

PROJECT ADMINISTRATION DATA SHEET☒ XX

ORIGINAL

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REVISION NO. _____

Project No. E-19-681 (R6175-OA0)GTRC/~~EXX~~DATE 7 /31 /86Project Director: G.W. Poehlein and F.J. SchorkSchool/~~Lab~~ ChESponsor: National Science FoundationType Agreement: Grant No. CBT-8604407Award Period: From 8/1/86 To 10/31/87 (Performance) 10/31/87 (Reports)

Sponsor Amount:

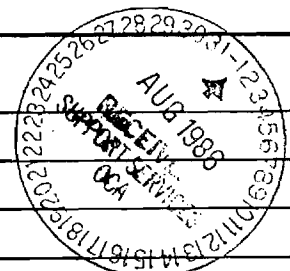
This ChangeTotal to DateEstimated: \$ _____ \$ 32,600Funded: \$ _____ \$ 32,600Cost Sharing Amount: \$ 16,400 Cost Sharing No: E-19-341Title: Engineering Research Equipment Grant: Equipment in Support of Polymer Research
Engineering.ADMINISTRATIVE DATAOCA Contact John B. Schonk ext. 4820

1) Sponsor Technical Contact:

2) Sponsor Admin/Contractual Matters:

Maria BurkaC.T. HenneyNational Science FoundationNational Science FoundationEng/CBTDGC/EngWashington, DC 20550Washington, DC 20550202/357-9606202/357-9626Defense Priority Rating: N/AMilitary Security Classification: N/A(or) Company/Industrial Proprietary: N/ARESTRICTIONSSee 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 GITCOMMENTS:No funds may be expended after 7/31/87.COPIES TO:

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SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 7/26/88

Project No. E-19-681 (R6175-OA0) School ChE

Includes Subproject No.(s) N/A

Project Director(s) G. W. Poehlein & F. J. [unclear] GTRC/GMX

Sponsor National Science Foundation Grant # CBT-8604407

Title Engineering Research Equipment Grant: Equipment in Support of Polymer Research Engineering

Effective Completion Date: 10/31/87 (Performance) 1/31/88 (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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sent to Project Director ☒
- ☒ Govt. Property Inventory & Related Certificate
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PART I-PROJECT IDENTIFICATION INFORMATION

1. Institution and Address Georgia Tech Research Corp. Georgia Institute of Technology Atlanta, Georgia 30332-0420	2. NSF Program Eng. Research Equip. Grant	3. NSF Award Number CBT-86 04407
	4. Award Period From 8/1/86 To 10/31/87	5. Cumulative Award Amount \$32,600

6. Project Title


"Equipment in Support of Polymer Reaction Engineering"

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

Funds allocated under this grant were combined with substantial Institute cost sharing funds to purchase equipment in support of the research efforts of the Polymerization Reaction Engineering Group at the Georgia Institute of Technology. Specific major expenditures include:

- * Malvern Autosizer II dynamic light scattering instrument for latex particle size analysis (\$24,700)
- * Gas chromatograph for residual monomer determination during copolymerization. (\$3,000)
- * Parts for construction of a hydrodynamic chromatograph for latex particle size analysis. (\$10,300)
- * Paar digital densitometer for on-line determination of monomer conversion. (\$4,000)
- * UV/Visible spectrophotometer for latex particle number analysis and general use. (\$2,700)
- * Miscellaneous equipment in support of polymerization reaction engineering research. (\$6,800)

PART III-TECHNICAL INFORMATION (FOR PROGRAM MANAGEMENT USES)

1. ITEM (Check appropriate blocks)	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses	X				
b. Publication Citations	X				
c. Data on Scientific Collaborators	X				
d. Information on Inventions	X				
e. Technical Description of Project and Results					
f. Other (specify)					
2. Principal Investigator/Project Director Name (Typed) Gary W. Poehlein F. Joseph Schork	3. Principal Investigator/Project Director Signature 			4. Date 10/10/87 10/14/87	

PART IV - SUMMARY DATA ON PROJECT PERSONNEL

NSF Division Chem., Biochem., & Thermal Eng.

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

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

*U.S. Citizens/ Permanent Visa	PI's/PD's		Post- doctorals		Graduate Students		Under- graduates		Precollege Teachers		Others	
	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.	Male	Fem.
American Indian or Alaskan Native												
Asian or Pacific Islander												
Black, Not of Hispanic Origin												
Hispanic												
White, Not of Hispanic Origin	2											
Total U.S. Citizens	2											
Non U.S. Citizens	0											
Total U.S. & Non- U.S. . .	2											
Number of individuals who have a handicap that limits a major life activity.	0											

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

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

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

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

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

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

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

**National Science Foundation
Engineering Research Equipment Grant
Number CBT-8604407**

Equipment in Support of Polymer Reaction Engineering

Principal Investigators

**Gary W. Poehlein
F. Joseph Schork
School of Chemical Engineering
Georgia Institute of Technology**

INTRODUCTION

Grant Number CBT-8604407 was awarded to allow the purchase of a Micromeritics Flowsizer hydrodynamic chromatograph (HDC) and a high-resolution gas chromatograph. Both pieces of equipment were meant to support the research efforts of the Principal Investigators in the field of polymerization reaction analysis, while the gas chromatograph was to be employed in determining residual monomer concentrations during copolymerization. Two factors have allowed us to greatly expand the scope of the purchases possible under this grant. The first was the availability of additional cost-sharing funds from the Georgia Tech Research Corporation. The second was a decision on the part of the Principal Investigators not to purchase the Micromeritics Flowsizer. After extensive discussions with person knowledgeable in the field of HDC, it was decided that a hydrodynamic chromatograph could be custom built in our laboratory for a fraction of the cost of the Flowsizer. In addition, building our own unit allowed us to incorporate the best features of previous designs, including the Flowsizer.

FUNDS AVAILABLE

The following funds were available for purchase of equipment under this grant:

NSF Grant Number CBT-860447	\$32,600
Georgia Tech Research Corporation Cost Sharing	16,400
Georgia Tech Research Corporation Supplemental Grant	8,000
TOTAL AVAILABLE FUNDS	\$57,000

EQUIPMENT PURCHASED

Items of equipment purchased under this grant are listed below with the approximate purchase price:

Malvern Autosizer II	\$24,700
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Parts for construction of a custom-built hydrodynamic chromatograph:

LDC UV/Visible Detector	4,500
IBM PC/XT for data acquisition	2,500
Milton Roy Minipump	1,200
Miscellaneous parts and fittings	2,600
Total	10,800
High-Resolution Gas Chromatograph	8,000
Metering Pumps (4) for general use	4,300
Paar Digital Densitometer	4,000
UV/Visible Spectrophotometer for general use	2,700
pH Meter for general use	800
Amicon Latex Concentrator	800
Miscellaneous Equipment	900
TOTAL EXPENDITURES	\$57,000

A brief explanation of the justification of the purchase of the above items follows.

Upon the recommendation of other scientists in the field of emulsion polymerization, we decided to purchase the Malvern Autosizer II dynamic light scattering instrument. The instrument is capable of determining the particle size distribution of materials in the latex range. The entire analysis can be completed in under two minutes, and requires only appropriate dilution of the sample. This instrument will be used for routine

characterization of latex products prepared in our laboratory. It is not meant to be a replacement for the HDC, since light scattering results are of questionable validity for bimodal particle size distributions. Rather, dynamic light scattering will be used as a supplement to particle size analysis via HDC.

Justification for the purchase of a hydrodynamic chromatograph remains as in the original proposal. Construction of a custom unit has resulted in significant cost savings, and the incorporation of improved techniques of data handling. The HDC has been constructed and we will soon begin evaluation of its capabilities.

The justification for the high-resolution gas chromatograph remains as in the original proposal. The unit is in routine use in conjunction with emulsion copolymerization research currently under way.

Four metering pumps have been purchased to upgrade our two continuous polymerization units and to add a third. A digital densitometer has to be purchased to allow on-line monitoring of monomer conversion on the planned third unit. This capability is available and in routine use on the two existing units. Miscellaneous additional equipment has been purchased in support of the construction of the third unit.

A UV/Visible spectrophotometer has been purchased for general use, but also for determination of latex particle number via turbidity measurements. Particle number, when combined with particle size distribution data from dynamic light scattering or HDC, provides a complete characterization of the particle

distribution in an emulsion-polymerized product.

A pH meter and Amicon Latex Concentrator have been purchased for general use in emulsion polymerization research.

UTILIZATION

Equipment purchased under this grant have been used in conjunction with research supported under the following grants, as well as in research supported by industrial grants and funds provided by the Georgia Tech Research Corporation.

"Emulsion Kinetics and Continuous Reactor Processes,"
G. W. Poehlein, NSF Grant No. CBT-8413987

"Continuous Miniemulsion Polymerization," F. J. Schork, NSF
Grant No. CBT-8419914

"Kinetic Model for Non-Uniform Emulsion Polymer Particles,"
G. W. Poehlein, Petroleum Research Fund/American Chemical
Society

An overview of recent and current research in polymerization reaction engineering at Georgia Tech is provided in the attached supplement, "Research in Polymerization Reaction Engineering."

RESEARCH
in
POLYMERIZATION REACTION ENGINEERING

Program Directed by

Dr. Gary W. Poehlein

Dr. F. Joseph Schork

School of Chemical Engineering

Georgia Institute of Technology

Atlanta, Georgia 30332

U.S.A.

INTRODUCTION

Currently, approximately 200 billion pounds of synthetic polymeric materials are produced per year throughout the world. These materials are made through numerous chemical mechanisms in a wide variety of reactor configurations. The benefits of improved operation in such a large market are obvious. In addition, the current trend toward specialty chemicals is impacting the polymer field as manufacturers move toward high value-added specialty polymers with unique properties aimed at very specific markets. This sort of business, while profitable, requires tight control of polymer properties to meet highly specific end-use applications. Such tight control may be obtained through a combination of understanding of the chemistry and physics of the polymerization process; optimization of the polymerization reactor configuration and operation; and monitoring and digital control of the polymerization. Polymerization reactions are especially benefited by optimization and control since polymers are in general "products by process." That is to say that the history of the polymerization is written in the molecular weight distribution, the degree of branching, and the copolymer composition distribution. The end-use properties, in turn, are determined by the molecular structure of the polymer. The manipulation of the molecular structure of the polymer during polymerization can be described as polymerization reaction engineering, and involves kinetics, mathematical modeling, reactor design, optimization measurement, and control.

The Polymerization Reaction Engineering Research Program at Georgia Tech is focused on improvements in understanding and operation of solution, suspension and emulsion polymerization systems. The major emphasis is on emulsion polymerization, one of the most important and widely used commercial methods for converting unsaturated monomers into polymeric materials. A wide variety of commodity and specialty products are produced by emulsion polymerization. Product properties and application performance are subject to control via an extremely broad range of formula

variations and reaction engineering alternatives. Development of a fundamental understanding of the physical and chemical mechanisms of emulsion polymerization is important for product and process innovations; for the more complex speciality latexes.

RESEARCH PROGRAMS

Areas of recent and current research include the following:

Solution Polymerization

1. Direct Control of Molecular Weight Distribution during Polymerization.
2. Adaptive Control of a Continuous Polymerization Reactor.
3. Adaptive Optimizing Control of a Semibatch Polymerization Reactor.
4. Closed-Loop Dynamics of Continuous Polymerization Reactors.

Emulsion Polymerization

5. Polymerization Kinetics in Continuous Reactors.
6. Polymerization in Nonuniform Latex Particles.
7. Particle Nucleation Phenomena.
8. Emulsion Polymerization with Acid Monomers.
9. Semibatch Emulsion Polymerization with Nonionic Surfactants.
10. Continuous Miniemulsion Polymerization.
11. Dynamic Optimization of the Semibatch Emulsion Polymerization Process.
12. Control of a Continuous Emulsion Polymerization Reactor.

Details on each of these areas is provided below:

1. Direct Control of Molecular Weight Distribution During Polymerization

This study focuses on the control of the molecular weight distribution during

solution polymerization of methyl methacrylate in a continuous stirred tank reactor. The simulated model includes the leading moments of the chain length distribution, and direct control of the molecular weight distribution assuming complete state feedback is evaluated. In spite of the non-linearities in the model, a linear quadratic optimal controller with integral state feedback is successfully designed for the system.

2. Adaptive Control of a Continuous Polymerization Reactor:

In this study, a multivariable adaptive control strategy is applied to a digital simulation describing the continuous solution polymerization of methyl methacrylate. The reactor model illustrates unusual process dynamics such as multiple steady states, limit cycles, and steady state instabilities. This dissipative behavior results from the autocatalytic nature of polymerization reactions owing primarily to the "gel effect."

The self-tuning regulator of Vogel and Edgar is applied to this model. The controller is based upon pole-zero placement and includes compensation for variable and multiple delays. Parameter estimation for the controller is performed by recursive least squares. Initiator concentration in the feed and the reactor jacket temperature are used to effectively control the monomer concentration and the temperature in the reactor.

3. Adaptive Optimizing Control of a Semibatch Polymerization Reactor:

Control of a semibatch reactor involves driving the reaction from an initial state to a specified final state in some manner which is judged to be the "best" in terms of productivity or product quality. In most cases, this "best" trajectory is approximated empirically through the wisdom of experience. A logical improvement on this strategy is to employ optimal control to drive the reaction along a trajectory which maximizes some predetermined objective functional. Such a procedure requires an accurate model of the process which is often not available.

To deal with this lack of knowledge about the process, an on-line, linear,

time-series model was utilized which relates the current states to the previous states and controls. A discrete optimizing control algorithm is applied, based on the current time series model of the reaction system, to calculate the optimal controls to be applied to the polymerizer. These controls are optimal for the current interval only, subject to the constraints of the process model and objective function; no attempt is made to optimize the entire trajectory. It has been found that this process of adaptive modelling and optimizing control yields a suboptimal trajectory which results in marked improvement over current polymerization practice. The flexibility of the algorithm allows for simultaneous regulation and batch time minimization in a multivariable framework.

This algorithm has been applied, in simulation, to the free radical solution polymerization of methylmethacrylate in a semibatch configuration. Control variables used are the reactor jacket coolant temperature and initiator feed rate to the reactor.

Simulation results indicate the flexibility and effectiveness of the adaptive optimizing algorithm. Adaptive optimizing control of temperature is as effective as simple proportional temperature control, while optimizing control of conversion and temperature results in good temperature control and reduced batch time.

The case of most significant practical importance is that of control of monomer conversion and average molecular weight, since reduction of batch time without control of molecular weight may result in unacceptable polymer quality. Results indicate the following improvements over conventional operating practices: reduced initiator consumption, reduced batch time, good control of average molecular weight, and reduced product polydispersity. The noted improvements are even more significant when batch-to-batch variations in monomer reactivity are considered.

4. Closed-Loop Dynamics of Continuous Polymerization Reactors

Recent studies describing the bifurcation characteristics of open-loop chemical systems, namely the exothermic CSTR, verify the existence of multiple steady states and

reveal other structures such as limit cycles and isola. This analysis enhances the understanding of the behavior of complex nonlinear systems. Likewise, from the viewpoint of process control, a similar analysis would be beneficial in characterizing the dynamic structures in closed-loop systems. It is known that conventional feedback control, specifically the integral mode, can induce dissipative structures such as unstable states and limit cycles not observed in the open-loop process. In this study, the bifurcation characteristics of an isothermal polymerization of methylmethacrylate in a CSTR will be determined for both the open and closed loop configurations. A comparison will be made between the open-loop dynamic behavior and the system under conventional, and adaptive feedback control. Utilizing the information obtained from the bifurcation analysis, qualitative and quantitative judgments may be made regarding the operating range and reliability of feedback control.

5. Polymerization Kinetics in Continuous Reactors

The study of emulsion polymerization in continuous reactors has been an active interest 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 speciality latexes. Present efforts involve copolymerization studies in a reactor system comprising a tubular prereactor followed by a series of two CSTRs. The focus of present and future work will involve measurement of reaction rate, particle size distribution, composition of the copolymer formed in each reactor, and molecular weights. These measurements will 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

partocile morphology. Present work involves copolymerization studies with styrene-methyl acrylate and styrene-acrylonitrile systems. 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 from copolymerization reactions and the use of functional monomers that are water soluble. 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.

6. Polymerization in 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 effectively 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 recent 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, which are described in Paper 12 Appendix II, 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.

Our present research efforts have been focused on utilizing the 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.

7. Particle Nucleation Phenomena

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 is just beginning.

A number of nucleation theories have been published and our first efforts have involved an attempt to unify various concepts into rather general models. Conventional and emulsifier-free systems have been considered in the preliminary modeling work. Early results have produced some simplified models that seem to be able to simulate literature data. Future efforts will include model refinement and experimental work.

8. 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 some preliminary process development research with ethyl acrylate-methacrylic acid comonomers in which up to

78 mole % of the water-soluble monomer, MAA, was used. The fact that typical, non-viscous latexes with very little water-soluble polymer were formed was somewhat surprising.

The EA-MAA latexes could be produced in batch and continuous reactor systems. We have not, however, had time to pursue a number of important questions resulting from the preliminary work. The questions are related to

- * Water-phase reactions: What is happening in the continuous phase and how can these components of the reaction be modeled?
- * Polymer product: What are the compositional parameters of polymer molecules that may be formed partially in each of two phases? Can these compositional parameters be controlled by selection of monomers and reaction conditions? Our future work will be aimed at trying to obtain a better understanding of polymerization reactions and the products formed when acid monomers such as IA, AA and MAA are used with conventional hydrophobic monomers. Research will involve polymerizations over a broad range of acid monomer compositions.

Some effort will also be devoted to studying the properties of the copolymers formed from such systems. The molecules could be rather blocky and have some unusual properties and application potential.

9. Semibatch Emulsion Polymerization with Nonionic Surfactants

Primary efforts will emphasize development of a particle nucleation and growth model adequately representing the semi-batch emulsion polymerization of vinyl acetate with polyvinyl alcohol (PVOH) as an emulsifier and stabilizer. The complexity of this

system necessitates consideration of both micellar and homogeneous nucleation, coagulation of primary and mature particles, radical desorption, grafting and PVOH adsorption and stabilizing characteristics. Supplemental empirical correlations relating turbidity/particle size, surface tension/free PVOH concentration and density/conversion will be generated to augment 'first principle' models, providing a model verifiable via computer simulation and experimentation.

As time and opportunity permit, on-line measurements and adjustable parameters indicated by the model will be investigated in a particle nucleation and growth control strategy. Controller performance may be evaluated by computer simulation and actual polymerizations incorporating typic industrial disturbances.

10. Continuous Miniemulsion Polymerization

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

Conclusions from previous studies concerning the importance of the cosurfactant to obtaining stable distributions of small monomer droplets have been confirmed. Experimental polymerizations in a CSTR have shown that, at low residence times, the classic emulsions oscillate in conversion whereas the miniemulsions do not. The

conversion oscillations in classic emulsion polymerization are due to the alternating presence and absence of micelles in the reaction mixture. In the miniemulsions, the lack of oscillations clearly points to the reduced role of micelles. Further, the miniemulsions achieved a polymerization rate twice that of the classic emulsions. The particle size and conversion data indicate that more particles are present in the miniemulsions. The molecular weight data point to a significant degree of radical segregation in both systems. Other experimental data show that the polymerization rate in the miniemulsion system is a function of the concentration of monomer droplets in the emulsion. In the classic emulsion system, the polymerization rate is a function of the concentration of micelles.

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

11. Dynamic Optimization of the Semi-Batch Emulsion Polymerization Process

Appropriate concepts from modern control engineering and optimization theory in conjunction with a simple, comprehensive model of the well-established, yet poorly understood, emulsion polymerization system were used to establish an anticipatory operational algorithm to minimize production cost and maximize product quality and controllability.

The optimal recipe and feed-rate policy for the (semi-) batch emulsion polymerization of methylmethacrylate were tracked via suitable use of a 'tendency' model and data filtering, fitting and prediction methods. Optimal policies allowed

specified polymerization rate and average molecular weight distribution profiles to be followed, minimizing kettle time and interbatch product variability, subject to a maximum polymerization rate safety constraint. These policies were responsive to uncontrolled, unmonitored, unmodelled but relatively slow variations in reactant quality. Polymerization progress was observed solely by on-line densitometry, and the procedure was validated on the lab-bench scale.

12. Control of a Continuous Emulsion Polymerization Reactor

An improved reactor design for the emulsion polymerization process which incorporates the concepts of a plug flow pre-reactor and split feed operation has been described. The reactor configuration eliminates oscillations in the latex properties and offers potential savings in capital and operating costs.

The Vogel-Edgar multivariable controller has been applied to the reactor system, the major motivation being the strong nonlinearities exhibited by the emulsion process. The controller is successful in controlling the monomer conversion and average particle size in the presence of unmeasured disturbances. Satisfactory closed-loop performance is also obtained for the servo problem.

SUMMARY

Current and planned future research in polymerization reaction engineering at Georgia Tech will focus on the kinetics of the polymerization, mathematical modeling, design and optimization of reactor configurations, development of on-line sensors, and closed-loop control of polymerization reactors. The overall goal is the manipulation of the reactor environment to produce polymer of specified molecular and morphological properties.

APPENDIX I

STUDENT PARTICIPANTS

Hsueh-Chi Lee, "Emulsion Polymerization in a Seed-Fed Continuous Stirred-Tank Reactor," PhD Dissertation, Georgia Institute of Technology (March 1985).

M.S. ChE, Georgia Institute of Technology (1981)

M.S. Chemistry, Emory University (1979).

B.S. ChE, Cheng-Kung University, Taiwan (1977)

Present Employer: Dow Chemical Company

Jeffrey Reinhardt, "Inverse Emulsion Polymerization," M.S. Thesis, Georgia Institute of Technology (1985)

B.S. ChE, Bucknell University (1983).

Present Employer: Self Employed

Beverly M. Tanner, "Optimal Control of Molecular Weight Distribution in a Continuous Polymerization Reactor," Ph.D. Dissertation, Georgia Institute of Technology (1985).

B.S. ChE, Auburn University (1983)

Present Employer: Dow Chemical Company

William E. Houston, "Adaptive Optimizing Control of a Semibatch Polymerization Reactor," M.S. Thesis, Georgia Institute of Technology (1986).

B.S. ChE, Georgia Institute of Technology (1978)

Present Employer: Lockheed Georgia

Kristina M. Kwalik, "Bifurcation Characteristics in Closed-Loop Polymerization Reactors," Ph.D. Dissertation in Progress, Georgia Institute of Technology (1988).

B.S. ChE, Lehigh University (1983)

M.S. ChE, Georgia Institute of Technology (1986)

Thesis: "Adaptive Control of a Continuous Polymerization Reactor"

A. K. Adebekun, "On-Line Estimation and Control of Molecular Weight Distribution," Ph.D. Dissertation in Progress, Georgia Institute of Technology (1989).

B.S. ChE, University Lagos, Lagos, Nigeria

M.S. ChE, Georgia Institute of Technology (1987)

Thesis: "On-Line Control of Molecular Weight Distribution"

Kyle Stuart Atkinson, "The Emulsion Copolymerization of Ethyl Acrylate with Methacrylic Acid," Undergraduate Research Project.

B.S. ChE, Georgia Institute of Technology (1987)

Darrell T. Barnette, "Continuous Miniemulsion Polymerization," Ph.D. Dissertation, Georgia Institute of Technology (December 1987)

M.S. ChE, Georgia Institute of Technology (1983)

B.S. ChE, Georgia Institute of Technology (1981)

Present Employer: Ciba Geigy

Chorng-Shyan Chern, "Emulsion Polymerization in Nonuniform Latex Particles" PhD Dissertation, Georgia Institute of Technology (1987).

M.S. ChE, University of New Hampshire (1984)

B.S. ChE, National Technical University, Taiwan (1980)

- Richard Norman Mead, "Emulsion Copolymerization in Continuous Reactor System," PhD Dissertation in Progress, Georgia Institute of Technology (1987).
 M.S. ChE, University of Florida (1983)
 B.S. ChE, North Carolina State University (1980).
- Mark J. Perri, "Optimal Control of a Semibatch Emulsion Polymerization Reactor," Ph.D. Dissertation in Progress, Georgia Institute of Technology (1987).
 B.S. ChE, University Delaware (1982)
- Glenn Lewis Shoaf, "Emulsion Polymerization with Acid Monomers," Ph.D. Dissertation in Progress, Georgia Institute of Technology (1987).
 M.S. ChE, Georgia Institute of Technology (12/1986).
 Thesis: "Feasibility Study for Continuous Emulsion Copolymerization of Ethyl Acrylate and Methacrylic Acid."
 B.S. ChE, North Carolina State University (1985)
- Zhi-Qiang Song, "Particle Nucleation in Emulsion Polymerization," Ph.D. Dissertation in Progress, Georgia Institute of Technology (1987).
 B.S. ChE, Zhejiang Univeristy, China (1982)
 M.S. ChE, Zhejiang University, China (1984)
 On leave from faculty of Zhejiang University, China
- Kwaku O. Temeng, "Adaptive Control of a Continuous Emulsion Polymerization Reactor," Ph.D. Dissertation, Georgia Institute of Technology (December 1987).
 B.S. ChE, Massachusetts Institute of Technology (1982)
 M.S. ChE, Georgia Institute of Technology (1984)
 Present Employer: E.I. DuPont de Nemours & Co.
- Cheryl Yvette Matthews, Initiating Ph.D. research in the area of control of particle number and size distribution in emulsion polymerization.
 M.S. ChE, Colloids, Polymers & Surfaces, Carnegie-Mellon University (1982)
 B.S. ChE, Colloids, Polymers & Surfaces, Carnegie-Mellon University (1980)

APPENDIX II

PUBLICATIONS RELATED TO POLYMERIZATION REACTION ENGINEERING RESEARCH

1. "High Swelling of Latex Particles Without the Utilization of Swelling Agents," L. H. Jansson, M. C. Wellons and G. W. Poehlein, J. Polym. Sci., Polym. Letters Ed., **21**, 937-943 (1983).
2. "On-Line Monitoring of Emulsion Polymerization Reactors," F. J. Schork in Science and Technology of Polymer Colloids, G. W. Poehlein, R. Ottewill and J. Goodwin, (ed.), Martinus Nijhoff Publishers, The Hague (1983).
3. "Mechanisms and Kinetics of Emulsion Polymerization," G. W. Poehlein, Ch. 2 in Polymer Colloids, T. Corner (Ed.), Applied Science Publishers, Ltd., London (1985).
4. "Latex Particle Size Distributions from Steady-State Continuous Stirred-Tank Reactor Systems," G. W. Poehlein, H-C Lee, and N. Stubicar, J. Polym. Sci., Polym. Sym. **72**, 207-220 (1985).
5. "Emulsion Polymerization," G. W. Poehlein, Ch. 6 in Applied Polymer Science, ACS Sym. Series 285, R. W. Tess, and G. W. Poehlein (Eds.), Washington, DC (1985).
6. "Continuous Polymerization in Miniemulsions," D. T. Barnette, and F. J. Schork, in Polymer Reaction Engineering, K. H. Reichert and W. Geisler, (ed.) Huthig & Wepf, Heidelberg, (1986).
7. "Computer Simulation of Continuous Miniemulsion Polymerization," C. M. Chen, L. Gothjelpsen and F. J. Schork, Polymer Process Engineering, **4**, No. 2, (1986).
8. "Continuous Tube-CSTR Reactor System for Emulsion Polymerization Kinetic Studies," H.-C. Lee and G. W. Poehlein, Chem. Engr. Sci., **41:4**, 1023-1030 (1986).
9. "Emulsion Polymerization," G. W. Poehlein, Chapter E in Encyclopedia of Polymer Science and Engineering, Vol. 6, 1-51, Wiley (1986).
10. "Free Radical Transport and Reactions in Emulsion Polymerization," G. W. Poehlein, H.-C. Lee and C.-S. Chern, 59-70 in Polymer Reaction Engineering, K.-H. Reichert and W. Geiseler (Eds.), Huthig & Wepf, Heidelberg (1986).
11. "Continuous Miniemulsion Polymerization," D. T. Barnette, F. J. Schork, Chem. Eng. Progress, **83** No. 6, 25-30, (1987).
12. "Polymerization in Nonuniform Latex Particles: Distribution of Free Radicals," C.-S. Chern and G. W. Poehlein, J. Polym. Sci., Part A, 617-635 (1987).
13. "Adaptive Predictive Control of a Semibatch Polymerization Reactor," W. E. Houston and F. J. Schork, Polymer Process Engineering **5**, No. 1, 119-147, (1987).
14. "Emulsion Polymerization in a Seed-Fed Continuous Stirred Tank Reactor: Influence of Transfer Reactions," H.-C. Lee and G. W. Poehlein, Polym. Process Engr., **5(1)**, 37-74 (1987).
15. "Feedback Control of Molecular Weight Distribution During Continuous

Polymerization," B. M. Tanner, A. K. Adebekun and F. J. Schork, Polymer Process Engineering, 5, No. 1, 75-118, (1987).

16. "Reaction Kinetics of Vinyl Acetate Emulsion Polymerization," C. S. Chern and G. W. Poehlein, J. Appl. Polym. Sci., 33, 2117-2136 (1987).
17. "Continuous Miniemulsion Polymerization," D. T. Barnette and F. J. Schork, Encyclopedia of Chemical Processing and Design, John J. McKetta, (ed.), Marcel Dekker, New York (in press).
18. "A Kinetic Model for Curing Reactions of Epoxides with Amines," C.-S. Chern and G. W. Poehlein, Polym. Eng. Sci. (in press).
19. "Adaptive Pole-Placement Control of a Continuous Polymerization Reactor," K. M. Kwalik and F. J. Schork, Chem Eng. Commun., (in press).
20. "Kinetics of Grafting in Solution Polymerization," Chem. Eng. Communications, (in press).

APPENDIX III

CONFERENCE PAPERS, LECTURES & SEMINARS

1. "On-Line Monitoring of Emulsion Polymerization Reactors," F. J. Schork, NATO Advanced Study Institute on Polymer Colloids, Bristol, U.K., July, 1982.
2. "Adaptive Control of a Continuous Polymerization Reactor," K. M. Kwalik and F. J. Schork, American Control Conference, Boston, June, 1985.
3. "Emulsion Polymerization in a Seed-Fed CSTR/Chain Transfer Effects," H.-C. Lee and G. W. Poehlein, Paper a, Sym. on Polym Reactors, AIChE National Meeting, Chicago, November, 1985.
4. "Use of Continuous Reactor System to Study Radical Transport Phenomena in Emulsion Polymerization," G. W. Poehlein, 1985 Gordon Conference on Polymer Colloids, Tilton, NH (July 10, 1985).
5. "Continuous Polymerization in Miniemulsions," D. T. Barnette and F. J. Schork, 1986 Berlin Workshop on Polymer Reaction Engineering, Berlin, FRG, October, 1986.
6. "Continuous Miniemulsion Polymerization," D. T. Barnette and F. J. Schork, AIChE Annual Meeting, Miami Beach, November, 1986.
7. "Polymerization in Non-Uniform Latex Particles," C.-S. Chern and G. W. Poehlein, Paper 160b, Sym. on Polym. React. Engr., AIChE National Meeting, Miami, FL, November 1986.
8. "Kinetics of Grafting in Semi-Batch Emulsion Polymerization," C.-S. Chern and G. W. Poehlein, ACS Ruber Division Meeting, Atlanta, GA, October 1986.
9. "Grafting Kinetics in Emulsion Polymerization," C.-S. Chern and G. W. Poehlein, ACS Colloid Division Meeting, Atlanta, GA, June 1986.
10. "Adaptive Optimizing Control of a Semibatch Polymerization Reactor," W. E. Houston and F. J. Schork, AIChE Annual Meeting, Miami Beach, November, 1986.
11. "Use of Continuous Reactors for Emulsion Polymerization Kinetic Studies," 2nd Berlin International Workshop on Polym. Reaction Engr., Berlin, West Germany (October 1, 1986).
12. "Emulsion Polymerization Reaction Engineering," G. W. Poehlein, Institut fur Polymerchemie Erich Correns, Teltow, East Germany, Invited lecture (September 30, 1986).
13. "Emulsion Polymers and Emulsion Polymerization," G. W. Poehlein, 75th Anniversary Lecture Series, Purdue University, November 1986.
14. "Direct Control of Molecular Weight Distribution During Continuous Polymerization," AIChE Spring Meeting, Houston, March, 1987.
15. "Adaptive Control of Emulsion Polymerization in a Seeded Stirred Tank Reactor," K. O. Temeng and F. J. Schork, American Control Conference, Minneapolis, June, 1987.

APPENDIX IV

AVAILABLE FACILITIES AND RESOURCES

The Polymerization Reaction Engineering Laboratories at Georgia Institute of Technology are equipped with a number of batch, semi-batch and continuous reactor systems. Appropriate temperature and reagent flow control equipment is available to permit a wide range of reactor configurations and operating procedures.

Analytical equipment within the Laboratory includes standard items for gravimetric analysis, a GC for measurement of dynamic residual monomer, dynamic light scattering for particle size analysis, uv/visible spectrophotometry, devices for on-line measurement of density and surface tension, and an HDC unit for particle size distribution measurements.

Major equipment items available to support future research includes electron microscopes, NMR, FTIR, GC-Mass Spec and various computers. Close relationships with several industrial organizations and with the Emulsion Polymers Institute at Lehigh University also expand our measurement and preparation capabilities.

16. Graduate Seminars on Emulsion Polymer Topics, G. W. Poehlein, Clemson University (January 20, 1987) University of South Carolina (November 20, 1986) University of Akron (February 28, 1985).
17. Industrial Seminars on Emulsion Polymer Topics, G. W. Poehlein, Dow Chemical Co., Midland, MI (November 15, 1985) DSM Resins BV, Holland (September 29, 1986) Eastman Kodak Co., Rochester, NY (October 17, 1985) United Merchants Co., Langley, SC (April 29, 1986).
18. "Emulsion Polymerization Mechanisms and Kinetics," and "Emulsion Polymerization Reaction Engineering," G. W. Poehlein, two lectures given each year in short course at Lehigh University (June) and Davos, Switzerland (August).
19. Graduate Seminars on Polymerization Reaction Engineering, F. J. Schork, Auburn University (1984) University of Maryland (1986).
20. "Monitoring and Control of Emulsion Polymerization Reactors," F. J. Schork, lecture given each year in a short course in Davos, Switzerland.