRANT PROJECT |
|---|---|---|
| C.-S. Chern | Georgia Tech and NSF | 9/1/86 - 6/15/87 |
| Richard Mead | Georgia Tech & S. C. Johnson Co. | 9/1/86 - 8/31/87 |
| | | |
| | | |

* For graduate students, indicate the College or University attended prior to graduate work. For postdoctoral fellows, give the name of the Ph. D. granting institution.

** (during the period stated in preceding column)

Revised 6/82

Georgia Tech

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

September 13, 1988

The Petroleum Research Fund
American Chemical Society
1155 Sixteenth Street, NW
Washington, DC 20036

REFERENCE: PRF GRANT #17638-AC7

Gentlemen:

I have enclosed the following components of the final report on my PRF grants.

1. Research Progress Report
2. Bibliographic Citations (1) with reprint
3. Personnel Statement

The financial statement will be mailed shortly. Copies of publications currently in press will be sent after publication.

Sincerely,

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

cc: Steve Watt (OCA)

PERSONNEL STATEMENT

PRF# 17638-AC7 REPORTING PERIOD Sept. 1, 1986 TO Aug. 31, 1988

GRANTEE INSTITUTION Georgia Institute of Technology DEPARTMENT Chemical Engineering

PRINCIPAL INVESTIGATOR(S) G. W. Poehlein

GRANT PROJECT TITLE Kinetic Model for Non-Uniform Emulsion Polymer Particles

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| NAME | TITLE OR ACADEMIC APPOINTMENT | PREVIOUS EDUCATION & DEGREES* | COUNTRY OF PERMANENT RESIDENCE | PERIOD OF SUPPORT (MONTHS) | PERCENT OF SUPPORT FROM PRF ** | DEGREES RECEIVED (IF ANY) DURING REPORTING PERIOD |
|---|---|---|---|---|---|---|
| Zhi-Qiang Song | GRA | BS & MS from Zhetiang Univ in China | China | 22 mos. | 40% | PhD June 1988 |
| | | | | | | |
| Christopher Smith | Undergrad Student Assist. | | USA | Summer 88 | 100% | |
| | | | | | | |

List other co-workers on grant project not directly supported with ACS - PRF funds:

| NAME | SOURCE OF SUPPORT | DATES ASSOCIATED WITH GRANT PROJECT |
|---|---|---|
| C.-S. Chern | Georgia Tech and NSF | 9/1/86-6/15/87 |
| Richard Mead | Georgia Tech & S. C. Johnson Co. | 9/1/86-12/30/87 |
| | | |
| | | |

* For graduate students, indicate the College or University attended prior to graduate work. For postdoctoral fellows, give the name of the Ph. D. granting institution.

** (during the period stated in preceding column)

Revised 6/82

THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 17638-AC7



PREPARED BY

Gary W. Poehlein

Date September 13, 1988

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Fill in information requested above for each page.

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# 17638-7 Kinetic Model for Non-Uniform Emulsion Polymer Particles

Gary W. Poehlein, Georgia Institute of Technology

Research on the mechanisms and kinetics of emulsion polymerization has included two areas: (i) grafting reactions and (ii) particle nucleation. The grafting studies have been based, in part, on earlier work (1) on the non-uniform distribution of free radicals in the monomer-swollen latex particles. The first extension of this work was development of a kinetic model for latex particles with two phases (2). This model was then used to calculate grafting efficiencies in emulsion polymerization (3). Good agreement was obtained with previously published and new experimental data.

Grafting in emulsion polymerization can only involve oligomeric radicals or radicals generated by chain transfer reactions (e.g., monomer or solvent) when water-soluble initiators are used. Such is not the case in solution, bulk or suspension polymerization because the initiator free radicals can contact the polymer. Studies of solution polymerization of styrene in the presence of polybutadiene indicate that the initiator radical can be the most important grafting species (4).

Particle nucleation is an important mechanism in emulsion polymerization. Song (5) has studied this complex phenomena in both the presence and absence of emulsifiers and chain transfer agents. New theories which consider two separate stages of the nucleation period have been developed for transient particle concentration (6) and the final steady-state number (7). Additional work has been completed on nucleation in emusifier-free systems, with and without chain transfer agents (5,8,9).

THE PETROLEUM RESEARCH FUND

REPORT ON ACTIVITY ASSISTED BY

GRANT, PRF # 17638-AC7



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(1) Chern, C. S., Poehlein, G. W. J. Polym. Sci., Part A (1987) 25, 617.

(2) Chern, C. S., Poehlein, G. W. J. Polym. Sci., Part A, (1988) in press.

(3) Chern, C. S., Poehlein, G. W. J. Polym. Sci., Part A (1988) in press.

(4) Chern, C. S., Poehlein, G. W., Chem. Engr. Comm. (1988) in press.

(5) Song, Z., "Emulsion Polymerization Kinetics," Ph.D. Dissertation, School of Chemical Engineering, Georgia Institute of Technology (6/1988)

(6) Song, Z., Poehlein G. W., J. Macromol. Sci.-Chem. (1988) A25(4), 403.

(7) Song, Z., Poehlein, G. W., J. Macromol. Sci.-Chem. (1988) accepted.

(8) Song, Z., Poehlein G. W. J. Coll. Interface Sci. (1988) accepted.

(9) Song, Z., Poehlein, G. W. J. Coll. Interface Sci. (1988) accepted.

**BIBLIOGRAPHIC INFORMATION** PRF# 17638-AC7

**Please refer to instructions. Fill in information requested on each card. Type (double space) complete reference for one article in space below.**

**PRINCIPAL INVESTIGATOR(S)** Gary W. Poehlein

SONG, Z., POEHLEIN, G. W.

"Particle Formation in Emulsion Polymerization: Transient Particle Concentration," J. Macromol.Sci.-Chem. (1988) A25(4) 403.