

15:14:56

OCA PAD AMENDMENT - PROJECT HEADER INFORMATION

04/07/93

Active

Project #: E-19-645 Cost share #: A-65-311 Rev #: 5
Center # : 10/24-6-R7197-0A0 Center shr #: 10/22-1-F7197-0A0 OCA file #:
Contract#: CTS-9023240 Mod #: ADM. REVISION Work type : RES
Prime # : Document : GRANT
Contract entity: GTRC

Subprojects ? : Y CFDA: 47.041
Main project # : PE #: N/A

Project unit: CHEM ENGR Unit code: 02.010.114
Project director(s):
POEHLEIN G W CHEM ENGR (404)894-3090

Sponsor/division names: NATL SCIENCE FOUNDATION / GENERAL
Sponsor/division codes: 107 / 000

Award period: 910501 to 941031 (performance) 950131 (reports)

Sponsor amount	New this change	Total to date
Contract value	0.00	249,827.00
Funded	0.00	249,827.00
Cost sharing amount		24,981.00

Does subcontracting plan apply ? : N

Title: EMULSION AND DISPERSION POLYMERIZATION

PROJECT ADMINISTRATION DATA

OCA contact: Jacquelyn L. Tyndall 894-4820

Sponsor technical contact Sponsor issuing office

MARIA BURKA MARIAN C. SCHEINER
(202)357-9606 (202)357-9626

NATIONAL SCIENCE FOUNDATION NATIONAL SCIENCE FOUNDATION
1800 G STREET, N.W. 1800 G STREET, N.W.
WASHINGTON, D.C. 20550 WASHINGTON, D.C. 20550

Security class (U,C,S,TS) : U ONR resident rep. is ACO (Y/N): N
Defense priority rating : N/A NSF supplemental sheet
Equipment title vests with: Sponsor GIT X
NONE PROPOSED

Administrative comments -
ISSUED TO CORRECT REVISION #3, AMENDMENT 03. FUNDS WILL BE REBUDGETED IN
SUBPROJECT E-19-X19 DUE TO THE NEW OVERHEAD RATE OF 44.9%.

15:14:56

SUBPROJECTS OF MAIN PROJECT E-19-645

04/07/93

Project number

Spon/Div

Project Director

Project Unit

Total Contract

Total Funded

E-19-X19

107/000

61,913.00

CHEM ENGR

61,913.00

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 11/15/94

Project No. E-19-645_____ Center No. 10/24-6-R7197-0A0_

Project Director POEHLEIN G W_____ School/Lab CHEM ENGR_____

Sponsor NATL SCIENCE FOUNDATION/GENERAL_____

Contract/Grant No. CTS-9023240_____ Contract Entity GTRC

Prime Contract No. _____

Title EMULSION AND DISPERSION POLYMERIZATION_____

Effective Completion Date 941031 (Performance) 950131 (Reports)

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

Comments _____
LETTER OF CREDIT APPLIES. 98A SATISFIES PATENT REQUIREMENT. _____

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 Management	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other _____	N
_____	N

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT (SUBPROJECTS)

Closeout Notice Date 11/15/94

Project No. E-19-645

Center No. 10/24-6-R7197-0A0_

Project Director POEHLEIN G W _____

School/Lab CHEM ENGR _____

Sponsor NATL SCIENCE FOUNDATION/GENERAL _____

Project # E-19-X19	PD POEHLEIN G W	Unit 02.010.114	T
GRANT # CTS-9023240	MOD#	BR DTD 940819	CHEM ENGR *
Ctr # 10/24-6-R7197-0A1	Main proj # E-19-645	OCA CO	JLB
Sponsor-NATL SCIENCE FOUNDAT	/GENERAL		107/000
EMULSION AND DISPERS			
Start 910501	End 941031	Funded	61,913.00
		Contract	61,913.00

LEGEND

1. * indicates the project is a subproject.
 2. I indicates the project is active and being updated.
 3. A indicates the project is currently active.
 4. T indicates the project has been terminated.
 5. R indicates a terminated project that is being modified.
-



Georgia Institute of Technology

A UNIT OF THE UNIVERSITY SYSTEM OF GEORGIA

ATLANTA, GEORGIA 30332-0370

(404) 894-4826

OFFICE OF VICE PRESIDENT
FOR INTERDISCIPLINARY PROGRAMS

January 22, 1992

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 progress report for 1991. Please let me know if you would like any additional material. Best regards for 1992.

Sincerely,

Gary W. Poehlein
Vice President for Interdisciplinary
Programs

GWP:g
Enclosure

cc: OCA w/ report

ANNUAL PROGRESS REPORT

NATIONAL SCIENCE FOUNDATION GRANT NO. CTS-9023240

GEORGIA TECH PROJECT NUMBER E-19-645

PROJECT TITLE: Emulsion and Dispersion Polymerization

PROJECT DIRECTOR: Gary W. Poehlein

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

INTRODUCTION

The high points of 1991 were the completion of doctoral dissertations by two students who are listed below. This work was started under a previous grant. A summary of the research, a list of publications and presentations, and plans for year two comprise the remainder of this report.

DEGREES GRANTED

- Ph.D. - David M. Lange, "Emulsion Polymerization with Functional Monomers in Continuous Reactors," School of Chemical Engineering, Georgia Institute of Technology (1991). Dr. Lange is currently employed by Ameripol Sympol Co. in Port Neches, Texas.
- Ph.D. - Cheryl Matthews Gilmore, "Particle Nucleation and Growth in a Polymerically Stabilized Emulsion Polymerization System," School of Chemical Engineering, Georgia Institute of Technology (1991). Dr. Gilmore is a part-time postdoctoral student with Prof. Schork (Ga. Tech) and a full-time mother to two children who were born during her doctoral studies.

RESEARCH SUMMARIES

Emulsion Copolymerization with Functional Monomers: Emulsion polymerization is a heterogeneous process with an aqueous continuous phase. The reaction mechanisms and kinetics in a copolymerization system become more

complicated when one monomer has significant solubility in water. Emulsion copolymerization reactions with styrene and carboxylic acid monomers (acrylic and methacrylic) were carried out in batch and continuous reactor systems with and without latex seed particles. Experimental work included measurement of the phase distributions of the various recipe ingredients as well as polymerization rates and product characteristics – particle concentrations and size distributions.

The data were analyzed with the aid of mechanism-based reactor models -- batch and continuous. The results clearly demonstrated that the acid monomers increase the transport of free radicals out of the monomer-swollen polymer particles which are the major sites for the polymerization reactions. The responsible mechanisms are chain transfer to the hydrophilic acid monomer followed by diffusion of the monomer radical into the continuous aqueous phase. In seeded systems this results in a reduction in polymerization rate because of a decrease in the average number of free radicals in the polymer particles. Polymerization rates often increase in unseeded systems because the acid monomers help to stabilize more particles.

The results of this work include a range of experimental data, tuned reactor models and fundamental parameters related to phase thermodynamics and reaction mechanisms. Additional work is being focused on the nature of the copolymer molecules which are partially formed in each of the two phases.

Poly(Vinyl Alcohol)-Stabilized Emulsion Polymerization of Vinyl Acetate: Emulsion polymerization reactions with polymeric stabilizers are commercially important (e.g., PVOH-stabilized VAc systems) but not nearly as well understood as the more common systems which utilize anionic surfactants. First, stabilization with polymers is more complex. Second, chain transfer reactions involving the stabilizing polymer molecules can generate a complex molecular mix.

The major focus of this work was to model the PVOH (actually partially hydrolyzed PVAc -- 88% hydrolyzed to OH)-stabilized emulsion polymerization of vinyl acetate -- an important commercial process. Model components included nucleation via grafting with the dissolved PVOH as well as via propagation reactions in the aqueous phase (homogeneous nucleation). Flocculation and particle growth components were also included.

The model parameters were tuned with new experimental data and literature results. The major conclusion was that grafting to the PVOH is not a major particle nucleation mechanism as is commonly believed. Most grafting of PVAc onto PVOH occurs after the particles are formed and the PVOH is associated with the surfaces of these particles.

PAPERS AND PRESENTATIONS

Published (Attached):

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

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

"Kinetic Analysis of Seeded Emulsion Polymerization of Vinyl Acetate," D.M. Lange, G.W. Poehlein, S. Hayashi, A. Komatsu and T. Hirai, *J. Polym. Sci., Part A, Poly. Chem.*, 29, 785-792 (1991).

"Emulsion Polymerization and Latex Technology: Past Achievements and Future Directions," G.W. Poehlein, *Chapter One, 5(3)* (Sept 1991). -- *Chapter One* is an AIChE publication with papers aimed at students. Hence, this is not a research publication.

Accepted:

"Characterization of Styrene-Carboxylic Acid Monomer Emulsion Copolymerization," D.M. Lange and G.W. Poehlein, *Polym. Reaction Engr.*

"Modeling of Styrene-Carboxylic Acid Monomer Emulsion Copolymerization in a Series of Seed-Fed Continuous Stirred-Tank Reactors," D.M. Lange and G.W. Poehlein, *Polym. Reaction Engr.*

Prepared But Not Yet Reviewed:

"Modeling Poly(Vinyl Alcohol)-Stabilized Vinyl Acetate Emulsion Polymerization I. - Theory," C.M. Gilmore, G.W. Poehlein and F.J. Schork (1992).

"Modeling Poly(Vinyl Alcohol)-Stabilized Vinyl Acetate Emulsion Polymerization II. - Comparison with Experiments," C.M. Gilmore, G.W. Poehlein and F.J. Schork (1992).

Presentations:

"Emulsion Polymerization and Copolymerization in Continuous Reactor Systems," Preprint and invited paper, *International Symposium on Polymeric Microspheres*, Fukui, Japan (October 1991).

"Emulsion Polymerization Mechanisms and Kinetics," Short courses at Lehigh University (June 1991) and Davos, Switzerland (Aug. 1991) and at Lord Corporation, Cary, NC (Dec. 1991).

"Emulsion Polymerization Reaction Engineering," Short courses at Lehigh University (June 1991) and Davos, Switzerland (Aug. 1991).

"Continuous Reactors in Emulsion Polymerization," Invited presentation at meeting of North Carolina Chapter of ACS Polymer Division, Raleigh, NC (Dec. 1991).

RESEARCH PROGRESS AND PLANS

Present research and plans for the next year are primarily focused on developing a better understanding of reaction details in heterogenous free-radical polymerization systems. Emulsion and dispersion systems will be studied. Specific areas of study include:

- The formation of blocky copolymers in emulsion and dispersion polymerization. Molecules formed in these systems can be initiated in one phase and complete the growth process in a second phase. We are interested in the nature of the blocky molecules formed.
- Particle growth in dispersion polymerization can occur via reactions within the particles or by deposition of material formed in the continuous phase. Experiments will be used in conjunction with models to quantify particle growth phenomena.

Preliminary experiments have been carried out to study NMR spectra and composition of polymers formed from styrene and carboxylic acid monomers in bulk (low conversion) and emulsion polymerization. Work with mathematical models for these copolymerization systems has also been started.

STAFF

Dr. G. W. Poehlein, Principal Investigator
Dr. Shouting Wang, Postdoctoral Fellow
Mr. Pei-Hua Yang, Ph.D. Candidate (ChE)
Mr. Syed Ahmed, Ph.D. Candidate (ChE)
Mr. Ravindra Kshirsagar, M.S. Candidate (ChE)

Additional support from Georgia Institute of Technology, Dow Chemical Co. and GenCorp has helped to expand the NSF-funded program.

Kinetics of Emulsion Copolymerization with Acrylic Acids

GLENN L. SHOAF and GARY W. POEHLEIN*

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

SYNOPSIS

A kinetic model is presented that describes the reaction behavior of emulsion copolymerization systems where significant polymerization occurs in both the particle and aqueous phases. Equations for predicting aqueous-phase free-radical concentrations and aqueous-phase and particle-phase reaction rates are developed. A method for estimating the radical entry rate coefficient is also presented. The model is applied to two seeded carboxylated emulsion copolymerization systems, acrylic acid-styrene and methacrylic acid-styrene. Both experimental and predicted results reveal that the reaction behavior is greatly affected by the type of acid monomer, partition of monomer between the various phases, and locus of polymerization. The mechanism for the acrylic acid-styrene system is more complicated than that for the methacrylic acid-styrene system. Evidence suggests that the primary reaction locus in the acrylic acid-styrene system shifts from the particles to the aqueous phase after the hydrophobic monomer, styrene, has been consumed.

INTRODUCTION

Conventional emulsion polymer systems employ monomers that are relatively water insoluble such as styrene. The primary reaction locus is inside the polymer particles and aqueous-phase polymerization is usually negligible. Many industrial reaction systems, however, employ one or more monomers that have significant water solubility. The concentration and reaction of these monomers in the aqueous phase may be significant, and conventional emulsion polymerization kinetics do not apply to these systems.

Carboxylated copolymer latexes comprise an increasingly important class of industrial emulsion polymer systems involving water-soluble monomers. They are used widely for the production of paper coatings, textile coatings, and adhesives. Carboxylic acid monomers are often completely soluble in water. However, they will still distribute to varying extents into the organic phase depending on their relative hydrophobicity. Significant amounts of polymerization can occur in both the particle and aqueous phases.

Copolymerization Studies of Hydrophobic Monomers (i.e., Styrene) with Carboxylic Acid Monomers

Potentiometric and conductometric titration studies of copolymer latex systems containing acid monomers copolymerized with a more hydrophobic monomer such as styrene have been performed by a variety of workers including Fordyce and Ham,¹ Muroi,² Ceska,^{3,4} Sakota and Okaya,⁵ Vijayendran,⁶ Egusa and Makuuchi,⁷ and Gasper and Tan.⁸ Most of these studies were aimed at determining the distribution of the acid groups between the aqueous phase, particle surface, and particle interior and the effects of these distributions on the rate of polymerization, particle stability, and particle generation.

The most frequently studied acid monomers copolymerized with styrene (or other hydrophobic monomers) are itaconic acid (IA), acrylic acid (AA), and methacrylic acid (MAA), listed in order of increasing hydrophobic nature. The amount of acid found buried inside the particle core increases with hydrophobicity of the monomer. Hydrophobic monomers diffuse into the particle, polymerize, and become a part of the particle core more easily than hydrophilic monomers. Hydrophilic acid monomers such as IA must be carried to the particle surface by oligomeric radicals that have polymerized in the

* To whom correspondence should be addressed.

aqueous phase.³ Very little IA monomer normally becomes incorporated within the particle core. The concentration of IA in the free aqueous phase is, therefore, greater than MAA when equal amounts are charged. The incorporation of AA into the particle core is intermediate between IA and MAA.^{2,6-9}

Ceska copolymerized IA, AA, and MAA with styrene in separate reactions. Copolymerization rates were found to increase with the presence of carboxylic monomers in the order IA < AA < MAA.^{2,3} The rate increased as the hydrophobicity of the monomer increased. The increase in overall reaction rate with hydrophobicity of the acid monomer may be related to two factors. First, the more hydrophobic acid monomers may become incorporated earlier in the reaction and thus stabilize a greater number of particles. Second, the more hydrophobic acid monomer partitions to a greater extent into the particles where the reaction rate is fastest.

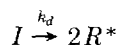
Seeded reactions were utilized in this study in order to study the kinetics of carboxylated styrene emulsion systems without the complicated particle nucleation phenomena. A constant particle number was maintained by using a large concentration of seed particles to capture oligomers before significant secondary nucleation could occur. Small amounts of surfactant were used to stabilize existing particles while minimizing the chances for further particle nucleation. Examination of reaction samples with a transmission electron microscope revealed no signs of secondary nucleation under the conditions used in this study.

THEORY

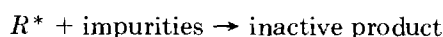
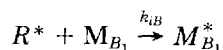
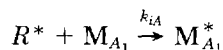
Emulsion Copolymerization Kinetics

The basic initiation and propagation reactions for copolymerization of two monomers, M_A and M_B , are shown below.

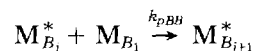
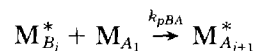
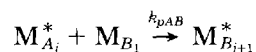
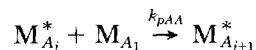
Initiator decomposition



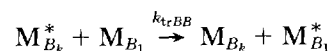
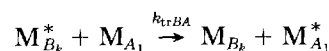
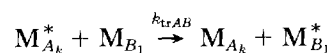
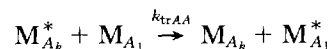
Monomer initiation



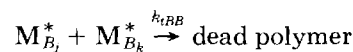
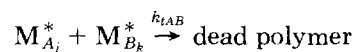
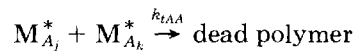
Propagation



Monomer chain transfer



Termination



j refers to the number of monomer units of either type A or B in the oligomeric chain, whereas the A or B refers only to the type of monomer unit at the end of the chain.

It is unlikely that initiator radicals will be found inside the particles since they are most likely to react before entering a polymer particle. The chain transfer reactions are most important in the particle phase since the formation of single monomer radicals may lead to the exit or "desorption" of radicals from the particles. The rate of entry and exit of free radicals significantly affects the concentration of radicals in the particles and in the aqueous phase and thus the rates of reaction in each phase.

Nomura et al.¹⁰ developed rate equations for emulsion copolymerization inside the polymer particles. Eqs. (1), (2), and (3) give the reaction rates for monomer A, monomer B, and total monomer, respectively.

$$R_{pA} = -dM_A/dt = k_{pAA}[M_A]_p N_{A^*} + k_{pBA}[M_A]_p N_{B^*} \quad (1)$$

$$R_{pB} = -dM_B/dt \\ = k_{pBB}[M_B]_p N_{B^*} + k_{pAB}[M_B]_p N_{A^*} \quad (2)$$

$$R_{p\text{tot}} = R_{pA} + R_{pB} \quad (3)$$

where N_{A^*} and N_{B^*} are the number of particles per volume of water containing A and B radicals, respectively. Note that eqs. (1) and (2) do not include polymerization in the aqueous phase.

Nomura et al.¹⁰ used eq. (4) to express the composition of copolymer formed in the particles.

$$\frac{dM_A}{dM_B} = \frac{[M_A]_p (r_A [M_A]_p + [M_B]_p)}{[M_B]_p (r_B [M_B]_p + [M_A]_p)} \quad (4)$$

They also assumed that the change in concentration of A^* and B^* radicals with time is slow when compared to the time scale of the complete reaction. Hence,

$$k_{pBA}[M_A]N_{B^*} = k_{pAB}[M_B]N_{A^*} \quad (5)$$

They then defined an average number of respective radicals per particle.

$$\bar{n}_A = N_{A^*}/N_T, \quad \bar{n}_B = N_{B^*}/N_T, \quad \bar{n}_I = N_{I^*}/N_T$$

and

$$\bar{n}_t = (N_{A^*} + N_{B^*} + N_{I^*})/N_T$$

where N_{I^*} is the number of particles containing an initiator radical.

The number of initiator radicals is relatively small, and when water-soluble initiators are used, these radicals are not likely to enter the hydrophobic polymer particles so that

$$\bar{n}_t \approx \bar{n}_A + \bar{n}_B + \bar{n}_I \cong \bar{n}_A + \bar{n}_B \quad (6)$$

\bar{n} may be calculated using a procedure developed by Ugelstad and Hansen¹¹ that involves the method of continuous fractions.

After various algebraic manipulations, copolymerization rates can be written.

$$R_{pA} \\ = \frac{[1/(1+A)](k_{pAA}[M_A]_p + k_{pAB}[M_B]_p)\bar{n}_t N_p}{N_A} \quad (7)$$

$$R_{pB} \\ = \frac{[A/(1+A)](k_{pBA}[M_A]_p + k_{pBB}[M_B]_p)\bar{n}_t N_p}{N_A} \quad (8)$$

where

$$A = \frac{\bar{n}_B}{\bar{n}_A} = \frac{k_{pAA}}{k_{pBB}} \frac{r_B}{r_A} \frac{[M_B]_p}{[M_A]_p} \quad (9)$$

Aqueous-Phase Free-Radical Concentration in Emulsion Copolymerization Systems

Emulsion copolymerization, which includes at least one monomer with a high degree of water solubility, probably involves a significant amount of reaction in the aqueous phase. A kinetic model of emulsion copolymerization for these types of systems requires that the concentration of free radicals in the aqueous phase be known. A useful expression for obtaining the aqueous-phase free-radical concentration developed in collaboration with Mead¹² can be derived by the following method.

Reactions affecting all aqueous-phase radical species are listed in Table I. Corresponding rate expressions are also shown. An expression for the rate of change of initiator free-radical species can be written as follows:

$$\frac{d[I^*]}{dt} = \text{rate of formation by decomposition of } I_2$$

- rate of monomer initiation
- rate of termination with other I^* radicals
- rate of termination with oligomer radicals
- rate of capture by particles
- + rate of desorption from particles
- rate of capture by monomer droplets
- rate of capture by micelles

Due to the high concentration of monomer relative to the concentration of initiator radicals, it is unlikely that termination between two initiator radicals will occur. The initiator free radical is very reactive and has a short lifetime. Therefore, the third and last four terms of the previous expression may be neglected. The resulting expression is given by

Table I Reactions Affecting Aqueous-Phase-Radical Species

1.	• decomposition	$I_2 - k_D \rightarrow 2I^*$	$R_d = 2fk_d[I_2]$
2a.	• monomer initiation	$I^* + A_w - k_{IA} \rightarrow R_{1A}^*$	$R_{1A} = k_{jA}[A]_w[I^*]$
2b.		$I^* + B_w - k_{IB} \rightarrow R_{1B}^*$	$R_{1B} = k_{jB}[B]_w[I^*]$
3.	• deactivation	$I^* + \text{impurities} \rightarrow \text{dead prod}$	$R_{\text{deac}} = 2(1-f)k_d[I_2]$
4a.	• termination	$I^* + I^* - k_{twII} \rightarrow I_2$	$R_{twII} = 2k_{twII}[I^*]^2$
4b.		$I^* + R_{jA}^* - k_{twIA} \rightarrow I - R_{jA}^*$	$R_{\text{term}} = 2k_{twIA}[R_{jA}^*][I^*]$
4c.		$I^* + R_{jB}^* - k_{twIB} \rightarrow I - R_{jB}^*$	$R_{\text{term}} = 2k_{twIB}[R_{jB}^*][I^*]$
5a.	• propagation	$R_{jA}^* + A_w - k_{pAA} \rightarrow R_{j+1A}^*$	$R_{pAA} = k_{pAA}[R_{jA}^*][A]_w$
5b.		$R_{jA}^* + B_w - k_{pAB} \rightarrow R_{j+1B}^*$	$R_{pAB} = k_{pAA}[R_{jA}^*][B]_w$
5c.		$R_{jB}^* + A_w - k_{pBA} \rightarrow R_{j+1A}^*$	$R_{pBA} = k_{pBA}[R_{jB}^*][A]_w$
5d.		$R_{jB}^* + B_w - k_{pBB} \rightarrow R_{j+1B}^*$	$R_{pBB} = k_{pBB}[R_{jB}^*][B]_w$
6a.	• capture of init.	$I^* + P - k_{cI} \rightarrow P_1^*$	$R_{cI} = k_{cI}N_p[I^*]$
6b.	and oligomer radi-	$R_{jA}^* + P - k_{cIA} \rightarrow P_A^*$	$R_{cA} = k_{cIA}N_p[R_{jA}^*]$
6c.	cals by particles	$R_{jB}^* + P - k_{cIB} \rightarrow P_B^*$	$R_{cB} = k_{cIB}N_p[R_{jB}^*]$
7a.	• desorption of	$P_1^* - k_{desI} \rightarrow I^* + P$	$R_{\text{desI}} = k_{\text{desI}}(N_p\bar{n}/N_A)$
7b.	radicals from	$P_A^* - k_{desA} \rightarrow R_{jA}^* + P$	$R_{\text{desA}} = k_{\text{desA}}(N_p\bar{n}/N_A)$
7c.	particles	$P_B^* - k_{desB} \rightarrow R_{jB}^* + P$	$R_{\text{desB}} = k_{\text{desB}}(N_p\bar{n}/N_A)$
8a.	• termination of	$R_{iA}^* + R_{jA}^* - k_{twAA} \rightarrow O_{i+j}$	$R_{\text{term}} = 2k_{twAA}[R^*]^2$
8b.	oligomer radicals	$R_{iA}^* + R_{jB}^* - k_{twAB} \rightarrow O_{i+j}$	$R_{\text{term}} = 2k_{twAB}[R_{iA}^*][R_{jB}^*]$
8c.		$R_{iB}^* + R_{jB}^* - k_{twBB} \rightarrow O_{i+j}$	$R_{\text{term}} = 2k_{twBB}[R_{iB}^*]^2$
9a.	• capture of	$I^* + D - k_{cDI} \rightarrow P_{DI}^*$	$R_{cDI} = k_{cDI}N_D[I^*]$
9b.	radicals by	$R_{jA}^* + D - k_{cDA} \rightarrow P_{DA}^*$	$R_{cDA} = k_{cDA}N_D[R_{jA}^*]$
9c.	droplets	$R_{jB}^* + D - k_{cDB} \rightarrow P_{DB}^*$	$R_{cDB} = k_{cDB}N_D[R_{jB}^*]$
10a.	• capture of	$I^* + M_c - k_{McI} \rightarrow P_{MI}^*$	$R_{McI} = k_{McI}N_{MC}[I^*]$
10b.	radicals by	$R_{jA}^* + M_c - k_{McA} \rightarrow P_{MA}^*$	$R_{McA} = k_{McA}N_{MC}[R_{jA}^*]$
10c.	micelles	$R_{jB}^* + M_c - k_{McB} \rightarrow P_{MB}^*$	$R_{McB} = k_{McB}N_{MC}[R_{jB}^*]$

$$\frac{d[I^*]}{dt} = 2fk_d[I_2] - 2k_{IA}[A]_w[I^*] + 2k_{IB}[B]_w[I^*] - 2k_{twI}[R_{\text{tot}}^*][I^*] \quad (10)$$

A balance on the monomer radicals ($j = 1$) is given below.

$$\frac{d[R_1^*]}{dt} = \text{rate of initiation of monomer molecules}$$

- rate of formation of $j = 2$ mers
- rate of termination with initiator radicals
- rate of termination with oligomer radicals
- rate of capture by particles
- rate of capture by drops, micelles
- + rate of desorption from particles

Capture by monomer droplets is usually negligible, and if the surfactant level is kept below its critical micelle concentration, micelles will not be present in the system. Applying the assumption that the identity of a radical A^* or B^* is independent of chain length gives

$$R_{1A}^* = \frac{R_1^*}{1 + A_w} \quad (11)$$

$$R_{1B}^* = \frac{A_w R_1^*}{1 + A_w} \quad (12)$$

A_w is a term introduced by Nomura that assumes that the probability of a radical ending with an A^* or B^* unit is independent of chain length, and that the rate of change in the proportion of the radicals is small over the course of the reaction period. A_w is defined by

$$A_w = \frac{[R_{jB}^*]}{[R_{jA}^*]} = \frac{k_{pAA} r_B [B]_w}{k_{pBB} r_A [A]_w} \quad (13)$$

The rate expression for the monomer radicals can then be written by

$$\begin{aligned} \frac{d[R_1^*]}{dt} = & (k_{tA}[A]_w + k_{tB}[B]_w)[I^*] \\ & - \frac{R_{1^*}}{1 + A_w} [(k_{pAA} + A_w k_{pBA})[A]_w \\ & + (k_{pAB} + A_w k_{pBB})[B]_w] \\ & - 2\bar{k}_{twl}[R_1^*][I^*] - 2\bar{k}_{tw}[R_1^*][R_{tot}^*] \\ & - \bar{k}_{c1}[R_1^*]N_p + \bar{k}_{des}(N_p \bar{n}/N_a) \quad (14) \end{aligned}$$

where the average constants and overall radical concentration are given by the following expressions:

$$\bar{k}_{twl} = \frac{[R_{jA}^*]k_{twlA} + [R_{jB}^*]k_{twlB}}{[R_{jA}^*] + [R_{jB}^*]} \quad (15)$$

$$\bar{k}_{tw} = \frac{1}{(1 + A_w)^2} (k_{twAA} + A_w k_{twAB} + A_w^2 k_{twBB}) \quad (16)$$

$$\bar{k}_{c1} = \frac{k_{c1A}[R_{1A}^*] + k_{c1B}[R_{1B}^*]}{[R_{1A}^*] + [R_{1B}^*]} \quad (17)$$

Next, a balance is written on the j -mer radicals with $j > 1$.

$$\begin{aligned} \frac{d[R_{j^*}]}{dt} = & \text{rate of formation of } j\text{-mer} \\ & - \text{rate of formation of } j + 1 \text{ mer} \\ & - \text{rate of termination with initiator radicals} \\ & - \text{rate of termination with oligomer radicals} \\ & - \text{rate of capture by particles} \\ & - \text{rate of capture by drops, micelles} \\ & + \text{rate of desorption from particles} \end{aligned}$$

Again, capture by droplets and micelles is neglected relative to capture by seed particles. Desorption from latex particles is also unlikely if j is much larger than 1. The resulting rate expression is given by eq. (18). [Note that eq. (15) has been extended to include radicals of length j .]

$$\begin{aligned} \frac{d[R_j^*]}{dt} = & \frac{[R_j^*]}{1 + A_w} [(k_{pAA} + A_w k_{pBA})[A]_w \\ & + (k_{pAB} + A_w k_{pBB})[B]_w] \\ & - \frac{[R_{j+1}^*]}{1 + A_w} [(k_{pAA} + A_w k_{pBA})[A]_w \\ & + (k_{pAB} + A_w k_{pBB})[B]_w] \\ & - 2\bar{k}_{twl}[R_j^*][I^*] - 2\bar{k}_{tw}[R_j^*][R_{tot}^*] \\ & - \bar{k}_{cj}[R_j^*]N_p \quad (18) \end{aligned}$$

where

$$\bar{k}_{cj} = \frac{[R_{jA}^*]k_{cjA} + [R_{jB}^*]k_{cjB}}{[R_{jA}^*] + [R_{jB}^*]} \quad (19)$$

$$[R_j^*] = [R_{jA}^*] + [R_{jB}^*] \quad (20)$$

The oligomers grow to a critical length beyond which capture by particles is assumed to occur. This critical length is denoted by j_{cr} . Therefore, the system of equations developed consists of j_{cr} equations. The steady-state assumption must be applied in order to solve the j_{cr} system of equations. The derivatives are all set to zero and the j_{cr} equations are summed yielding

$$\begin{aligned} 2fk_d[I_2] - 2\bar{k}_{twl}[R_{tot}^*][I^*] - 2\bar{k}_{tw} \sum_{j=1}^{j_{cr}-1} [R_j^*][R_{tot}^*] \\ - N_p \sum_{j=1}^{j_{cr}-1} \bar{k}_{cj}[R_j^*] + \bar{k}_{des} \left(\frac{N_p \bar{n}}{N_a} \right) \\ - \frac{[R_{j_{cr}-1}^*]}{1 + A_w} [(k_{pAA} + A_w k_{pBA})[A]_w \\ + (k_{pAB} + A_w k_{pBB})[B]_w] = 0 \quad (21) \end{aligned}$$

One may then define \bar{k}_c , an average radical capture constant, as was done by Ugelstad and Hansen.¹¹

$$\bar{k}_c = \sum_{j=1}^{j_{cr}-1} \frac{k_{cj}[R_j^*]}{[R_{tot}^*]} \quad (22)$$

and rewrite the expression for the average termination constant,

$$2\bar{k}_{tw} \sum_{j=1}^{j_{cr}-1} [R_j^*][R_{tot}^*] = 2\bar{k}_{tw}[R_{tot}^*]^2 \quad (23)$$

A more simplified equation then follows:

$$2fk_d[I_2] - 2\bar{k}_{tw}f[R_{tot}^*][I^*] - 2\bar{k}_{tw}[R_{tot}^*]^2 - \bar{k}_c N_p [R_{tot}^*] + \bar{k}_{des} \left(\frac{N_p \bar{n}}{N_A} \right) - \frac{[R_{jcr-1}^*]}{1 + A_w} [(k_{pAA} + A_w k_{pBA})[A]_w + (k_{pAB} + A_w k_{pBB})[B]_w] = 0 \quad (24)$$

This equation is of the same form as that derived by Ugelstad and Hansen¹¹ for homopolymerization. Two additional assumptions can be made to simplify this expression.

1. If seed is present, flocculation of oligomers onto seed particles should be great enough that few oligomer species can reach the critical chain length needed for homogeneous nucleation of particles. Therefore, $[R_{jcr-1}^*]$ should be very small (especially compared to $[R_{tot}^*]$), and the last term can be neglected.
2. If the initiator is very reactive (i.e., potassium persulfate), and if the concentration of monomer(s) in the aqueous phase is significant (i.e., significantly water-soluble monomers such as carboxylic acids), $[I^*]$ should be small, and the second term can also be neglected.

These simplifications lead to

$$2fk_d[I_2] - 2\bar{k}_{tw}[R_{tot}^*]^2 - \bar{k}_c N_p [R_{tot}^*] + \bar{k}_{des} (N_p \bar{n} / N_A) = 0 \quad (25)$$

Application of the quadratic formula leads to a direct solution for $[R_{tot}^*]$.

$$[R_{tot}^*] = \frac{\sqrt{(\bar{k}_c N_p)^2 + 8\bar{k}_{tw}(\bar{k}_{des} N_p \bar{n} / N_A + 2fk_d[I_2])} - \bar{k}_c N_p}{4\bar{k}_{tw}} \quad (26)$$

Expression for Diffusion-Controlled Aqueous-Phase Copolymerization

The rationale used in the previous derivation of $[R_{tot}^*]$ can be used in deriving an expression for diffusion-controlled aqueous-phase copolymerization

in an emulsion system. The rate expression is given by

$$R_{paq} = - \frac{(d[A]_{aq} + d[B]_{aq})}{dt} = k_{pAA}[A^*]_{aq}[A]_{aq} + k_{pAB}[A^*]_{aq}[B]_{aq} + k_{pBA}[B^*]_{aq}[A]_{aq} + k_{pBB}[B^*]_{aq}[B]_{aq} \quad (27)$$

A steady-state concentration is assumed for each type of radical.

$$k_{pBA}[B^*]_{aq}[A]_{aq} = k_{pAB}[A^*]_{aq}[B]_{aq} \quad (28)$$

Steady state is also assumed for the total concentration of radicals, which normally leads to an expression of the form

$$R_{initiation} = R_{termination} \quad (29)$$

However, as shown in the previous discussion involving an emulsion system, radical capture by latex particles and radical desorption from latex particles are important. Therefore, eq. (29) must be modified to

$$R_{initiation} = R_{termination} + R_{capture} - R_{desorption} \quad (30)$$

which leads to

$$R_i = 2\bar{k}_{tw}([A^*]_{aq} + [B^*]_{aq})^2 + \bar{k}_c([A^*]_{aq} + [B^*]_{aq})N_p - \bar{k}_{des}(N_p \bar{n} / N_A) \quad (31)$$

Rearranging and solving for the free radical concentration gives

$$[A^*]_{aq} + [B^*]_{aq} = [R_{tot}^*]_{aq} = \frac{\sqrt{(\bar{k}_c N_p)^2 + 8\bar{k}_{tw}(R_i + \bar{k}_{des} N_p \bar{n} / N_A)} - \bar{k}_c N_p}{4\bar{k}_{tw}} \quad (32)$$

Solving for $[B^*]_{aq}$ from eq. (28) yields

$$[B^*]_{aq} = \frac{k_{pAB}[A^*]_{aq}[B]_{aq}}{k_{pBA}[A]_{aq}} \quad (33)$$

and substituting this result into eq. (32) and rearranging gives an expression for $[A^*]_{aq}$:

$$[A^*]_{aq} = \frac{\sqrt{(\bar{k}_c N_p)^2 + 8\bar{k}_{tw}(R_i + \bar{k}_{des} N_p \bar{n} / N_A)} - \bar{k}_c N_p}{4\bar{k}_{tw}(1 + k_{pAB}[B]_{aq} / k_{pBA}[A]_{aq})} \quad (34)$$

Let $r_A = k_{pAA}/k_{pAB}$ and $r_B = k_{pBB}/k_{pBA}$. Then substituting eqs. (33) and (34) into eq. (27) and rearranging leads to an expression for the rate of reaction in the aqueous phase.

$$R_{p\text{aq}} = \frac{\sqrt{(\bar{k}_c N_p)^2 + 8\bar{k}_{tw}(R_i + \bar{k}_{\text{des}} N_p \bar{n}/N_A) - \bar{k}_c N_p}}{4\bar{k}_{tw}(r_A [A]_{\text{aq}}/k_{pAA} + r_B [B]_{\text{aq}}/k_{pBB})} \times (r_A [A]_{\text{aq}}^2 + 2[A]_{\text{aq}}[B]_{\text{aq}} + r_B [B]_{\text{aq}}^2) \quad (35)$$

Separate expressions for each monomer can be derived for the aqueous-phase copolymerization rate. These expressions are more useful than eq. (35) for calculating the aqueous-phase copolymer composition. The derivation begins with eq. (27). Again, the steady-state assumption for the total concentration of free radicals and the assumption that the identity of an A^* or B^* radical is independent of chain length leads to

$$k_{pBA} [B^*]_{\text{aq}} [A]_{\text{aq}} = k_{pAB} [A^*]_{\text{aq}} [B]_{\text{aq}} \quad (36)$$

By definition,

$$A = \frac{[B^*]_{\text{aq}}}{[A^*]_{\text{aq}}} = \frac{k_{pAB} [B]_{\text{aq}}}{k_{pBA} [A]_{\text{aq}}} \quad (37)$$

The total aqueous-phase concentration is equivalent to the sum of each type of free-radical species.

$$[R_{\text{tot}}]_{\text{aq}} = [A^*]_{\text{aq}} + [B^*]_{\text{aq}} \quad (38)$$

Algebraic manipulation of eqs. (37) and (38) lead to expressions for $[A^*]_{\text{aq}}$ and $[B^*]_{\text{aq}}$.

$$[A^*]_{\text{aq}} = \frac{1}{1+A} [R_{\text{tot}}^*]_{\text{aq}} \quad (39)$$

$$[B^*]_{\text{aq}} = \frac{A}{1+A} [R_{\text{tot}}^*]_{\text{aq}} \quad (40)$$

Breaking eq. (27) into two parts leads to

$$R_{pA\text{aq}} = k_{pAA} [A^*]_{\text{aq}} [A]_{\text{aq}} + k_{pBA} [B^*]_{\text{aq}} [A]_{\text{aq}} \quad (41)$$

$$R_{pB\text{aq}} = k_{pAB} [A^*]_{\text{aq}} [B]_{\text{aq}} + k_{pBB} [B^*]_{\text{aq}} [B]_{\text{aq}} \quad (42)$$

Finally, substitution of eqs. (39) and (40) into eqs. (41) and (42) and rearrangement yield reaction rate expressions for the aqueous phase in terms of measurable parameters where $[R_{\text{tot}}^*]_{\text{aq}}$ is given by eq. (26).

$$R_{pA\text{aq}} = \frac{k_{pAA} + Ak_{pBA}}{1+A} [R_{\text{tot}}^*]_{\text{aq}} [A]_{\text{aq}} \quad (43)$$

$$R_{pB\text{aq}} = \frac{k_{pAB} + Ak_{pBB}}{1+A} [R_{\text{tot}}^*]_{\text{aq}} [B]_{\text{aq}} \quad (44)$$

The overall emulsion copolymerization model then takes the form

$$R_{p\text{tot}} = R_{pAp} + R_{pBp} + R_{pA\text{aq}} + R_{pB\text{aq}} \quad (45)$$

where the equations for rate of reaction in the particles are given by eqs. (7) and (8).

Transport of Radicals Out of Particles

Transport of free radicals from polymer particles, commonly referred to as radical desorption, is an important phenomenon in emulsion polymerization. The rate of transport of free radicals from particles greatly affects the free-radical concentration in both the particle and aqueous phases and thus affects the rate of reaction in each phase. The transport of free radicals to and from the particles was accounted for by Smith and Ewart¹³ in their original recursion equation reproduced here.

$$\begin{aligned} N_n [\rho_n/N + nk_{\text{des}} + n(n-1)k_t/V_p] \\ = N_{n-1}(\rho_n/N) + (n+1)k_{\text{des}}N_{n+1} \\ + (n+2)(n+1)(k_t/V_p)N_{n+2} \end{aligned} \quad (46)$$

where $N = \sum_{n=0}^{\infty} N_n$, and N_n is the number of polymer particles per unit volume of aqueous phase that contains n free radicals, ρ_n is the overall rate of radical absorption by the particles, V_p is the particle volume, k_{des} is a rate coefficient for radical desorption from the particles, and k_t is the radical termination constant in the particles.

Expressions for predicting the radical desorption coefficient, k_{des} , for homopolymerization systems have been developed by Ugelstad and co-workers,^{11,14,15} and Nomura and co-workers.¹⁶⁻¹⁸ Nomura et al.¹⁰ then developed expressions for predicting an average radical desorption coefficient, \bar{k}_{des} , for an emulsion copolymerization system. Nomura developed eq. (47) to predict the radical desorption coefficient for radical A and eq. (48) for radical B for the case where aqueous-phase termination is neglected as is common with conventional relatively water-insoluble monomer systems:

$$k_{\text{des}_A} = K_{oA} \frac{r_A c_{m_{AA}} [M_A]_p + c_{m_{BA}} [M_B]_p}{r_A ([M_A]_p + K_{oA} \bar{n} / k_{p_{AA}}) + [M_B]_p} \quad (47)$$

$$k_{\text{des}_B} = K_{oB} \frac{r_B c_{m_{BB}} [M_B]_p + c_{m_{AB}} [M_A]_p}{r_B ([M_B]_p + K_{oB} \bar{n} / k_{p_{BB}}) + [M_A]_p} \quad (48)$$

K_{oA} is defined by

$$K_{oA} = 12 D_{wA} \delta'_A / m_{dA} d_p^2 \quad (49)$$

where d_p is the particle diameter, D_{wA} is the diffusion coefficient of monomer A radicals in the aqueous phase, m_{dA} is the partition coefficient for monomer A radicals between the particle and water phases,

$$m_{dA} = \frac{[M_{A^*}]_p}{[M_{A^*}]_w} \quad (50)$$

and δ'_A is the ratio of water-side film mass-transfer resistance to overall mass-transfer resistance for monomer A radicals defined by

$$\delta'_A = \frac{1}{1 + 2D_{pA} / m_{dA} D_{pA}} \quad (51)$$

where D_{pA} is the diffusion coefficient of monomer A radicals in the polymer particles.

Nomura et al.¹⁰ state that if aqueous-phase termination is not neglected (as in the water-soluble acid-styrene monomer systems), then eqs. (47) and (48) are modified to the form given by

$$k_{\text{des}_A} = \frac{K_{oA}}{\bar{n}} \frac{r_A c_{m_{AA}} [M_A]_p + c_{m_{BA}} [M_B]_p}{r_A ([M_A]_p + K_{oA} / k_{p_{AA}}) + [M_B]_p} \quad (52)$$

$$k_{\text{des}_B} = \frac{K_{oB}}{\bar{n}} \frac{r_B c_{m_{BB}} [M_B]_p + c_{m_{AB}} [M_A]_p}{r_B ([M_B]_p + K_{oB} / k_{p_{BB}}) + [M_A]_p} \quad (53)$$

An overall average radical desorption coefficient, \bar{k}_{des} (1/s), is then calculated from

$$\bar{k}_{\text{des}} = \frac{k_{\text{des}_A}}{1 + A} + \frac{k_{\text{des}_B}}{1 + A} \quad (54)$$

where A is defined by

$$A = \frac{k_{p_{AA}} r_B [M_B]_p}{k_{p_{BB}} r_A [M_A]_p} \quad (55)$$

An alternate form of the desorption coefficient, \bar{k}'_{des} (cm²/s), which is volume independent, is shown in

$$\bar{k}'_{\text{des}} = V_p^{2/3} \bar{k}_{\text{des}} \quad (56)$$

where V_p is the average swollen particle volume (cm³). The values of \bar{k}_{des} (1/s) calculated for the styrene-carboxylic acid systems using the Nomura et al.¹⁰ model are consistent with the trend of values found for other similar monomer systems: styrene 0.02–0.05,^{19,12} styrene-methyl acrylate 0.06–1.4,¹² styrene-acrylonitrile 0.2–0.6,¹² and styrene-carboxylic acid 0.1–2.0. The values increase with the overall hydrophilicity of the monomer system.

Mead¹² has developed a model with analytical solutions for predicting the radical desorption coefficient in an emulsion copolymerization system that accounts for nonuniform distribution of free radicals within the particle. Chern²⁰ has developed a model that accounts for nonuniform distribution of both monomer free radicals and long-chain free radicals inside the particles, but Chern's model requires numerical integration for calculation of the radical desorption coefficient. Results from Mead¹² and Chern²⁰ reveal that the desorption coefficient increases as the diffusivity in the particle decreases because the free radicals tend to concentrate more at the particle surface than at the particle center when diffusion is slow. Slow diffusion effects are more likely to be prevalent with monomer systems such as the acrylates and methacrylates where the gel effect has been observed to be more significant relative to a styrene or acid-styrene monomer system. The effects of nonuniform radical distributions were not included in this work.

The gel effect was also included in the kinetic model for the acid-styrene systems using a development presented by Sundberg et al.²¹ However, the gel effect was determined to be insignificant with the recipes and conditions employed except at very high conversions (> 95%).²²

Estimation of Radical Entry Rate Coefficients

The average radical entry rate coefficient \bar{k}_c has been estimated for styrene emulsion homopolymerization by several workers with varying results. The mechanism for entry of radicals from the aqueous phase into the polymer particles is complex. The entry rate depends on particle surface effects, which may change over time, rates of radical initiation, rates of diffusion, as well as rates of radical transport from the particles. The mechanism becomes even more complex for copolymerization systems of monomers with different hydrophobicities due to changing copolymer compositions and thus changing hydrophobicities of the oligomeric radicals.

Gilbert et al.²³ and Feeney²⁴ determine the parameter ρ (1/s), which is the rate of entry as pre-

sented in the classical Smith-Ewart approach. They have developed a method for zero-one systems by which they calculate values of ρ_a and a desorption term, k , from the slope and intercept of batch conversion-time data in the steady-state region where $\rho = \rho_a + \alpha k \bar{n}$. α is shown to be 0 or -1. Given the particle concentration for their system, values of ρ may be converted to \bar{k}_c ($\text{cm}^3_{\text{aq}}/\text{s}$) by

$$\bar{k}_c = \frac{\rho}{N_p} 1000 \quad (57)$$

where N_p is the particle concentration in numbers of particles/ cm^3_{aq} . This calculation results in values between 10^{-18} to 10^{-16} cm^3/s for the styrene homopolymerization system depending on the particle radius, initiator concentration, and number of particles.

Gilbert and Napper's approach is relatively simple for it requires only batch conversion-time data for a series of recipes, and it does not require separate calculations to account for electrostatic repulsion or other particle surface effects. However, it is not easily extended to copolymerizations with water-soluble monomers because of assumptions needed to obtain the slope and intercept of the overall conversion-time curve during the steady-state period. Their results also depend on the nature of the particle surface, which may be much different in an acid-styrene system relative to a styrene homopolymerization system since the acid is hydrophilic and tends to concentrate at the particle surface. A particle surface covered predominantly with carboxyl groups may differ significantly from the surface of particles without carboxylic acid present in the system, and the nature of this surface may change as the copolymer composition changes throughout the course of the reaction.

Hansen and Ugelstad²⁵ present a more common approach to radical capture in terms of radical diffusion. A system involving irreversible absorption with no electrostatic effects is modeled by

$$\bar{k}_c = 4\pi D_w r \quad (58)$$

where D_w is the diffusivity of monomer in water, and r is the average particle radius.

Since radical desorption and surface effects do exist in most systems, this expression represents an overestimation of the radical capture rate. Therefore, they note that D_w must be modified to account for these phenomena. They report a value of D_w for styrene that leads to a \bar{k}_c of 4×10^{-13} (cm^3/s) for a particle with a diameter of 30–40 nm, which is

several orders of magnitude greater than the values obtained from the work of Gilbert and Napper.²³

Hansen and Ugelstad²⁵ include a discussion in which they rigorously develop expressions for a reversibility factor (U) and a factor that includes electrostatic effects (W'). This results in the expression for \bar{k}_c :

$$\bar{k}_c = 4\pi D_w F r \quad (59)$$

where $F = U/W'$.

A third approach for estimating \bar{k}_c for systems with significant aqueous-phase polymerization rates utilizes steady-state reaction data obtained either from reactions in a continuous stirred-tank reactor (CSTR) or from steady-state portion of the conversion-time curve obtained with most batch data. Continuous reactions were carried out in this work with MAA-styrene and AA-styrene systems using a seed-fed CSTR. Steady-state conversion results from a representative continuous run are presented in Figure 1 for the MAA-styrene system. Steady-state batch reaction rates for styrene were also obtained from the slope of the individual conversion-time curves for styrene for both the MAA-styrene and AA-styrene batch reaction systems at various monomer/water ratios.

The concentrations of the monomers in the particle and aqueous phases were calculated from the partition model using either steady-state conversion

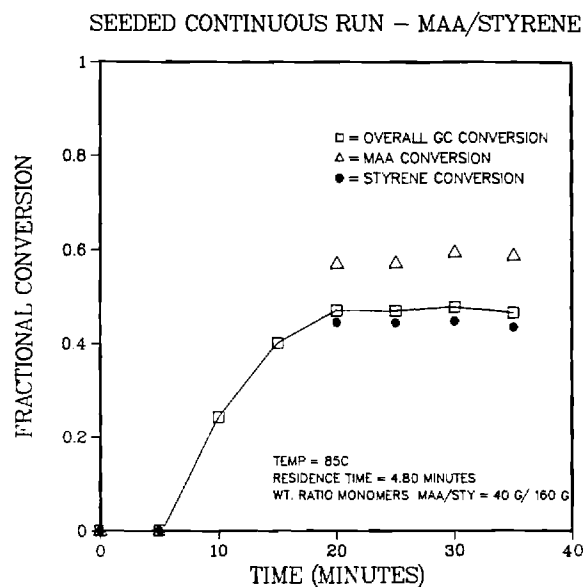


Figure 1 Steady-state conversion-time data for the reaction of MAA-styrene in a CSTR at 85°C with a residence time of 5.1 min (grams acid/grams total monomer = 0.10).

data from the continuous reactions or a selected point along the steady-state portion of the batch conversion curves. A value of \bar{n} was obtained by assuming that the rate of reaction of styrene in the aqueous phase is negligible compared to the rate in the particles. The steady-state rate of reaction of each monomer can be determined from individual monomer conversion measurements. If the reaction of styrene is assumed to take place primarily in the particles, \bar{n} may be calculated directly using

$$\bar{n} = \frac{R_{pB} N_A}{(N_p) \left(k_{pBB} \frac{A}{1+A} + k_{pAB} \frac{1}{1+A} \right) [B]_p} \quad (60)$$

where

$$A = \frac{k_{pAA} r_B [B]_p}{k_{pBB} r_A [A]_p}$$

\bar{k}_{des} may be estimated using equations developed by Nomura et al.¹⁰

Ugelstad and Hansen¹¹ present a method for calculating \bar{n} that accounts for reabsorption of radicals into the particles and aqueous-phase termination. A mass balance on the aqueous-phase free radicals for a batch system is given by

$$\begin{aligned} [R_c = \text{rate of capture (mol/L}_{aq} \text{ s)}] \\ R_c = \text{rate of formation} + \text{rate of desorption} \\ \quad - \text{rate of termination} \\ R_c = \frac{\bar{k}_c N_p [R_{tot}]_{aq}}{1000} = 2f k_d [I] + \bar{k}_{des} \bar{n} N_p / N_A \\ \quad + 2\bar{k}_{tw} [R_{tot}]_{aq}^2 \end{aligned} \quad (61)$$

This expression may be rewritten in terms of dimensionless variables as described by

$$\alpha_n = \alpha'_n + m\bar{n} - Y\alpha_n^2 \quad (62)$$

where

$$\alpha_n = \frac{R_c N_A^2 (V_p / V_{aq})}{k_{tp} N_p^2} \quad (63)$$

$$\alpha'_n = \frac{R_i N_A^2 (V_p / V_{aq})}{k_{tp} N_p^2} \quad (64)$$

$$m = \frac{k_{des} (V_p / V_{aq}) N_A}{N_p k_{tp}} \quad (65)$$

$$Y = \frac{2k_{tw} k_{tp} N_p^2}{N_A^2 \bar{k}_a^2 (V_p / V_{aq})} \quad (66)$$

\bar{n} may then be calculated from Bessel functions as given by

$$\bar{n} = \frac{a}{4} \frac{I_m(a)}{I_{m-1}(a)} \quad (67)$$

where $a = \sqrt{8\alpha_n}$. The Bessel functions may be solved by the method of continued fractions described by Ugelstad and Hansen.¹¹ All parameters in eqs. (63)–(66) are known from the reaction conditions or can be calculated using appropriate correlations except for the absorption coefficient, \bar{k}_a (1/s), which may be expressed as a function of the average capture coefficient, \bar{k}_c (cm³/s) by

$$\bar{k}_a = \frac{\bar{k}_c N_p}{1000} \quad (68)$$

Using the calculated value of \bar{k}_{des} obtained with the Nomura et al. model,¹⁰ \bar{k}_c may then be adjusted until the calculated \bar{n} matches the experimental value. This procedure is useful only in the range where the parameter Y is large (> 100) since \bar{n} is not very sensitive to changes in Y , and thus \bar{k}_c , when Y is small. Due to the large number of particles (N_p) and small particle size (diameter ≈ 30 – 40 nm), reasonably large values of Y (~ 100 – 900) were obtained under the reaction conditions employed in this work.

Both steady-state continuous reaction and batch reaction data were investigated. However, the results reported in this work are based primarily on data obtained from the steady-state region of batch conversion-time curves for both MAA–styrene and AA–styrene systems since reactions in CSTRs result in rather broad particle size distributions. Batch reactions only exhibit steady-state reaction rates over a limited reaction period. However, the particles in batch reactions are often monodisperse, which minimizes the effects of different particle sizes on the average rate of capture.

The dependence of \bar{n} on the average capture coefficient for various values of \bar{k}_{des} under the conditions of the reactions used in this study is shown in Figures 2 and 3 for the MAA–styrene and AA–styrene systems, respectively. \bar{n} increases as \bar{k}_c increases initially. When \bar{k}_c continues to increase, the parameter Y approaches zero, and further changes in \bar{k}_c , and thus Y , have little effect on \bar{n} . The value of \bar{n} for any given \bar{k}_c depends also on the rate of desorption represented by \bar{k}_{des} .

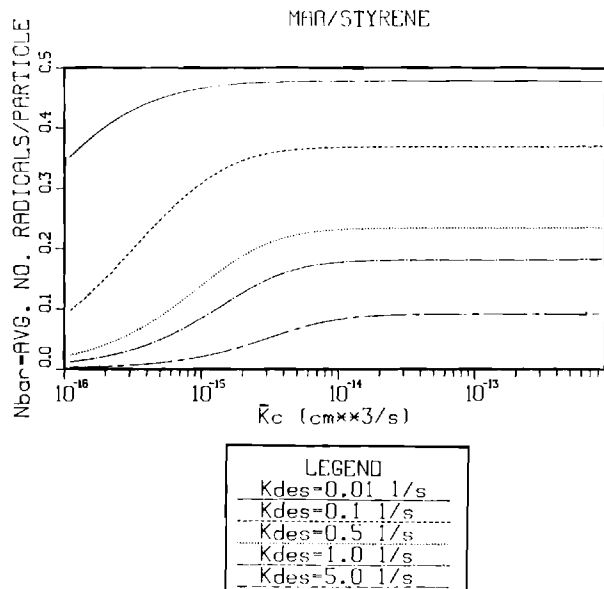


Figure 2 Dependence of \bar{n} on the average capture coefficient at various values of \bar{k}_{des} for the MAA-styrene system at an α'_n of 2.0×10^{-5} .

The dependence of the aqueous-phase free-radical concentration and the parameter Y on \bar{k}_c for each system are shown in Figures 4, 5, and 6. The aqueous-phase free-radical concentration, $[R_{tot}]_{aq}$, decreases with both \bar{k}_c and \bar{k}_{des} , as expected. The value of Y is greater for the AA-styrene system than for the MAA-styrene system due to the higher rate of termination of AA than MAA.

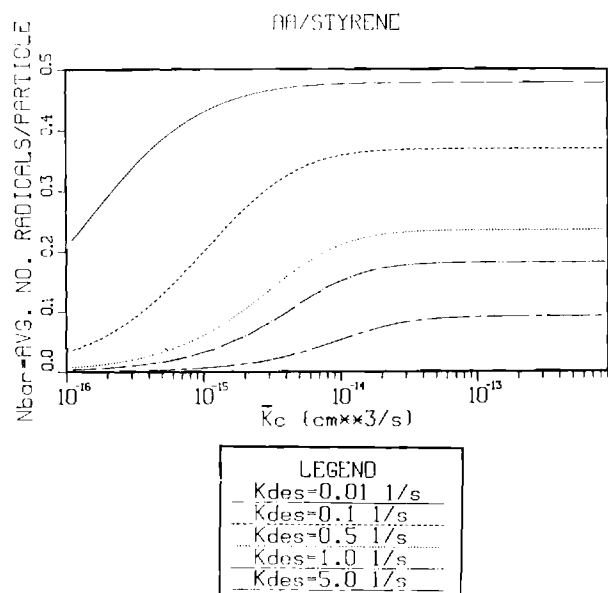


Figure 3 Dependence of \bar{n} on the average capture coefficient at various values of \bar{k}_{des} for the AA-styrene system at an α'_n of 1.7×10^{-5} .

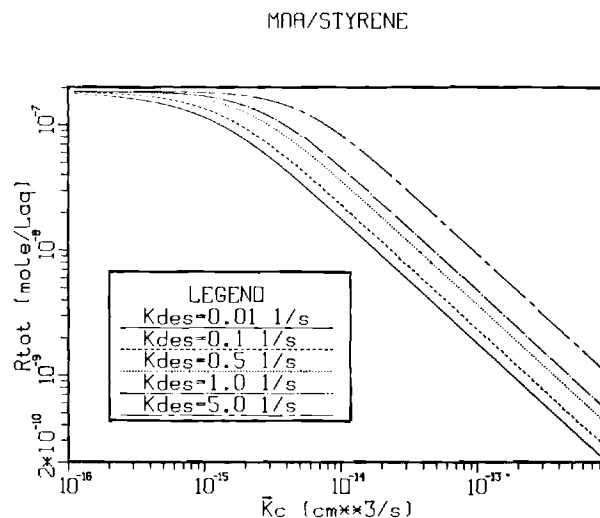


Figure 4 Dependence of the aqueous-phase free-radical concentration on the average capture coefficient at various values of \bar{k}_{des} for the MAA-styrene system at an α'_n of 2.0×10^{-5} .

Mead¹² used an approach for the MA-styrene system similar to the steady-state continuous reaction approach described earlier except he utilized particle size distribution data instead of reaction rate data, and he fit the parameter W defined by Ugelstad. His simulations resulted in \bar{k}_c values ranging between 2×10^{-17} and 2×10^{-15} cm^3/s . Analysis of the experimental data from the studies of the MAA-styrene and AA-styrene systems as discussed previously resulted in \bar{k}_c values ranging between 7

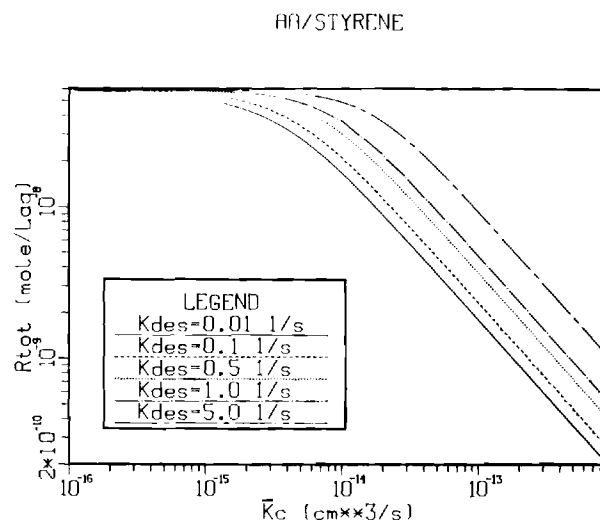


Figure 5 Dependence of the aqueous-phase free-radical concentration on the average capture coefficient at various values of \bar{k}_{des} for the AA-styrene system at an α'_n of 1.7×10^{-5} .

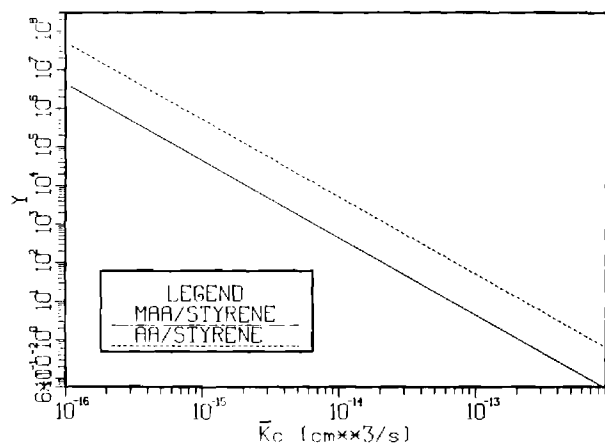


Figure 6 Dependence of dimensionless parameter Y on the average capture coefficient at various values of \bar{k}_c for the MAA-styrene (α'_n of 2.0×10^{-5}) and AA-styrene systems (α'_n of 1.7×10^{-5}).

$\times 10^{-15}$ and 7×10^{-14} cm^3/s . A summary of the reported values for the various systems is shown in Table II.

It is apparent that there is a great deal of discrepancy in the values of \bar{k}_c reported. Values of \bar{k}_c obtained for the acid-styrene systems are larger than values obtained for the MA-styrene system, which in turn are also larger than the range reported by Gilbert and Napper²³ and Feeney²⁴ for the styrene homopolymerization system. It is unclear why the capture rate constant tends to increase when a more hydrophilic monomer is added to the system. However, one factor that may contribute to the increased capture rates is that the propagation constants also increase in the same order as the hydrophilicity for these monomers (styrene < MA < MAA < AA). A faster propagation reaction would increase the rate of growth of an oligomer radical to the critical chain length at which capture is most likely to occur. Evidence of this phenomenon is obtained from results reported by Hawket et al.²⁶ where they show qualitatively that the capture efficiency for more water-soluble monomers (methyl methacrylate, vinyl acetate, vinyl chloride, and acrylonitrile) is higher than that for styrene due to their faster rates of propagation to reach the critical chain length required for capture to occur. An opposing factor to increased rate of capture is the fact that a more hydrophilic monomer will require a greater critical chain length before it becomes "hydrophobic" enough to make capture likely. However, the results from these acid-styrene studies as well as the MA-styrene system imply that the effect of an increased rate of propagation to the critical chain length needed for capture

is greater than the effect of having to grow to a longer chain length before becoming hydrophobic enough to be captured when compared to results from the styrene studies (with the exception for the value of \bar{k}_c obtained for styrene based on Hansen and Ugelstad's²⁵ results).

An additional factor that may have large effects on the rate of capture is the nature of the particle surface. Both steric and electrostatic effects play an important role in determining how easily an oligomer radical will penetrate through the surface of the particle. Therefore, addition of other components that may contribute to surface effects such as surfactant or initiator should be considered before applying reported values for capture coefficients to a particular reaction system. In addition, the character of the surface may change over the reaction period in copolymerization systems, especially when monomers such as itaconic acid, AA or MAA are utilized. These monomers tend to concentrate at the particle surface due to their hydrophilic nature. Therefore, a styrene seed particle with a hydrophobic surface may eventually become coated by the hydrophilic monomer as the reaction proceeds. This coating may significantly change the character of the particle surface, which in turn may affect the rate at which oligomeric radicals diffuse from the aqueous phase to the particle interior.

The estimates of \bar{k}_c reported in this work for the MAA-styrene and AA-styrene systems were obtained with a relatively simple experimental approach. This approach may be applied to many similar monomer systems in order to obtain order-of-magnitude estimates for the average capture coefficients under a given set of reaction conditions. The resulting values, however, depend on the accuracy of the experimental data as well as the accuracy of the parameters utilized in the copolymerization rate equations for calculating \bar{n} and \bar{k}_{des} , and they do not reflect potential effects from the changing nature of the particle surface throughout the reaction period. Therefore, more rigorous approaches for determin-

Table II Reported Values of Capture Coefficients for Several Monomer Systems

Source	System	\bar{k}_c (cm^3/s)
23	Styrene	10^{-18} – 10^{-16}
12	MA-styrene	2×10^{-17} – 2×10^{-15}
This work	MAA-styrene	7×10^{-15} – 7×10^{-14}
	AA-styrene	—
25	Styrene	3×10^{-13}

ing \bar{k}_c for copolymer systems with water-soluble monomers are needed.

Nevertheless, the general approach used in this study appears to give reasonable estimates for \bar{k}_c . The average values obtained for the acid-styrene systems correspond to the trend of increasing \bar{k}_c with increasing propagation rate (and increasing hydrophilicity) exhibited by other monomer systems, and when used in the batch copolymerization model, these same values result in the best fits of the experimental batch copolymerization data. Values of \bar{k}_c in the range reported by Mead¹² and Gilbert and Napper²³ are too small to provide reasonable fits of conversion-time data for the MAA-styrene and AA-styrene systems, unless unreasonably low values for \bar{k}_{des} are used in the copolymerization model.

EXPERIMENTAL

Acrylic acid, methacrylic acid, and styrene monomer (all > 90% pure) were used as received. Potassium persulfate and sodium dodecyl sulfate were also used as received. Carboxylated styrene seed particles (28 nm diameter) were supplied by Dow Chemical, Midland, Michigan. High-purity nitrogen (> 99%) was employed.

All of the batch reactions utilized monomers that contained a small amount of inhibitor added by the manufacturer to prevent polymerization during shipping. Removal of inhibitor is unnecessary for most batch runs since the only effect in most cases is the occurrence of an induction period at the beginning of the reaction during which the inhibitor is consumed. The reaction then proceeds in normal fashion. (Due to the low levels of inhibitor in the monomers and the high reaction temperatures, no induction period was observed for the reactions performed in this study.) This assumption was checked by performing a MAA-styrene run using "cleaned" monomers and comparing the results to runs made with "uncleaned" monomers. Styrene was cleaned

for this run by washing with 5.0 wt % KOH solution followed by filtration through an alumina packing, and the MAA was distilled under vacuum. No difference was observed in the conversion-time behaviors.

The standard recipe for each of the seeded emulsion copolymerization reactions is given in Table III.

All emulsion polymerization reactions were run at 85°C in a nitrogen-purged, agitated, 1.0-L glass vessel similar to the reactor used for the solution polymerizations. The following procedure was used for each run. Carboxylated, styrene seed latex was mixed for 24–48 h with an anionic-cationic ion exchange resin (Bio-Rex MSZ 501) in order to remove excess surfactant. The amount of surfactant removed from the seed was determined gravimetrically. Deionized water, "cleaned" seed, and SDS (an amount combined with the SDS remaining in the seed latex to give a concentration of 4.0 mmol/L_{aq}) was added to the reactor. Nitrogen was bubbled into the reactor and heating was begun by pumping hot water through an internal stainless-steel coil. When the reactor temperature reached approximately 85°C, styrene was slowly added through a dropping funnel. The acid monomer was then slowly added in the same manner. Fast addition of either monomer would tend to "shock" the seed, resulting in coagulation. The nitrogen purge line was pulled to the top level of the emulsion after the monomer addition to prevent polymer from coagulating at the interface of the nitrogen bubbles.

Samples of 20–25 mL were extracted with a syringe, immediately injected into a chilled hydroquinone solution, and immersed in an ice bath to quench the reaction. The overall conversion was measured gravimetrically by drying about 5 g of each sample overnight in an oven and performing a mass balance on the dried solids.

Individual monomer conversions were obtained by gas chromatography (GC) using a Varian 3300 with a 12-ft stainless-steel column packed with Gas

Table III Standard Recipe for Carboxylated Emulsion Batch Copolymerizations

K ₂ S ₂ O ₈	5.0 mmol/L _{aq}
Sodium dodecyl sulfate (SDS)	4.0 mmol/L _{aq} (CMC = 9.0 mmol/L _{aq})
Seed (particle diameter ~ 28 nm)	~ 30 g of solid polymer ~ 4.0 × 10 ¹⁸ particles/L _{aq}
Monomer	200 g total
Acid-styrene ratios	0/200, 20/180, 40/160, 70/130
DI water	Balance to give 1000 g total reaction mass

Chrom 254, 80–100 mesh packing. (The packed column was supplied by Alltech Associates in Deerfield, Illinois.) The column was operated at 220°C, and an internal standard was used in each sample.

Seeded continuous reactions were run in a 0.25-L glass, jacketed continuous stirred-tank reactor (CSTR). "Cleaned" monomers were used for all continuous runs. Monomer, water, and cleaned seed were preemulsified, purged with nitrogen, held in a glass vessel with constant stirring. Potassium persulfate was dissolved in water, purged, and stored in a second glass vessel. The mixtures were pumped separately into the CSTR using calibrated peristaltic pumps. The CSTR was heated by a hot water–ethylene glycol mixture that was pumped through the external jacket. A thermocouple, digital temperature controller, and water–ethylene glycol bath as already described were utilized to maintain a constant reaction temperature. Samples were collected from the overflow of the reactor at various time intervals and the conversion was measured using both GC and gravimetric analysis.

RESULTS AND DISCUSSION

Seeded Styrene Homopolymerization

Seeded reactions with styrene alone were initially performed at 85°C using the standard recipe shown in Table II. Unseeded homopolymerization reactions of styrene often require several hours to reach high conversion. However, the use of seed particles can cause the reaction to occur much more quickly as observed with the experimental conversion data shown in Figure 7. The primary reason for using seeded reactions was to avoid particle nucleation so that the study could be more easily focused on the reaction kinetics.

The seeded styrene homopolymerization was modeled with the basic emulsion polymerization reaction rate equation.

$$R_p = k_p [M]_p \bar{n} \frac{N_p}{N_A} \quad (69)$$

A k_p value of 900 L/mol s was used for the propagation constant for styrene at 85°C.²⁷ This value was determined from an Arrhenius-type plot based on experimental k_p values for styrene obtained over a large range of temperatures by a variety of different workers. The amount of swelling of the particles was based on work with styrene polymerization systems performed by Jansson.²⁸ Results of this work sug-

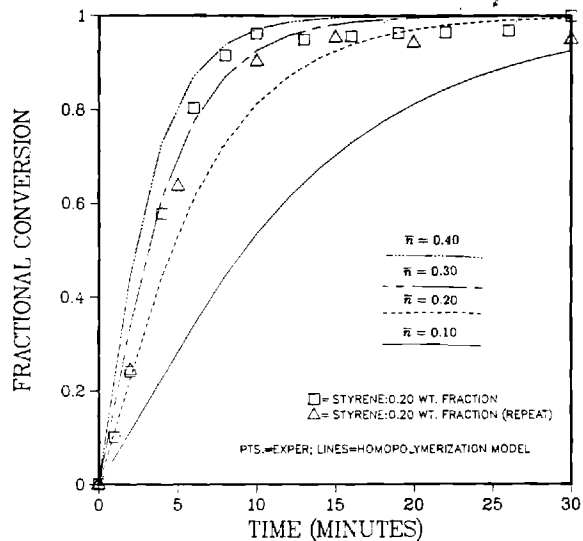


Figure 7 Experimental and predicted conversion-time data for a seeded emulsion homopolymerization of styrene.

gested that the volume ratio of monomer to polymer in the particles should be ≈ 1.5 during interval II based on the average particle sizes. Interval III was assumed to begin when the total volume of monomer in the system became less than 1.5 times the volume of polymer. All of the styrene was then assumed to be inside the particles. The average number of radicals per particle, \bar{n} , was varied from 0.1 to 0.4. A value of \bar{n} of 0.30 gives the best overall fit to the experimental data as revealed in Figure 7. However, \bar{n} will vary with conversion. Therefore, in the emulsion copolymerization model \bar{n} is calculated separately throughout the conversion period using the method developed by Ugelstad and Hansen¹¹ referred to earlier.

Seeded Emulsion Copolymerization of MAA–Styrene and AA–Styrene Systems

Batch seeded emulsion copolymerization reactions of MAA–styrene and AA–styrene were run at 85°C using the standard recipe given in Table III. Conversion-time measurements were made using gas chromatography and gravimetric analyses. Three weight ratios of acid/styrene were used: 20/180, 40/160, and 70/130. Conversion-time results for the 40/160 acid/styrene weight ratios along with the model predictions are shown in Figures 8 and 9 for the MAA–styrene and AA–styrene systems, respectively.

The reactions with the acids are rapid, with nearly complete conversion attained in about 10–20 min. However, these reactions are somewhat slower than

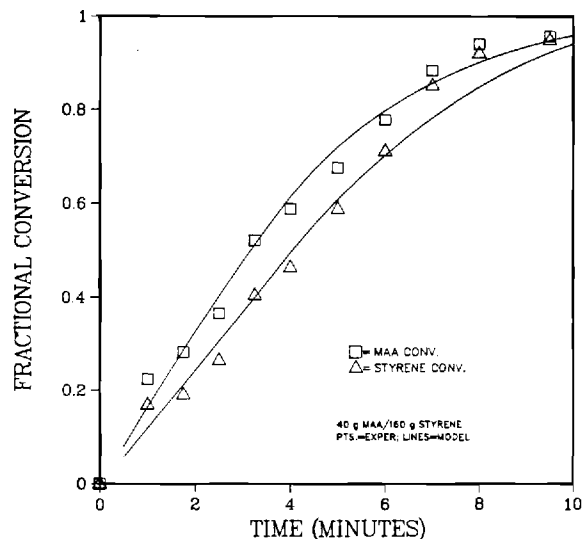


Figure 8 Comparison of predicted and experimental conversion-time data for the seeded batch emulsion copolymerization of MAA-styrene at a weight ratio of 40 g MAA/160 g styrene using a variable value of \bar{k}_{des} .

the homopolymerization of styrene under the same reaction conditions and particle concentrations. MAA reacts more quickly than does AA despite the fact that its propagation constant is less than that of AA. One reason for the faster rate with MAA is attributed to the fact that it is more hydrophobic than AA so that it distributes to a greater extent inside the particles where the monomer and free-radical concentrations are generally higher. MAA conversion becomes high at about the same time as styrene. However, for the same ratios of acid-styrene, the AA conversion significantly lags that of styrene. A substantial portion of AA does not react until most of the styrene monomer has been depleted. The primary reaction locus in the AA-styrene reaction may actually shift from the particles to the aqueous phase after the styrene has been depleted from the system. Additional experiments designed for more thorough investigation of the reaction mechanism for the AA-styrene system will be discussed later.

Model Assumptions for Seeded Batch Copolymerizations of MAA-Styrene and AA-Styrene Emulsion Systems

Simulations of seeded batch emulsion copolymerizations of MAA-styrene and AA-styrene systems were conducted with the model equations developed in the previous sections. Assumptions and conditions used in the model are as follows.

1. The reaction system is seeded and the particle number remains constant. Any new particles formed due to homogeneous nucleation flocculate onto preexisting particles due to the large particle concentration ($\approx 4.0 \times 10^{18}$ particles/ L_{aq}) in the system.
2. All aqueous-phase polymer flocculates onto the polymer particles. Because a relatively small amount of overall polymer is formed in the aqueous phase, this assumption has little effect on the predicted conversion-time behavior. Calculations based on the assumption that all of the aqueous-phase polymer remains in the aqueous phase gives almost identical results.
3. The average number of radicals per particle, \bar{n} , was calculated from a relation developed by Ugelstad and Hansen¹¹ as discussed in the previous section.
4. The average radical capture constant, \bar{k}_c , was determined from separate batch and continuous reaction studies and was assumed constant throughout the reaction period.
5. The desorption constant, \bar{k}_{des} , varied with monomer concentrations in the aqueous and particle phases, and it was calculated using a model proposed by Nomura et al.¹⁰ as modified to account for aqueous-phase polymerization.

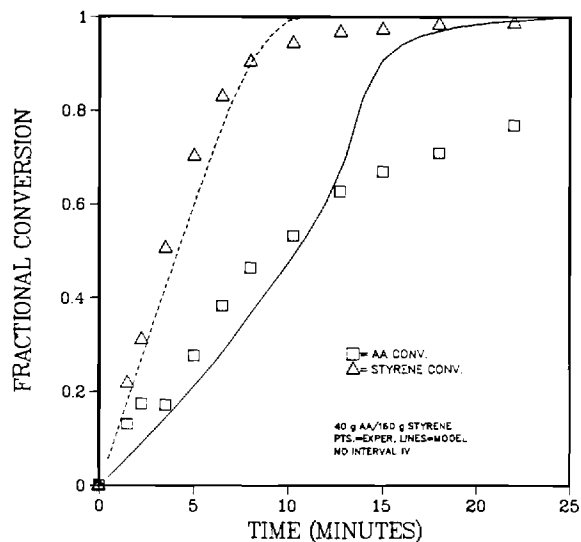


Figure 9 Experimental (points) and predicted (line) conversion-time data for the AA/styrene (40/160 g) seeded emulsion copolymerization system at 85°C. The model assumes that reaction occurs in both the particle and aqueous phases throughout the conversion period (i.e., no interval IV).

6. Values for diffusivities in water of each monomer were calculated using the Wilke–Chang correlation.³⁴ Values for the diffusivities in the polymer particles were assumed to be approximately 0.1 times the diffusivity in water.^{12,19}
7. Values of chain transfer constants in the range reported for methyl acrylate (0.01×10^{-4} to 0.4×10^{-4} ,²⁷) were used for MAA and AA. Values for chain transfer constants (c_{m_i}) for the MAA and AA are not available in the literature. However, the structure of MAA and AA are similar to that of methyl acrylate (MA) as shown in Figure 10. Therefore, values for chain transfer constants used in the model for MAA and AA were chosen within the range reported for MA in the literature. Values used in the model for styrene were, likewise, restricted to the range reported for styrene in the literature (0.5×10^{-4} to 1.8×10^{-4}).²⁷
8. Values for cross-chain transfer constants were assumed to be 0.1 times the chain transfer constants for each monomer (i.e., $c_{m_{AB}} = 1/10 c_{m_{BB}}$ and $c_{m_{BA}} = 1/10 c_{m_{AA}}$). Values of cross-chain transfer constants ($c_{m_{ij}}$) are also not available in the literature. Since the difference in hydrophobicity between styrene and MAA or AA is so large, these monomers are not likely to associate with each other as much as with “like” monomer molecules. The cross-chain transfer between the acid–styrene molecules is probably much lower than between acid–acid or styrene–styrene molecules. The model results were not very sensitive to the selection of $c_{m_{ij}}$. Therefore, this assumption is not very critical.
9. The concentration of styrene monomer in the aqueous phase was based on values reported by Brown and Taylor³⁵ that were dependent on the concentration of acid in the aqueous phase. (Due to the low concentration of styrene in the aqueous phase and its subsequent small effect on the mass balances in the partition model, it was difficult to obtain accurate predictions of the aqueous-phase concentration of styrene from the partition model. Therefore, more accurate values obtained from the literature were used in the simulations in order to obtain accurate predictions of desorption constants without significantly affecting the overall mass balances calculated by the partition model).

Partition of the monomers between the aqueous, particle, and droplet phases is predicted through a combination of mass balances and thermodynamic free-energy relations that depend on the volume of each phase, the volume of monomer, and interaction between the monomers, polymer particles, monomer droplets, and aqueous phase. Interaction parameters employed in the thermodynamic equations were obtained from separate independent experiments. Details of these monomer partition calculations are presented by Shoaf²² and Shoaf and Poehlein.³⁶

Values for the various parameters used in the kinetic model are listed in Table IV.

The chain transfer constant, c_{MAA} , used for AA was smaller than that used for MAA (4). The chain transfer constant is defined by eq. (70), which relates the rate of chain transfer to the rate of propagation for a given monomer:

$$c_{M_i} = k_{tr}/k_{p_i} \quad (70)$$

Litt³⁷ suggests that radical transfer for the vinyl acetate monomer is to the vinyl group, and Mead,¹² by analogy, states that the vinyl group of MA may also provide a stable site for chain transfer. Except for the carboxyl group, the structures of MAA and AA are similar to MA, which again suggests that the most likely site for chain transfer is the vinyl group. However, the extra methyl group on the vinyl carbon with MAA helps to stabilize a free radical more than the hydrogen atom on the AA molecule. Therefore, MAA is more likely to release a hydrogen and stabilize the resulting radical species than AA, which maintains a stronger hold on the vinyl hydrogens. This fact suggests that k_{tr} should be greater for MAA than for AA. In addition, the propagation constant, k_p , is significantly greater for AA than for

CHEMICAL STRUCTURES

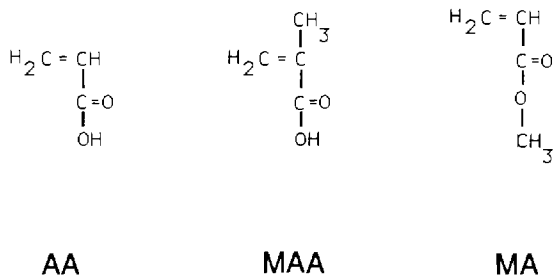


Figure 10 Chemical structure of AA, MAA, and MA monomers.

Table IV Values for Parameters Used in Seeded Emulsion Copolymerization Simulation ($T = 85^\circ\text{C}$)

Parameter	Monomer	Value	Source
k_p (L/mol s)	MAA	15,900	Experiment, 29
	AA	76,900	Experiment, 29
	Styrene	900	27
k_t (L/mol s)	MAA	0.1×10^8	30, 31
	AA	1.0×10^8	30, 31
	Styrene	2.5×10^8	27
r_A	MAA	0.55	32, 33
	Styrene	0.25	32, 33
r_B	AA	0.1	32, 33
	Styrene	0.9	32, 33
c_{mAA}	MAA	0.25×10^{-1}	27
c_{mAA}	AA	0.25×10^{-5}	27
c_{mBB}	Styrene	$0.5\text{--}1.0 \times 10^{-4}$	27
\bar{k}_c (cm ³ /s)	MAA/Sty	2.0×10^{-14}	This work
	AA/Sty	7.0×10^{-14}	This work
N_p (part/L _{reactor})		3.0×10^{18}	$\approx 4.0 \times 10^{18}$ (part/L _{aq})

MAA. These results suggest that the chain transfer constant, c_{mAA} , should be smaller for AA than for MAA. Results of the model simulations revealed that better fits of the experimental data were obtained when the value of c_{mAA} for AA was smaller than that for MAA. Therefore, the values used in the model were selected within the range reported for methyl acrylate, but a somewhat lower value was used for AA than for MAA (Table IV).

MAA–Styrene: Conversion Profiles and Reaction Rates

The overall model for the MAA–styrene system is shown to predict the experimental data quite well for a range of monomer concentrations using no adjustable parameters as shown in Figures 8, 11, and 12 for the 20/180, 40/160, and 70/130 MAA/styrene ratios, respectively. Good fits of the conversion-time behavior for both MAA and styrene are obtained over the full range of conversion. Typical model predictions of the rates of reaction of styrene in the particle phase and MAA in both particle and aqueous phases for the 40/160 recipe are shown in Figure 13. The aqueous-phase polymerization rate of MAA is less than the polymer-phase polymerization rate by more than an order of magnitude for all three monomer ratios. However, it is still significant, especially when considering the effects that small amounts of acids have on product properties. The aqueous-phase polymerization rate of styrene is several orders of magnitude less than the aqueous-phase polymerization rate of MAA, and it is not

shown in Figure 13. Prediction of other important parameters such as \bar{n} , \bar{k}_{des} , R_{tot} , particle diameter, and copolymer compositions are discussed in detail by Shoaf.²²

AA–Styrene: Conversion Profiles and Reaction Rates

Typical model results for the AA–styrene system are presented in Figure 9. A reasonable fit of the 40/160 experimental data is obtained until the sty-

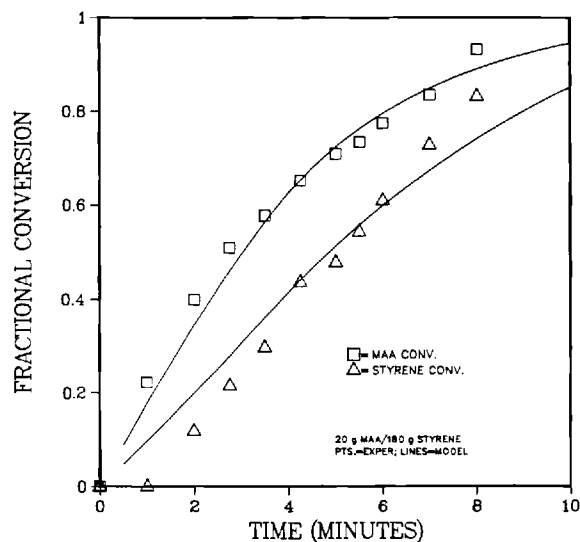


Figure 11 Comparison of predicted and experimental conversion-time data for the seeded batch emulsion copolymerization of MAA/styrene at a weight ratio of 20 g MAA/180 g styrene using a variable value of \bar{k}_{des} .

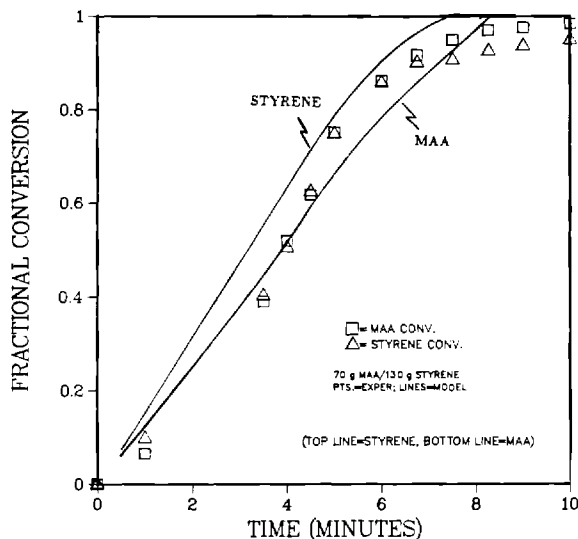


Figure 12 Comparison of predicted and experimental conversion-time data for the seeded batch emulsion copolymerization of MAA/styrene at a weight ratio of 70 g MAA/130 g styrene using a variable value of k_{des} .

rene disappears. The model at this point overestimates the reaction rate of AA. The model predicts that the AA reaction in the particles accelerates once the styrene is depleted due primarily to the large propagation constant of the AA radicals with AA monomer (76,900 L/mol s) relative to the cross-propagation constant for styrene radicals with AA monomer ($k_{pBA} = 1000$ L/mol s). The experimental reaction rate of AA does not accelerate after styrene has reached high conversions.

AA is very hydrophilic and does not partition to a large extent into the particles. The slow reaction rate of AA relative to the model predictions observed after styrene has been depleted is more representative of the reaction rate expected in the aqueous phase where the monomer and free-radical concentrations are usually lower than in the particles. Determining the primary reaction locus during this phase of the reaction may be important for understanding the mechanism for the seeded AA-styrene reaction, especially after the styrene has been consumed.

Interval IV in Emulsion Copolymerization

The reaction locus in most conventional emulsion systems is almost exclusively inside the polymer particles. Systems that contain both a hydrophobic and a hydrophilic monomer may exhibit reaction in both the aqueous and particle phases. (Some reaction may also occur in the monomer droplets. How-

ever, due to the small number of droplets relative to the number of polymer particles, reaction in the droplet phase is usually negligible, except in mini-emulsions.) Kawaguchi³⁸ showed that with the styrene-acrylamide system, the reaction locus actually started in the aqueous phase (where almost 99% of the acrylamide was located), moved to the polymer particles as styrene became incorporated into the oligomeric radicals, then moved back into the aqueous phase after the styrene was depleted.

The AA-styrene system is very similar to the acrylamide-styrene system except that a larger amount of AA partitions into the particles than does acrylamide. The reaction locus in the AA-styrene system is probably located in both the aqueous and particle phases initially, but there is evidence to suggest that the locus shifts back into the aqueous phase after the styrene is depleted. The seeded copolymerization model predicts the styrene conversion fairly well to high conversions as shown in Figure 9. However, the model predictions for AA conversion diverge from the experimental values after the styrene has been depleted. This result suggests that the reaction locus may shift back into the aqueous phase once the concentration of styrene in the system becomes very low.

If the aqueous phase is not saturated with styrene monomer, the oligomers would be very hydrophilic and thus unlikely to diffuse into the polymer particles. Also since polyAA tends to build up on the surface of the particles based on numerous titration studies reported in the literature,^{2,5,7} the particles may possess a coating of hydrophilic polyAA that

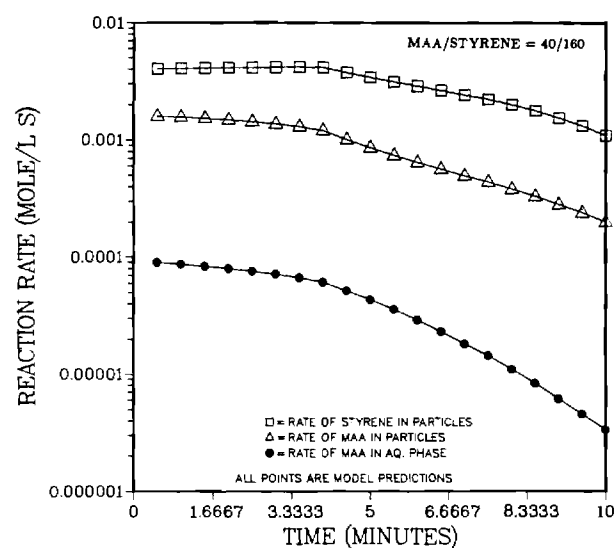


Figure 13 Predicted reaction rates of MAA and styrene as a function of time for an acid/styrene ratio of 40/160.

would tend to trap hydrophilic oligomer radicals, thus preventing their penetration into the polymer particles. The reaction would then occur exclusively in the aqueous phase. The point near the end of the reaction where the reaction locus shifts to the aqueous phase will be referred to as interval IV. Figure 14 provides a physical description of the system during interval IV.

One assumption made in the preceding analysis is that reaction of AA in the particles should be faster than reaction of AA in the aqueous phase. To test this assumption, styrene was removed from the system and a seeded homopolymerization of AA was conducted using the same initiator and initial monomer concentrations as used in a previous unseeded solution polymerization of AA. The resulting data was modeled assuming (i) only aqueous-phase polymerization and (ii) both aqueous-phase and particle-phase polymerization. A reasonable fit of the data was obtained for case (i) with f_{eff} set to 0.35 as shown in Figure 15. (The model for this case was analogous to an emulsion homopolymerization model. It included effects of monomer partitioning, radical capture, and desorption by the particles. Thus it was not limited to the simple solution polymerization case.) When particle-phase poly-

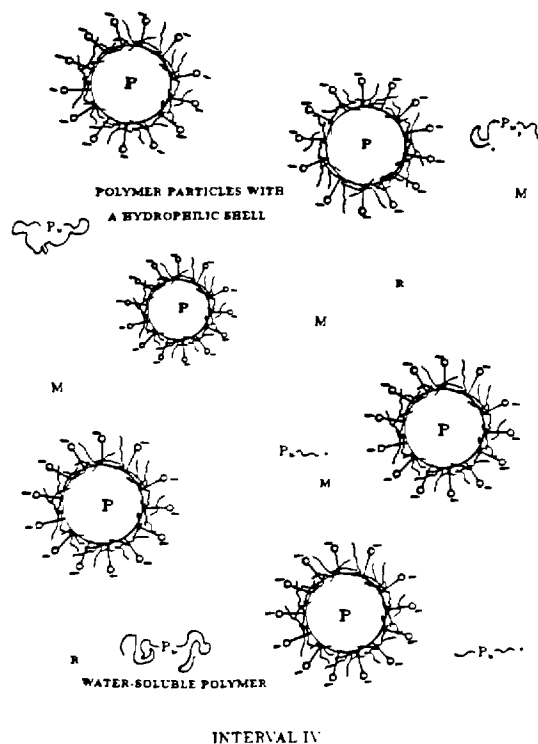


Figure 14 Emulsion copolymerization system during interval IV (P = polymer; M = monomer; R = free radical).

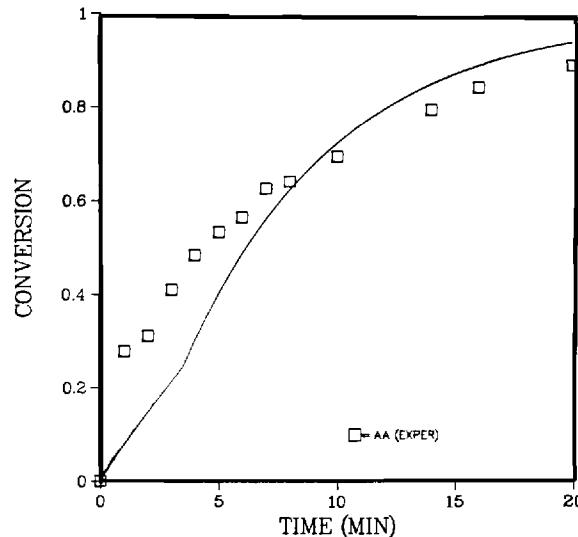


Figure 15 Model simulation of seeded homopolymerization of AA assuming only aqueous-phase polymerization. Particle number = $4 \times 10^{16}/L_{aq}$, $f_{eff} = 0.35$.

merization was also included in the model, the predicted reaction rate was much greater than that observed unless the average number of radicals per particle was set to very low values, less than 0.0005. (See Fig. 16.) Therefore, if significant AA reactions were taking place in the particle phase, the model predicts that the reaction rate would be much higher than the rate observed.

When the seeded homopolymerization data for AA was plotted along with the unseeded homo-

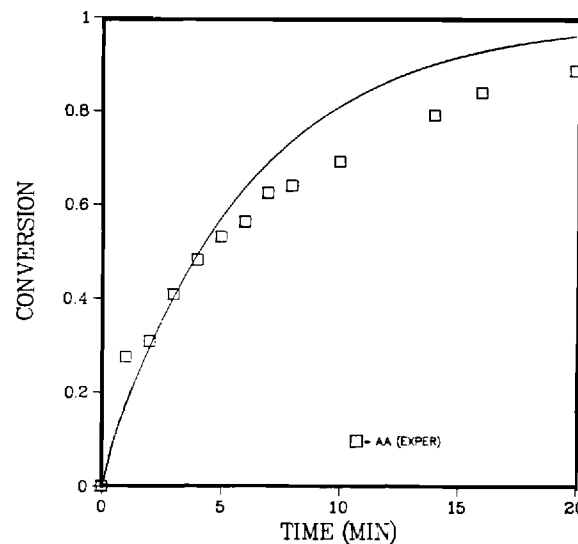


Figure 16 Model simulation of seeded homopolymerization of AA assuming both aqueous-phase and particle-phase reactions (particle number = $4 \times 10^{16}/L_{aq}$, $f_{eff} = 0.35$, and $\bar{n} = 0.0005$).

polymerization data (Fig. 17), the curves were almost identical. This result suggests that without the presence of styrene, the AA oligomer radicals do not penetrate the particles and initiate reaction in the particle phase.

A semibatch run of AA-styrene was performed to further test this conclusion. The precept was that if part of the styrene is fed to the reactor later in the reaction period, the styrene should help pull the oligomer radicals into the particles and thus increase the polymerization rate of AA relative to the case where essentially all of the styrene in the system has been depleted. Thirty-five percent of the styrene was fed over a 17-min period starting at 6 min into the reaction. All of the AA was added at the beginning of the reaction. Figure 18 shows the styrene concentration profiles for the batch and semibatch runs. The data show that a significant concentration of styrene was present in the reactor over the continuous addition period as desired. The AA concentration profiles, however, for both the batch and semibatch runs were almost identical as revealed in Figure 19. (Monomer concentrations were based on the final volume of the reaction contents for these runs.) The AA did not tend to react faster at higher conversions when in the presence of styrene as first expected.

The initial conclusion is that the styrene was unable to pull the radicals into the particles where both AA and styrene should react. However, since the styrene concentration does not build up during the continuous feed period, it must have reacted, and

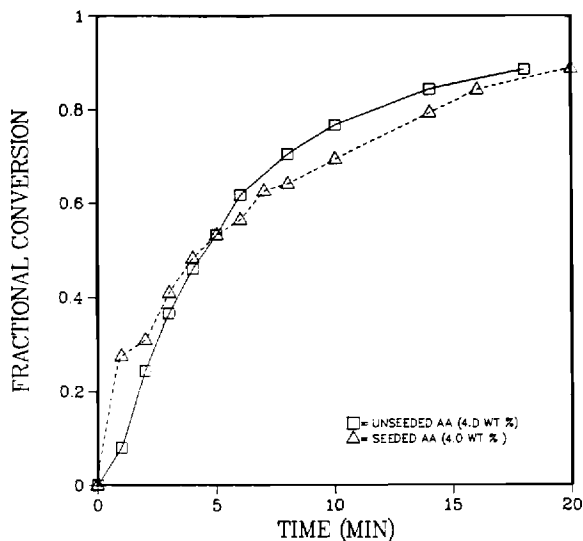


Figure 17 Comparison of conversion-time data for the homopolymerization of AA in a seeded and unseeded reaction system.

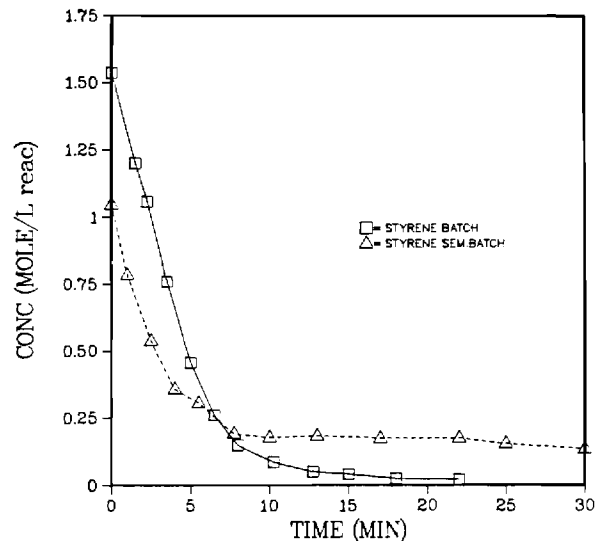


Figure 18 Styrene concentration for a batch and semibatch AA/styrene (40/160 g) seeded copolymerization. Thirty-five percent of the total styrene was fed continuously over a 17-min period starting at 6 min.

this reaction inevitably takes place inside the particles along with the AA monomer. However, the AA reaction rate does not show an increase.

A closer look at the reaction rate equations reveals that the presence of a significant amount of styrene in the particles may prevent the AA reaction rate from rising as expected in the semibatch case. This result can be obtained by calculating parameter A ,

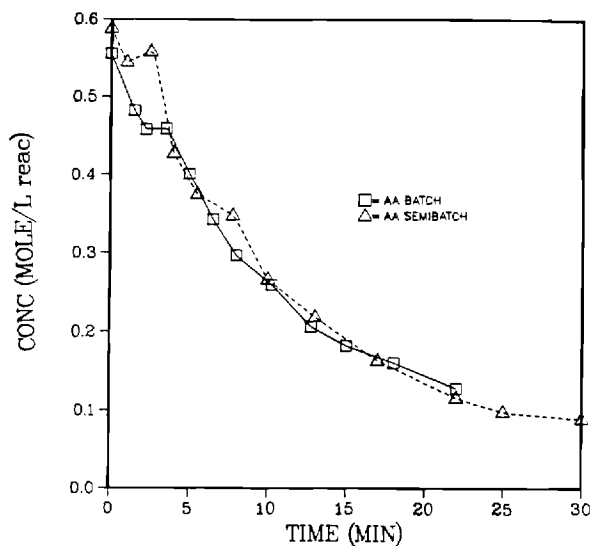


Figure 19 AA concentration for a batch and semibatch AA/styrene (40/160 g) seeded copolymerization. Thirty-five percent of the total styrene was fed continuously over a 17-min period starting at 6 min.

which accounts for the relative reactivities of the two monomers. This parameter, A , is represented by the following expression:

$$A = \frac{k_{pAA} r_B [M_B]}{k_{pBB} r_A [M_A]} \quad (71)$$

where r_1 and r_2 are the reactivity ratios of the acid and styrene, respectively, k_{pi} is the propagation constant for monomer i , and $[M_i]$ is the concentration of monomer i . The rate of reaction of AA in the particles was calculated as a function of parameter A with the results given in Figure 20. Low values of A were obtained only when styrene was essentially depleted. The value of parameter A in the semibatch run corresponding to the time of continuous styrene feed was about 1000. Therefore, the styrene was probably reacting with AA in the particles, but due to the relative reactivities of the two monomers, the AA reaction rate was not noticeably increased as originally expected. The concentration of styrene in the particles must be very low in order to obtain a low value of A and a significant increase in the AA particle phase reaction rate. However, if the concentration of styrene in the system is too low, the oligomeric radicals may be so hydrophilic that they tend to remain in the aqueous phase.

Another factor that may inhibit the hydrophilic oligomers from entering the polymer particles is the presence of a hydrophilic coating of polymer that may surround the particles, especially after most of the styrene has reacted. Muroi,² Sakota and Okaya,⁵

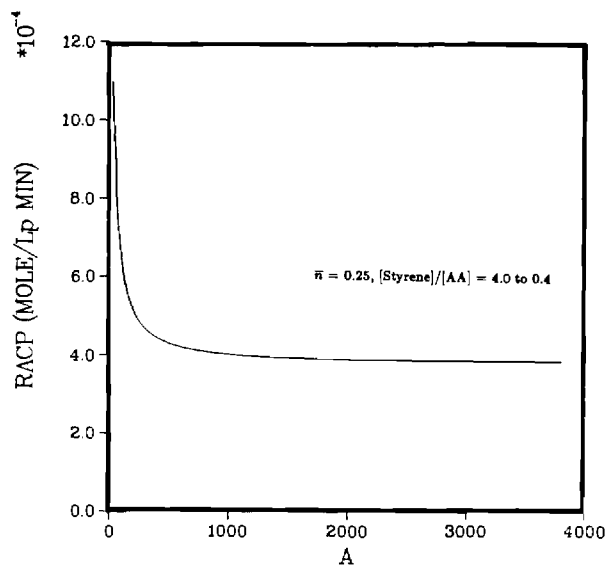


Figure 20 Dependence of AA reaction rate in the particles on the parameter A .

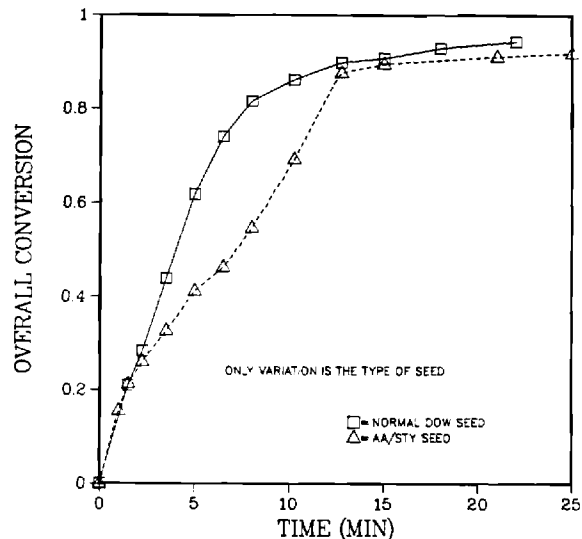


Figure 21 Effect of type of seed particles on the polymerization rate of the AA/styrene (40/160 g) system.

Egusa and Makuuchi,⁷ and others have clearly shown that carboxyl groups concentrate on the particle surface in acid-styrene reactions, especially when AA is used. If this hydrophilic coating were present on the particles at the start of the reaction, it may tend to decrease the overall reaction rate even when high concentrations of styrene are present.

Two AA-styrene (40/160) copolymerizations were performed in series to test this assertion. The initial reaction was carried to essentially complete conversion over a 3-h period. The final product was then used as seed for the second AA-styrene (40/160) copolymerization. The same reaction conditions including the same number of particles were used in both reactions. The objective was to try to start the second reaction with particles that had a high degree of hydrophilic polymer already coated onto the shell of the particles and observe whether the overall reaction rate was subsequently decreased. If the coating on the particles has no effect, the second reaction should be somewhat faster due to the larger seed particle size, since a larger particle size should lead to both a larger \bar{n} and a greater swelling of the particles with monomer²⁸ and thus a greater concentration of monomer inside the particles where the reaction is usually highest. The overall conversion data exhibited in Figure 21 for an AA-styrene run with normal seed particles is compared to overall conversion data obtained with the larger "AA-styrene" seed particles.

The reaction rate for the run with the AA-styrene seed particles is actually somewhat lower than the run with the normal seed particles suggesting that

the hydrophilic shell of polymer around the polymer particles may have inhibited the diffusion of oligomer radicals into the particles even though high concentrations of styrene were still present in the system.

The emulsion copolymerization model was modified to account for interval IV in the AA-styrene reaction. Once the conversion of styrene exceeded 0.999, all reaction in the particles was set to zero and only reaction in the aqueous phase was assumed to be significant. Partition calculations were made on the assumption that the amount of residual styrene was negligible. Therefore, only the partition of acid between the particle and aqueous phases was calculated. Results from the model, shown in Figures 22, 23, and 24 for the 20/180, 40/160, and 70/130 monomer ratios, respectively, reveal that interval IV calculations produce a much better match to the experimental data than when particle phase reaction of AA is included, as shown earlier for the 40/160 monomer ratio in Figure 9. However, the efficiency factor for radical formation had to be adjusted to 0.1 during the interval IV calculations to get the best fit of the data for all three runs.

The predicted and experimental results for both AA and styrene agree fairly well for the 20/180 and 40/160 recipes. The model predicts the styrene conversion behavior fairly well for the 70/130 recipe. However, the model underestimates the reaction rate of AA for this acid/styrene ratio. The AA monomer utilizes a more complex reaction mechanism than

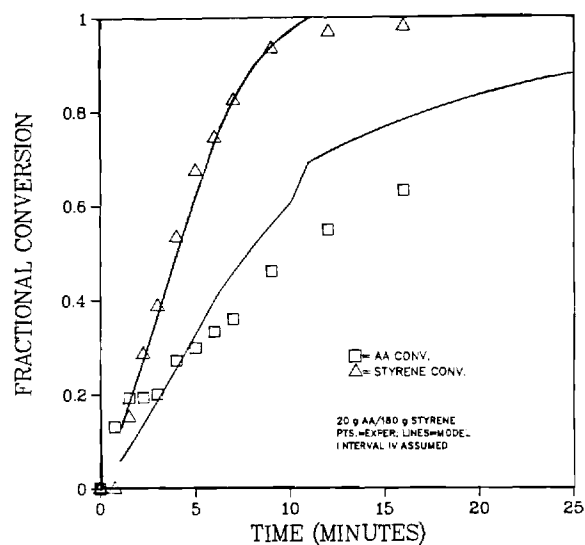


Figure 22 Comparison of predicted and experimental conversion behavior for a seeded, batch AA/styrene (20/180 g) copolymerization assuming that particle-phase reaction rates are negligible during interval IV.

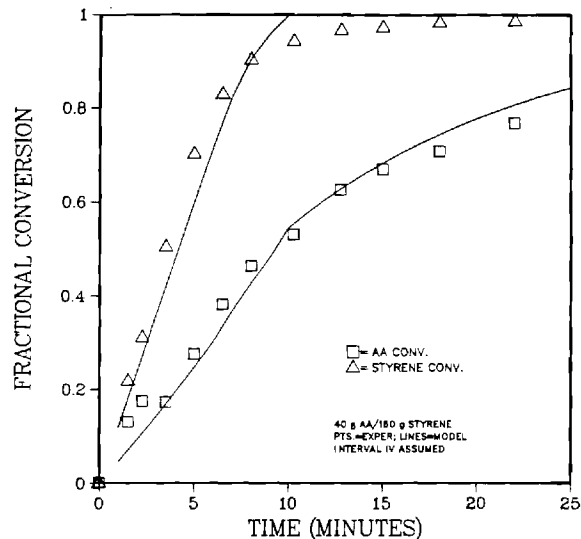


Figure 23 Model prediction of an AA/styrene (40/160 g) seeded copolymerization assuming that particle-phase reaction rates are negligible during interval IV.

the MAA monomer. Since a large fraction of the total monomer in the 70/130 recipe is comprised of AA, complexities in the AA reaction mechanism, which are not included in the present model, may contribute more significantly to the large disagreement in the predicted and experimental AA conversion-time results for this recipe than for the other recipes that utilized a smaller fraction of AA.

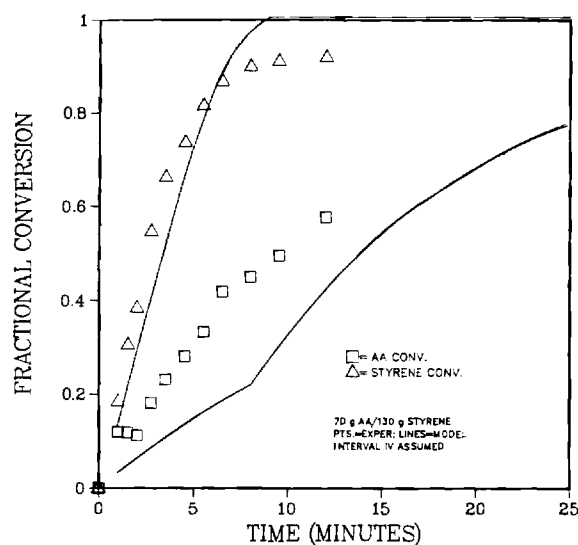


Figure 24 Comparison of predicted and experimental conversion behavior for a seeded, batch AA/styrene (70/130 g) copolymerization assuming that particle-phase reaction rates are negligible during interval IV.

Typical predicted rates of reaction of styrene in the particle phase and AA in both the particle and aqueous phases for the AA/styrene 40/160 recipe are exhibited in Figure 25. Though the values differ, the trends are the same for the other recipes examined in this work. There is a sharp increase in the predicted aqueous-phase reaction rates of AA and a sharp decrease in the predicted particle phase reaction rates at the beginning of interval IV. This sharp transition reflects the assumption that the reaction rates inside the particles become zero during interval IV (after the styrene conversion exceeds 99.9%) and that all of the reaction occurs in the aqueous phase. The actual system probably exhibits a much smoother transition of the primary reaction locus from the particle to the aqueous phase. However, since parameters such as \bar{k}_c , \bar{k}_{des} , \bar{n} , and the monomer partition will all be affected during this transition, the complexity of the system makes it extremely difficult to attempt to quantify all of these changes. Additionally, experimental verification of the predicted changes in each of these variables would be very onerous. Therefore, a step transition was implemented in the calculation when advancing from interval III to interval IV.

The decrease in reaction rate of AA after most of the styrene in the reactor has been depleted may be due in part to a decrease in the hydrophobicity of the oligomer radicals. It may also be due to the presence of a hydrophilic polymer coating, which surrounds the polymer particle and inhibits the penetration of hydrophilic oligomeric radicals into the particle core where additional reaction could occur.

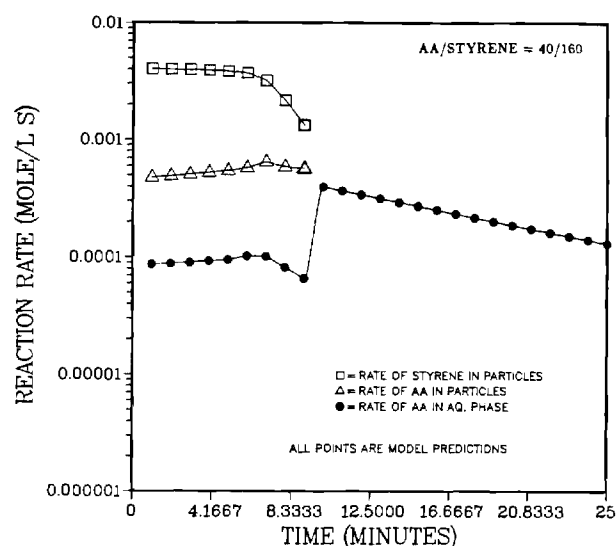


Figure 25 Predicted reaction rates of AA and styrene as a function of time for an acid/styrene ratio of 40/160.

Both explanations result in an overall decrease in the rate of diffusion of oligomer radicals and monomer into the polymer particle and a shift of the primary reaction locus into the aqueous phase. The fact that the AA reaction rate at high conversion is much slower than that expected if AA reacted significantly in both phases supports the concept of an interval IV in the AA styrene emulsion copolymerization system. Though the model presented in this work represents advances in quantitatively predicting the reaction rates of a seeded AA-styrene batch emulsion copolymerization, it is clear that this reaction system is not completely understood.

CONCLUSIONS

An overall kinetic model that includes reaction in both particle and aqueous phases has been developed for predicting batch copolymerization rates in seeded acid-styrene emulsion systems. The model utilizes thermodynamic partition equations to calculate the concentration of monomer in the aqueous, droplet, and particle phases. Radical capture coefficients are estimated from experiment, and radical desorption coefficients may be calculated using a model developed for copolymerization by Nomura et al.¹⁰ The kinetic model predicts the MAA-styrene conversion-time behavior quite well for a range of initial monomer concentrations. The model results in good predictions of the AA-styrene conversion-time behavior until the point where the styrene is almost entirely consumed. The predicted reaction rate of AA then exceeds the experimental rate.

The primary reaction locus in the AA-styrene system may shift into the aqueous phase after the styrene has been consumed. This shift in the primary reaction locus may be attributed to two main effects: (i) the increase in hydrophilicity of the oligomeric radicals due to depletion of styrene, which decreases the driving force for the radicals to penetrate into the hydrophobic particle core, and (ii) the potential barrier for penetration of these oligomeric radicals due to a buildup of polyAA on the surface of the polymer particles. Modification of the overall kinetic model to account for interval IV behavior leads to better predictions of the conversion-time behavior for the AA-styrene system.

Funding for this work was provided by Dow Chemical, Midland, Michigan, and the National Science Foundation under Grant No. CBT-8717926.

NOMENCLATURE

A	parameter relating the relative reactivities of monomer i and monomer j
c_{mij}	chain transfer constant of oligomer i with monomer j
CMC	critical micelle concentration (mol/L _{aq})
d_p	particle diameter (cm)
D_w	diffusion coefficient of monomer in water (cm ² /s)
D_p	diffusion coefficient of monomer in polymer (cm ² /s)
f	initiator efficiency factor
$I_m(a)$	Bessel function
$[I]$	initiator concentration (mol/L)
j_{cr}	critical chain length for oligomers at which capture is likely to occur
\bar{k}_a	rate coefficient for absorption of radicals by particles (1/s)
\bar{k}_c	average radical capture coefficient (cm ³ /s)
k_d	initiator decomposition rate coefficient (1/s)
\bar{k}_{des}	average radical desorption coefficient (1/s)
k'_{des}	volume-independent desorption coefficient (cm ² /s)
k_I	initiation constant of monomer from initiator radicals (L/mol s)
k_p	propagation constant (L/mol s)
k_{pji}	propagation constant of monomer i with monomer j (L/mol s)
k_t	termination constant (L/mol s)
\bar{k}_{tij}	average termination constant of radical i with radical j (L/mol s)
k_{tr}	monomer chain transfer constant (L/mol s)
k_{tw}	termination constant in the aqueous phase (L/mol s)
$[M]$	concentration of monomer (mol/L)
m	dimensionless parameter used in calculating \bar{n}
m_{di}	partition coefficient of monomer i between the particle and aqueous phases
\bar{n}	average number of free radicals per particle
N_A	Avogadro's number (6.02×10^{23} /mol)
N_n	number of particles containing n free radicals
N_p	concentration of polymer particles (no./L _{aq})
r_i	reactivity ratio = k_{pji}/k_{pji}
R_c	rate of capture of oligomer radical by particles (mol/L _{aq} s)

R_i	rate of initiation (mol/L _{aq} s)
R_p	rate of polymerization (mol/L _{aq} s)
SDS	sodium dodecyl sulfate (anionic surfactant)
T	temperature (°C)
t	time (s)
V	volume (cm ³)
Y	dimensionless parameter used in calculating \bar{n}

Greek Symbols

α_n	dimensionless parameter used in calculating \bar{n}
α'_n	dimensionless parameter used in calculating \bar{n}
ρ_a	rate of absorption of radicals into particles (1/s)
ρ_i	rate of generation of free radicals in the aqueous phase (mol/L _{aq} s)

Subscripts

aq	aqueous phase
A	monomer A (acid)
B	monomer B (styrene)
I	initiator
m	monomer
p	polymer or particle phase
P	polymer or copolymer
T or tot	total
w	water or aqueous phase

REFERENCES

1. R. G. Fordyce and G. E. Ham, *J. Am. Chem. Soc.*, **69**, 695 (1947).
2. S. Muroi, *J. Poly. Sci.*, **10**, 713 (1966).
3. W. Ceska, *J. Appl. Poly. Sci.*, **18**, 427 (1974a).
4. W. Ceska, *J. Appl. Poly. Sci.*, **18**, 2493 (1974b).
5. K. Sakota and T. Okaya, *J. Appl. Poly. Sci.*, **21**, 1035 (1977).
6. B. R. Vijayendran, *J. Appl. Poly. Sci.*, **23**, 893 (1979).
7. S. Egusa and K. Makuuchi, *J. Poly. Sci.*, **20**, 863 (1982).
8. S. P. Gasper and J. S. Tan, in *Water Soluble Synthetic Polymers: Properties and Behavior*, ed. P. Molyneux, Vol. I, CRC Press, Cleveland, OH, 1983.
9. F. L. Martin and A. E. Hamielec, *J. Appl. Polym. Sci.*, **27**, 489 (1982).
10. M. Nomura, K. Yamamoto, I. Horie, and K. Fujita, *J. Appl. Polym. Sci.*, **27**, 2483 (1982).
11. J. Ugelstad and F. K. Hansen, *Rubber Chem. Tech.*, **49**, 536 (1976).

12. R. N. Mead, Ph.D. Thesis, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA (1987).
13. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
14. J. Ugelstad, P. C. Mork, and J. O. Aasen, *J. Polym. Sci. A-1*, **5**, 2281 (1967).
15. J. Ugelstad and P. C. Mork, *Br. Polym. J.*, **2**, 31 (1970).
16. M. Nomura, M. Harada, K. Nakagowara, W. Eguchi, and S. Nagata, *J. Chem. Eng. Jpn.*, **4**, 160 (1970).
17. M. Nomura, M. Harada, W. Eguchi, and S. Nagata, *J. Appl. Polym. Sci.*, **15**, 675 (1971).
18. M. Nomura, H. Kojima, M. Harada, W. Eguchi, and S. Nagata, in *Emulsion Polymerization*, ed. I. Piirma and J. C. Gardon, *ACS Symposium Series*, **24**, 102 (1976).
19. H. C. Lee, Ph.D. Thesis, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA (1985).
20. C. S. Chern, Ph.D. Thesis, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA (1987).
21. D. C. Sundberg, J. Y. Hsieh, S. K. Soh, and R. F. Baldus, in *Emulsion Polymers and Emulsion Polymerization*, ed. D. R. Basset and A. E. Hamielec, *ACS Symposium Series* (1981).
22. G. L. Shoaf, Ph.D. Thesis, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA (1989).
23. R. G. Gilbert and D. H. Napper, *JMS - Rev. Macromol. Chem. Phys.*, **c23**, 127 (1983).
24. P. J. Feeney, Ph.D. Dissertation, Department of Physical Chemistry, University of Sydney, Sydney, Australia (1986).
25. F. K. Hansen and J. Ugelstad, *J. Polym. Sci.: Polym. Chem. Ed.*, **16**, 1953 (1978).
26. B. S. Hawkett, D. H. Napper, and R. G. Gilbert, *J. Polym. Sci.: Polym. Chem. Ed.*, **19**, 3173 (1981).
27. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 2nd ed., Wiley, New York, 1975.
28. L. Jansson, Masters Thesis, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA (1983).
29. G. Blauer, *J. Polym. Sci.*, **11**, 189 (1953).
30. V. F. Gromov, N. I. Galperina, T. O. Osmanov, P. M. Khomikovskii, and A. D. Abkin, *Eur. Polym. J.*, **16**, 529 (1980).
31. V. G. Popov, D. A. Topchiev, V. A. Kabanov, and V. A. Kargin, *Vysokomol. soyed.*, **A14**(1), 117 (1972).
32. R. Z. Greenley, *J. Macromol. Sci.-Chem.*, **A14**(4), 427 (1980).
33. F. V. Loncar, Ph.D. Thesis, Emulsion Poly. Inst., Lehigh University Bethlehem, PA (1985).
34. C. R. Wilke and P. Chang, *AIChE J.*, **1**(2), 264 (1955).
35. C. W. Brown and G. A. Taylor, *J. Appl. Polym. Sci.*, **13**, 629 (1969).
36. G. L. Shoaf and G. W. Poehlein, *I.E. and C. Fundamentals*, to appear.
37. M. H. Litt, R. Patsiga, and V. T. Stannett, *J. Polym. Sci., A-1*, **8**, 3607 (1970).
38. H. Kawaguchi, Y. Ohtsuka, and Y. Sugi, *J. Appl. Polym. Sci.*, **26**, 1637 (1981).

Received March 6, 1990

Accepted May 14, 1990

Solution and Emulsion Polymerization with Partially Neutralized Methacrylic Acid

GLENN L. SHOAF and GARY W. POEHLEIN*

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

SYNOPSIS

Polymerizations of partially neutralized methacrylic acid (MAA) were performed in both solution and emulsion systems. Polymerizations of MAA in solution were performed at an overall degree of neutralization ranging between 0 and 1. The rate of polymerization of the acid is found to decrease as the degree of neutralization increases due to increased electrostatic repulsion of the dissociated acid species (anions). The degree of neutralization of the unreacted monomer increases as the conversion increases. A kinetic model based on a copolymerization mechanism is used to describe the reaction behavior. Partially neutralized methacrylic acid was also polymerized with styrene in a seeded emulsion system. The reaction rates of both the acid and styrene decrease as the overall degree of neutralization increases. A previously developed emulsion copolymerization kinetic model is extended to account for reaction of the anions and used to investigate the overall "terpolymerization" of the acid, anions, and styrene.

INTRODUCTION

Carboxylic acid monomers such as methacrylic acid (MAA), acrylic acid (AA), and itaconic acid (IA) are used in a large number of commercial latex products including paper coatings, textile coatings, and adhesives. These monomers are completely soluble in water. Therefore, even in an emulsion polymerization, they react to a significant extent in the aqueous phase. A kinetic model to describe emulsion copolymerization of carboxylated styrene systems was developed by Shoaf and Poehlein.¹ Formation of many of the commercial products using these monomer systems requires strict control of the pH of the reacting system to attain the desired properties in the final product. Often small amounts of base, such as sodium hydroxide, are added that partially neutralize the acid, thus forming anionic species. Partial neutralization of a carboxylic acid monomer such as AA or MAA reduces the overall reactivity of the monomer due to electrostatic effects of the anions. The reduced reactivity of the partially dissociated monomer has been clearly shown by

Katchalsky and Blauer,² Pinner,³ and Kabanov et al.⁴

Mechanisms for polymerization of methacrylic acid in solution for both the unneutralized and partially neutralized cases are examined in this work. Kinetic models are used to describe the reaction behavior of both the undissociated acid and the anion. Effects of the degree of neutralization on the partition behavior and reaction rates are also examined for the MAA-styrene emulsion system. A kinetic model describing the emulsion polymerization behavior of the acid, anion, and styrene in both the particle and aqueous phases is developed and used to investigate the reaction mechanism for this complicated "terpolymerization" system.

THEORY

Polymerization of Carboxylic Acids

Free-radical solution polymerization of AA and MAA has been studied by several workers including Katchalsky and Blauer,² Pinner,³ Blauer,⁵ Galperina et al.,⁶ Gromov et al.,⁷ and Mishra and Bhadani.⁸ Kinetic information such as reaction rates, propagation and termination constants, activation ener-

* To whom correspondence should be addressed.

gies plus various effects of solvents and acid dissociation on these parameters have been determined through these studies. A variety of initiator systems as well as solvent species were used.

Galperina et al.⁶ and Gromov et al.⁷ studied the effect of solvent on radical polymerization of AA, MAA, and fluoracrylic acid. The solvents were water, formamide, and dimethylsulphoxide (DMSO). The initial rates of polymerization were proportional to the first power of the monomer concentration and the one-half power of the initiator concentration. The rate, therefore, could be described by the basic kinetic equation for free-radical polymerization.

$$R_p = k_p \left(\frac{2fk_d[I]}{2k_t} \right)^{1/2} [M] \quad (1)$$

k_p is the propagation constant, k_t is the termination constant, k_d is the initiator decomposition constant, f is the initiator efficiency factor, and $[M]$ and $[I]$ are the monomer and initiator concentrations, respectively. Values for k_p , k_t , and activation energies were reported for a range of temperatures. The reactions in water were carried out at low pH (2.2 and below) so that very little of the acid was dissociated. The monomer concentrations ranged from about 2 to 8 wt %.

The dependence of rate on pH, as reported by Plochocka,⁹ is illustrated in Figure 1. The rate of polymerization decreases sharply up to pH 6 to 7. This decrease in rate is not surprising since the degree of neutralization (and thus the concentration of anions) increases sharply between pH 4 and 5.

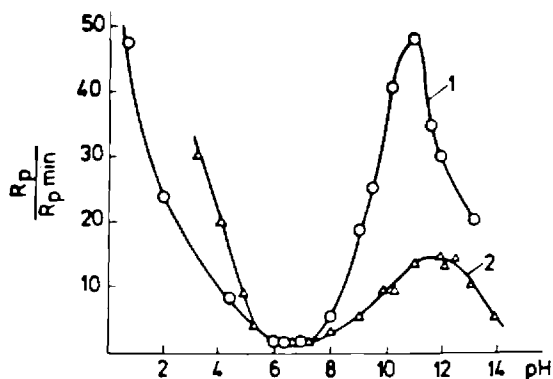


Figure 1 Relative rates of polymerization vs. pH adjusted by an addition of NaOH for MAA (1) and AA (2) at 60°C. Curve 1: $R_{pmin} \times 10^5 = 0.115$ mol/L/s, $[MAA] = 0.92$ mol/L, $[AIBN] = 5 \times 10^{-4}$ mol/L; curve 2: $R_{pmin} \times 10^5 = 0.43$ mol/L/s $[AA] = 1.2$ mol/L, $[AIBN] = 5 \times 10^{-3}$ mol/L. (Replotted from Plochocka⁹).

The rate then slowly increases to a maximum at a pH of 11 to 12. The increase in rate between a pH of 7 and 12 may be a result of cation binding by the carboxylate radical, which may decrease the electrostatic repulsion with an anionic monomer.⁹

Katchalsky and Blauer² developed general rate expressions for the homopolymerization of carboxylic acids. They noticed that at pH > 5.5 the polymerization rate approached zero, so they assumed that the dissociated species did not react. They proposed that the rate of reaction for a partially neutralized carboxylic acid system was proportional to the concentration of undissociated species as given by

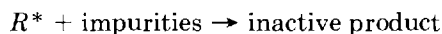
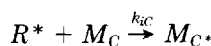
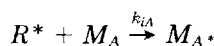
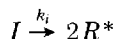
$$\frac{-d[M_{tot}]}{dt} = k_{p11} \left(\frac{fk_d}{k_{t11}} \right)^{1/2} [I]^{1/2} [M_{tot}] (1 - \alpha) \quad (2)$$

where $[M_{tot}]$ (mol/L) is the total concentration of monomer, k_{p11} is the propagation constant (L/mol s), k_{t11} is the termination constant (L/mol s), f is the initiator efficiency factor, k_d is the initiator decomposition constant, $[I]$ is the concentration of initiator, and α is the fraction of dissociation of the acid monomer.

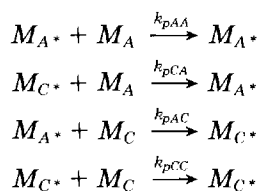
Pinner³ reported that the absence of polymerization at a pH of 5.5 was probably due to inactivation of H_2O_2 , the initiator used by Katchalsky and Blauer in their studies. Pinner showed that reaction occurs at pH as high as 13 is persulfate is used despite the ionization of the monomer. Blauer,⁵ in a later article, stated that his original assertion that ionized monomer is unable to propagate polymerization was in error. He performed runs using AIBN as initiator and obtained polymerization at a pH as high as 12. Blauer⁵ then asserted that the dependence of rate of MAA polymerization on the pH suggests that both un-ionized and ionized monomers and radicals do copolymerize.

Thus the acid (M_A) and anion (M_C) species do polymerize, but they exhibit very different reactivities. Therefore, Pinner³ proposed that the reaction mechanism is best described by the following set of copolymerization reactions:

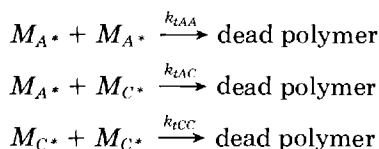
Initiation



Propagation



Termination



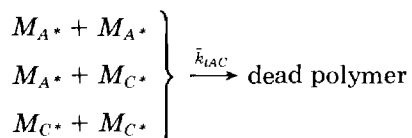
He used the rate equation based on chemical controlled termination to predict the reaction rate.

$$\begin{aligned} -\frac{d([M]_A + [M]_C)}{dt} \\ = \frac{(r_A[M]_A^2 + 2[M]_A[M]_C + r_C[M]_C^2)R_i^{1/2}}{r_A^2\delta_A^2[M]_A^2 + 2\phi r_A r_M \delta_A \delta_C [M]_A [M]_C + r_C^2\delta_C^2[M]_C^2} \quad (3) \end{aligned}$$

where $\delta_A^2 = k_{tAA}/k_{pAA}^2$, $\delta_C^2 = k_{tCC}/k_{pCC}^2$, $\phi = k_{tAC}/(k_{tAA}k_{tCC})^{1/2}$ = cross termination coefficient, and $R_i = 2fk_d[I]$.

The basic assumption for chemical controlled termination is that the termination reactions are dependent only on the nature of the end unit of the active radical chain. However, there is a great deal of uncertainty concerning the appropriate value for ϕ , which represents the relative tendency for two different types of radical chain ends to terminate.

Atherton and North¹⁰ later showed that many free-radical polymerization termination reactions are diffusion controlled, and the termination rate is independent of the nature of the active radical chain end. This approach utilizes a diffusion-controlled termination constant, \bar{k}_{tAC} , which depends on the monomer feed composition instead of using a constant ϕ factor.



\bar{k}_{tAC} is a function of the copolymer composition and for the ideal case, eq. (4) may be used.

$$\bar{k}_{tAC} = F_A k_{tAA} + F_C k_{tCC} \quad (4)$$

where F_i is the fraction of monomer i in the copolymer being formed.

The reaction rate equation developed by Atherton and North¹⁰ is given by

$$R_p = \frac{(r_A[M]_A^2 + 2[M]_A[M]_C + r_C[M]_C^2)R_i^{1/2}}{\bar{k}_{tAC}^{1/2} [(r_A[M]_A/k_{pAA}) + (r_C[M]_C/k_{pCC})]} \quad (5)$$

where r_A and r_C are the reactivity ratios of the undissociated species, and dissociated species as determined from Q and e values reported in the literature;¹¹ $[M_A]$ and $[M_C]$ are the concentrations of undissociated and dissociated species; and \bar{k}_{tAC} is an average termination constant.

The partially neutralized solution polymerization of MAA with the copolymerization reaction mechanism based on diffusion-controlled termination is the subject of the present study. The copolymerization of partially neutralized MAA, however, is unique because the undissociated and dissociated species are in dynamic equilibrium.

Any monomer unit along the polymer backbone may change from M_A to M_B and vice versa after polymerization. Such changes result from the equilibrium that exists between the undissociated and dissociated carboxyl groups of the monomer and polymer. When the monomer is combined into a polymer chain, the carboxyl group becomes less likely to release the H^+ ion and thus becomes a somewhat weaker acid relative to the single monomer molecule. Thus, the monomer and polymer exhibit different dissociation constants, and the "average" dissociation constant for the system changes as the relative amounts of monomer and polymer change. The net result is that after an M_A monomer unit reacts it may be converted to an M_B and then back to an M_A again due to the dynamic equilibrium process between the substituent carboxyl groups in the system. Therefore, the copolymer composition cannot be predicted in the conventional sense.

This equilibrium process is further complicated since the actual degree of neutralization of the unreacted monomer changes throughout the polymerization. This phenomenon occurs because the dissociation constant given by eq. (6) for the polymer differs from that of the acid:

$$K_{a_i} = \frac{[H^+][A_i^-]}{[HA_i]} \quad (6)$$

where $[H^+]$ is the concentration of hydronium ions, $[A_i^-]$ is the concentration of dissociated monomer i

molecules, and $[HA_i]$ is the concentration of undissociated monomer i molecules. The pK_a value for MAA and polyMAA are 4.36 and 7.0, respectively.¹² Because the pK_a values of the monomer and polymer differ by 2 to 3 units, the monomer may be considered to be a strong acid relative to the polymer. Hence, any dissociated monomer that reacts and becomes part of a polymer chain will develop a more basic character relative to the unreacted monomer molecules, so it may lose the Na^+ ion (assuming sodium hydroxide is the base used to neutralize a portion of the acid) and become reassociated with an H^+ ion. This equilibrium process will result in the dissociation of an additional monomer molecule. The net effect is that adding a base such as sodium hydroxide (NaOH) to a mixture of acid monomer and acid polymer tends to neutralize the acid monomer first. Since the amount of monomer decreases in a reacting system, but the amount of base is constant the effective degree of neutralization of the unreacted monomer will increase as the conversion increases. [Example: Add 1.0 mol of acid, 0.25 mol base ($DN_{overall} = 0.25$). After 0.75 mol of acid has reacted, the 0.25 mol of remaining acid will be completely neutralized (extreme case) resulting in $DN_{actual} = 1.0$.]

This changing DN of the unreacted monomer can greatly affect the reaction rates and copolymer compositions over the reaction period in a manner much different from the case where the DN of the unreacted monomer is assumed to remain the same. This assertion was confirmed experimentally by running a MAA reaction with an initial DN of about 0.59. The pH was allowed to change naturally (from 4.5 to 5.4) over the reaction period. The same reaction was then repeated, but trifluoroacetic acid was added throughout the reaction so as to maintain a constant pH (and thus constant DN of unreacted monomer) at the initial value of 4.5. Results from these runs shown in Figure 2 confirm that the reaction rate depends strongly on the DN of the system throughout the reaction period. The reaction with constant pH is much faster because the fraction of unreacted acid molecules that ionize does not increase during the reaction.

The following section describes a method for predicting the actual DN of the unreacted monomer over the entire conversion period. Equilibrium expressions for both the monomer (1) and polymer (2) are given by

$$K_{a_1} = \frac{[H^+][A_1^-]}{[HA_1]} \quad (7)$$

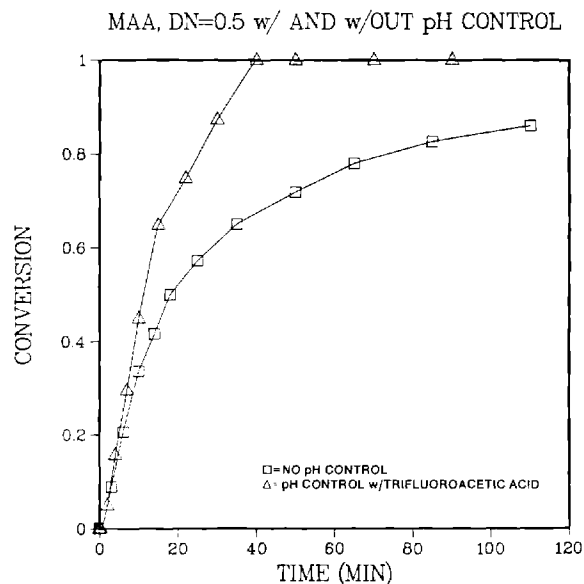


Figure 2 Comparison of reaction rates of 7.0 wt % MAA at initial DN of 0.59 with constant pH (pH control) and with naturally changing pH (no pH control).

$$K_{a_2} = \frac{[H^+][A_2^-]}{[HA_2]} \quad (8)$$

(This analysis assumes that an average K_a value may be used for the polymer. Actually, this value depends on the chain length and chain conformation of the polymer such that a distribution of K_a values corresponding to the distribution of polymer chain lengths and chain conformations better describes the actual system.) The ratio of the K_{a_i} values gives

$$\frac{K_{a_1}}{K_{a_2}} = \frac{x(y-z)}{(M_A - x - y)z} \quad (9)$$

Here, x is the moles of dissociated monomer, y is the moles of reacted monomer, z is the moles of dissociated polymer, and M_A is the initial moles of monomer charged.

The total moles of dissociated species is

$$[A_1^-] + [A_2^-] = x + z = (DN_0)M_A \quad (10)$$

where, DN_0 is the overall degree of neutralization, not the DN of the unreacted monomer.

Solving for z and substituting in eq. (9) gives

$$\frac{K_{a_1}}{K_{a_2}} = \frac{x[y - (DN_0)M_A + x]}{(M_A - x - y)\{(DN_0)M_A - x\}} \quad (11)$$

The value of x for any given value of y (obtained from the conversion) may be obtained by taking the positive root of this quadratic equation. The actual degree of neutralization of the unreacted monomer may then be obtained as a function of the moles of reacted monomer by

$$\text{DN}(y) = \frac{x}{M_A - y} \quad (12)$$

Emulsion Copolymerization Model with Aqueous-Phase Polymerization

An emulsion copolymerization model that accounts for polymerization in both the particle and aqueous phases was developed by Shoaf and Poehlein.¹ The particle-phase reaction rates were modeled using a development presented by Nomura et al.¹⁴ These equations are reproduced below:

$$R_{pA} = \frac{[1/(1+A)](k_{pAA}[M_A]_p + k_{pAB}[M_B]_p)\bar{n}_t N_p}{N_A} \quad (13)$$

$$R_{pB} = \frac{[A/(1+A)](k_{pBA}[M_A]_p + k_{pBB}[M_B]_p)\bar{n}_t N_p}{N_A} \quad (14)$$

where

$$A = \frac{\bar{n}_B}{\bar{n}_A} = \frac{k_{pAA} r_B [M_B]_p}{k_{pBB} r_A [M_A]_p} \quad (15)$$

An expression for predicting the aqueous-phase free-radical concentration was also developed.

$$[R_{\text{tot}}^*] = \frac{\sqrt{(\bar{k}_c N_p)^2 + 8\bar{k}_{tw}(\bar{k}_{\text{des}} N_p \bar{n}_t / N_A + 2f k_d [I_2])} - \bar{k}_c N_p}{4\bar{k}_{tw}} \quad (16)$$

This expression could then be used to predict the rates of reaction of both A and B monomers in the aqueous phases using

$$R_{pA\text{aq}} = \left(\frac{k_{pAA} + A k_{pBA}}{1 + A} \right) [R_{\text{tot}}]_{\text{aq}} [A]_{\text{aq}} \quad (17)$$

$$R_{pB\text{aq}} = \left(\frac{k_{pAB} + A k_{pBB}}{1 + A} \right) [R_{\text{tot}}]_{\text{aq}} [B]_{\text{aq}} \quad (18)$$

The overall emulsion copolymerization model then takes the form:

$$R_{p\text{tot}} = R_{pAp} + R_{pBp} + R_{pA\text{aq}} + R_{pB\text{aq}} \quad (19)$$

Details of the overall model development and methods of determining the various parameters in the rate equations are discussed by Shoaf and Poehlein.¹

Possible Approach for Modeling Emulsion Copolymerization with Carboxylic Acid Monomers at $\text{DN} > 0$

An extension of the preceding emulsion copolymerization model to account for the dissociated acid species obtained when the acid has been partially neutralized is now presented.

DN is defined as moles NaOH/moles acid fed. α_p is the fraction of acid in the particle phase that is dissociated, and α_{aq} as the fraction of acid in the aqueous phase that is dissociated. As long as the value of DN is greater than zero, then the overall system actually consists of three species: undissociated acid (A), styrene (B), and dissociated acid (C). (The α values are not equal to zero if no base is added. However, they are very small ($\approx 10^{-4.4}$) and may be approximated to be zero.) The following equations may be used to express the reaction rates in the particles.

$$R_{pA} = k_{pAA}[M_A]_p \bar{n}_A \frac{N_p}{N_A} + k_{pBA}[M_A]_p \bar{n}_B \frac{N_p}{N_A} + k_{pCA}[M_A]_p \bar{n}_C \frac{N_p}{N_A} \quad (20)$$

$$R_{pB} = k_{pBB}[M_B]_p \bar{n}_B \frac{N_p}{N_A} + k_{pAB}[M_B]_p \bar{n}_A \frac{N_p}{N_A} + k_{pCB}[M_B]_p \bar{n}_C \frac{N_p}{N_A} \quad (21)$$

$$R_{pC} = k_{pCC}[M_C]_p \bar{n}_C \frac{N_p}{N_A} + k_{pAC}[M_C]_p \bar{n}_A \frac{N_p}{N_A} + k_{pBC}[M_C]_p \bar{n}_B \frac{N_p}{N_A} \quad (22)$$

where $[M_A]_p$ is the concentration of undissociated acid in the particle, $[M_B]_p$ is the concentration of styrene in the particle, $[M_C]_p$ is the concentration of dissociated acid in the particle, N_p is the number of particles/ L_{aq} , k_{pji} is the propagation constant for radical i with monomer j , \bar{n}_j is the average number of j radicals/particle, and N_A is Avogadro's number.

The dissociated species, C, is treated like a third monomer in the above rate expressions. Nomura et al.¹⁴ give expressions for the change in n_j with time

for a copolymer system. Their analysis may be extended to include the dissociated species, C:

$$\begin{aligned} \frac{d\bar{n}_A}{dt} = & \frac{\rho_e w_a}{N_p} - 2k_{tpAA} \frac{\bar{n}_A^2}{\nu_p} - k_{tpAB} \frac{\bar{n}_A \bar{n}_B}{\nu_p} - k_{tpAC} \frac{\bar{n}_A \bar{n}_C}{\nu_p} \\ & - k_{desA} \bar{n}_A - (k_{pAB} + k_{mAB}) [M_B]_p \bar{n}_A \\ & + (k_{pBA} + k_{mBA}) [M_A]_p \bar{n}_B \\ & - (k_{pAC} + k_{mAC}) [M_C]_p \bar{n}_A \\ & + (k_{pCA} + k_{mCA}) [M_A]_p \bar{n}_C = 0 \quad (23) \end{aligned}$$

where ρ_e is the rate of adsorption of radicals by the particles, w_a is the probability of adsorbed radicals becoming an A radical, k_{mij} and k_{tvi} are chain transfer and termination constants, respectively, and k_{des} is a desorption constant.

Similar equations may be written for $d\bar{n}_B/dt$ and $d\bar{n}_C/dt$. Summation of these equations gives

$$\begin{aligned} \frac{d\bar{n}}{dt} = & \frac{d(\bar{n}_A + \bar{n}_B + \bar{n}_C)}{dt} \\ = & \frac{\rho_e}{N_p} - 2k_{tpAA} \frac{\bar{n}_A^2}{\nu_p} - 2k_{tpAB} \frac{\bar{n}_A \bar{n}_B}{\nu_p} - 2k_{tpBB} \frac{\bar{n}_B^2}{\nu_p} \\ & - 2k_{tpAC} \frac{\bar{n}_A \bar{n}_C}{\nu_p} - 2k_{tpBC} \frac{\bar{n}_B \bar{n}_C}{\nu_p} - 2k_{tpCC} \frac{\bar{n}_C^2}{\nu_p} \\ & - (k_{desA} \bar{n}_A + k_{desB} \bar{n}_B + k_{desC} \bar{n}_C) \quad (24) \end{aligned}$$

Nomura et al. note that the termination and desorption terms in eq. (24) are at most equal to ρ_e/N_p . If the rate of desorption is relatively small, $\rho_e \sim R_i$, and w_a is less than unity. Therefore, Nomura et al. state that the last terms (four in this case) in eq. (23) are dominating. ($\rho_e/N_p \approx 0.01$ to 1 and $k_p[M_i]_p \bar{n} \approx 100$ based on typical emulsion reaction systems.) The propagation constants are usually much greater in magnitude than the chain transfer rate constants ($k_p \gg k_m$) so eq. (23) can be simplified to

$$\begin{aligned} -k_{pAB} [M_B]_p \bar{n}_A + k_{pBA} [M_A]_p \bar{n}_B \\ - k_{pAC} [M_C]_p \bar{n}_A + k_{pCA} [M_A]_p \bar{n}_C = 0 \quad (25) \end{aligned}$$

Equilibrium between species A and C is described by

$$[M_A]_p = (1 - \alpha_p) [M_A]_{p_{tot}} \quad (26)$$

$$[M_C]_p = \alpha_p [M_A]_{p_{tot}} \quad (27)$$

where α_p is the degree of neutralization or fraction of dissociation of acid in the particles, and $[M_A]_{p_{tot}} = [M_A]_p + [M_C]_p$ is the total amount of acid species in the particles.

If this same relationship of dissociated and undissociated acid species applies to the radicals (i.e., the presence or absence of a radical is assumed not to affect whether the carboxyl group is dissociated or undissociated), then

$$\bar{n}_A = (1 - \alpha_p) \bar{n}_{A_{tot}} \quad (28)$$

$$\bar{n}_C = \alpha_p \bar{n}_{A_{tot}} \quad (29)$$

where $\bar{n}_{A_{tot}} = \bar{n}_A + \bar{n}_C$ is the total number of acid radicals.

Equation (25) may then be rewritten using the expressions given by eqs. (26) through (29). Rearrangement leads to the following expression:

$$\begin{aligned} A = & \frac{\bar{n}_B}{\bar{n}_{A_{tot}}} \\ = & \frac{k_{pAB} [M_B]_p + (k_{pAC} - k_{pCA}) \alpha_p [M_A]_{p_{tot}}}{k_{pBA} [M_A]_{p_{tot}}} \quad (30) \end{aligned}$$

Then,

$$\bar{n}_{A_{tot}} = \frac{1}{1 + A} \bar{n} \quad (31)$$

$$\bar{n}_A = (1 - \alpha_p) \frac{1}{1 + A} \bar{n} \quad (32)$$

$$\bar{n}_B = \frac{A}{1 + A} \bar{n} \quad (33)$$

$$\bar{n}_C = \alpha_p \frac{1}{1 + A} \bar{n} \quad (34)$$

Finally,

$$\begin{aligned} R_{pA} = & \left(k_{pAA} \frac{1 - \alpha_p}{1 + A} + k_{pBA} \frac{A}{1 + A} + k_{pCA} \frac{\alpha_p}{1 + A} \right) \\ & \times (1 - \alpha_p) [M_A]_{p_{tot}} \bar{n} \frac{N_p}{N_A} \quad (35) \end{aligned}$$

$$\begin{aligned} R_{pB} = & \left(k_{pBB} \frac{A}{1 + A} + k_{pAB} \frac{1 - \alpha_p}{1 + A} + k_{pCB} \frac{\alpha_p}{1 + A} \right) \\ & \times [M_B]_p \bar{n} \frac{N_p}{N_A} \quad (36) \end{aligned}$$

$$\begin{aligned} R_{pC} = & \left(k_{pCC} \frac{\alpha_p}{1 + A} + k_{pAC} \frac{1 - \alpha_p}{1 + A} + k_{pBC} \frac{A}{1 + A} \right) \\ & \times \alpha_p [M_A]_{p_{tot}} \bar{n} \frac{N_p}{N_A} \quad (37) \end{aligned}$$

Reaction Rate in the Aqueous Phase with $DN > 0$

The reaction rate in the aqueous phase is given by

$$\begin{aligned}
 R_{p_{aq}} &= -\left(\frac{d[M_A]_{aq} + d[M_B]_{aq} + d[M_C]_{aq}}{dt}\right) \\
 &= -\left(\frac{d[M_{A_{tot}}]_{aq} + d[M_B]_{aq}}{dt}\right) \\
 &= k_{p_{AA}}[M_A^*]_{aq}[M_A]_{aq} + k_{p_{AB}}[M_A^*]_{aq}[M_B]_{aq} \\
 &\quad + k_{p_{AC}}[M_A^*]_{aq}[M_C]_{aq} + k_{p_{BB}}[M_B^*]_{aq}[M_B]_{aq} \\
 &\quad + k_{p_{BA}}[M_B^*]_{aq}[M_A]_{aq} + k_{p_{BC}}[M_B^*]_{aq}[M_C]_{aq} \\
 &\quad + k_{p_{CC}}[M_C^*]_{aq}[M_C]_{aq} + k_{p_{CA}}[M_C^*]_{aq}[M_A]_{aq} \\
 &\quad + k_{p_{CB}}[M_C^*]_{aq}[M_B]_{aq} \quad (38)
 \end{aligned}$$

where $[M_j^*]_{aq}$ is the concentration of j radicals in the aqueous phase.

A steady-state concentration is assumed for each type of radical.

$$\begin{aligned}
 k_{p_{AB}}[M_A^*]_{aq}[M_B]_{aq} + k_{p_{AC}}[M_A^*]_{aq}[M_C]_{aq} \\
 = k_{p_{BA}}[M_B^*]_{aq}[M_A]_{aq} + k_{p_{CA}}[M_C^*]_{aq}[M_A]_{aq} \quad (39)
 \end{aligned}$$

$$\begin{aligned}
 k_{p_{BA}}[M_B^*]_{aq}[M_B]_{aq} + k_{p_{BC}}[M_B^*]_{aq}[M_C]_{aq} \\
 = k_{p_{AB}}[M_A^*]_{aq}[M_B]_{aq} + k_{p_{CB}}[M_C^*]_{aq}[M_B]_{aq} \quad (40)
 \end{aligned}$$

$$\begin{aligned}
 k_{p_{CA}}[M_C^*]_{aq}[M_A]_{aq} + k_{p_{CB}}[M_C^*]_{aq}[M_B]_{aq} \\
 = k_{p_{AC}}[M_A^*]_{aq}[M_C]_{aq} + k_{p_{BC}}[M_B^*]_{aq}[M_C]_{aq} \quad (41)
 \end{aligned}$$

In bulk or solution polymerizations the next step is to set the rate of initiation equal to the rate of termination.

$$R_i = R_{term}$$

However, in emulsion polymerization, capture and desorption of radicals must be taken into account.

$$R_i = R_{term} + R_{capture} - R_{des}$$

Substitution of the appropriate expression leads to

$$\begin{aligned}
 R_i = 2\bar{k}_{t_{ABC}}([M_A^*]_{aq} + [M_B^*]_{aq} + [M_C^*]_{aq})^2 \\
 + \bar{k}_c([M_A^*]_{aq} + [M_B^*]_{aq} + [M_C^*]_{aq})N_p \\
 - \frac{\bar{k}_{des}N_p\bar{n}}{N_A} \quad (42)
 \end{aligned}$$

where $\bar{k}_{t_{ABC}}$ is an average termination constant dependent on DN , and \bar{k}_c is an average capture constant. Since $[M_A^*]_{aq_{tot}} = [M_A^*]_{aq} + [M_C^*]_{aq}$, rearrangement gives

$$\begin{aligned}
 [R_{tot}]_{aq} &= ([M_A^*]_{aq_{tot}} + [M_B^*]_{aq}) \\
 &\quad [-\bar{k}_c N_p \\
 &\quad + \sqrt{(\bar{k}_c N_p)^2 + 8\bar{k}_{t_{ABC}}(R_i + \bar{k}_{des}N_p\bar{n}/N_A)}] \\
 &= \frac{4\bar{k}_{t_{ABC}}}{4\bar{k}_{t_{ABC}}} \quad (43)
 \end{aligned}$$

Initial experiments suggest that the partition of undissociated and dissociated species between the aqueous and particle phases is not the same. Therefore, a separate value for the fraction of acid in the aqueous phase, which is dissociated, denoted by α_{aq} , may have to be employed. Expressions for $[M_A^*]_{aq}$ and $[M_C^*]_{aq}$ are then obtained as follows:

$$[M_A^*]_{aq} = (1 - \alpha_{aq})[M_A^*]_{aq_{tot}} \quad (44)$$

$$[M_C^*]_{aq} = \alpha_{aq}[M_A^*]_{aq_{tot}} \quad (45)$$

Substitution of eqs. (44) and (45) into eq. (39) and then rearrangement leads to expressions for $[M_A^*]_{aq_{tot}}$ and $[M_B^*]_{aq}$.

$$[M_A^*]_{aq_{tot}} = \frac{[R_{tot}]_{aq}}{1 + G} \quad (46)$$

$$[M_B^*]_{aq} = \frac{[R_{tot}]_{aq}G}{1 + G} \quad (47)$$

where

$$G = \frac{k_{p_{AB}}[M_B]_{aq} + \alpha_{aq}[M_A]_{aq_{tot}}(k_{p_{AC}} - k_{p_{CA}})}{k_{p_{BA}}\alpha_{aq}[M_A]_{aq_{tot}}} \quad (48)$$

Substitution of these expressions for the total acid and styrene radical concentrations into eq. (49) gives a final expression for the rate of reaction in the aqueous phase, which involves only two measurable parameters ($[M_A]_{aq_{tot}}$ and $[M_B]_{aq}$), but which accounts for the reaction of three different species (providing that the value for α in each phase is known).

$$\begin{aligned}
 R_{p_{aq}} &= \left[k_{p_{AA}}(1 - \alpha_{aq})^2 + \left(\frac{k_{p_{AA}}}{r_{AC}} + \frac{k_{p_{CC}}}{r_{CA}} \right) \alpha_{aq}(1 - \alpha_{aq}) \right. \\
 &\quad \left. + k_{p_{CC}}\alpha_{aq}^2 \right] [M_A^*]_{aq_{tot}} [M_A]_{aq_{tot}} \\
 &\quad + \left[\frac{k_{p_{AA}}}{r_{AB}}(1 - \alpha_{aq}) + \frac{k_{p_{CC}}}{r_{CB}}\alpha_{aq} \right] [M_A^*]_{aq_{tot}} [M_B]_{aq}
 \end{aligned}$$

$$+ \left[\frac{k_{pBB}}{r_{BA}} (1 - \alpha_{aq}) + \frac{k_{pBB}}{r_{BC}} \alpha_{aq} \right] [M_{B^*}]_{aq} [M_A]_{aq, tot} + k_{pBB} [M_{B^*}]_{aq} [M_B]_{aq} \quad (49)$$

EXPERIMENTAL

Methacrylic acid and styrene monomers (all > 99% pure) were used as received. Potassium persulfate, sodium hydroxide, and sodium dodecyl sulfate were also used as received. Carboxylated styrene seed particles (28 nm diameter) were supplied by Dow Chemical, Midland, Michigan. High-purity nitrogen (> 99%) was employed.

The following procedure was used for all solution homopolymerizations of the acids. Deionized water was added to a 1.0-L glass reactor, and it was purged with nitrogen. The stirrer consisted of a paddle agitator with a 1.5 in. Teflon blade operated at about 600 rpm. Two separate stainless-steel coils were inserted into the reactor. Heating and cooling of the reactor contents was achieved by circulating hot and cold water through the respective coils. The coils and probes inserted into the reactor for temperature measurement and sampling also served as baffles, which improved mixing in the reactor. The reaction temperature was measured with a 316 stainless-steel type-T thermocouple (temperature range -210–160°C) connected to a time-proportioning digital temperature controller (OMEGA, Model 149) accurate to within 0.5°C. After the water and seed were brought to reaction temperature, the acid monomer was added, and then the initiator solution was injected. Samples were removed at selected times and injected into a chilled hydroquinone solution to short-stop the reaction. About 5 g of each sample were dried for gravimetric conversion analysis. Partially neutralized runs were conducted by adding enough sodium hydroxide solution to the reactor to obtain the desired initial degree of neutralization. Hydrochloric acid was then added to each

sample vial before drying to reassociate all acid in the sample. All of the acid would not volatilize unless it was completely undissociated due to the heavy cations that associated with the anionic acid species.

The standard recipe for each of the seeded emulsion copolymerization reactions is given in Table I.

All emulsion polymerization reactions were run at 85°C in a nitrogen purged, agitated, 1.0-L glass vessel similar to the reactor used for the solution polymerizations. The following procedure was used for each run. Carboxylated, styrene seed latex was mixed for 24–48 h with an anionic-cationic ion exchange resin (Bio-Rex MSZ 501) to remove excess surfactant. The amount of surfactant removed from the seed was determined gravimetrically. Deionized water, "cleaned" seed, and SDS (an amount that combined with the SDS remaining in the seed latex to give a concentration of 4.0 mmol/L_{aq}) was added to the reactor. Nitrogen was bubbled into the reactor and heating was begun by pumping hot water through an internal stainless-steel coil. When the reactor temperature reached approximately 85°C, styrene was slowly added through a dropping funnel. The acid monomer was mixed with an appropriated amount of 2M sodium hydroxide solution, then slowly added in the same manner. (Since diffusion of sodium hydroxide into the hydrophobic polymer particles is negligible, the monomer was partially neutralized before addition to the reactor.) Fast addition of either monomer would tend to "shock" the seed resulting in coagulation. The nitrogen purge line was pulled to the top level of the emulsion after the monomer addition to prevent polymer from coagulating at the interface of the nitrogen bubbles. The initiator solution was then injected.

The system was allowed to equilibrate for 1–2 min, and a sample was taken to make sure that thermal polymerization had not occurred. The relatively short equilibration time was utilized to minimize the risk of thermal polymerization occurring before addition of the initiator. Samples of 20–25 mL were extracted with a syringe at predetermined intervals

Table I Standard Recipe for Carboxylated Emulsion Batch Copolymerizations

K ₂ S ₂ O ₈	5.0 mmol/L _{aq}
Sodium dodecyl sulfate (SDS)	4.0 mmol/L _{aq} (CMC = 9.0 mmol/L _{aq})
Seed (particle diameter ~ 28 nm)	~ 30 g of solid polymer (~ 4.0 × 10 ¹⁸ particles/L _{aq})
Monomer (Acid/styrene ratios)	200 g total (0/200, 20/180, 40/160, 70/130)
DI water	Balance to give 1000 g total reaction mass

throughout the reaction period. The samples were immediately injected into a chilled hydroquinone solution and immersed in an ice bath to quench the reaction. The overall conversion was measured gravimetrically by adding either HCl or trifluoroacetic acid to each sample to reassociate the acid so that it would completely evaporate, then drying about 5 g of each sample overnight in an oven, and performing a mass balance on the dried solids.

Individual monomer conversions were obtained by gas chromatography (GC) using a Varian 3300 gas chromatograph with a 12-ft stainless-steel column packed with Gas Chrom 254, 80–100 mesh packing. (The packed column was supplied by Alltech Associates, Inc. in Deerfield, Illinois.) The column was operated at 220°C. The 5.0-mL reaction sample was diluted in a mixture of SDS solution, "uncleaned" seed, an internal standard solution, and a small amount of trifluoroacetic acid to reassociate all of the unreacted monomer so that it would completely volatilize in the column. The SDS solution and seed were added to help disperse the styrene homogeneously throughout the GC samples. Styrene is essentially insoluble (0.5 g/L) in water.

pH measurements were made using a Fisher digital pH meter with a combination electrode. A temperature probe was also immersed into the sample to account for temperature effects on the pH.

RESULTS AND DISCUSSION

Monomer Partitioning in Acid–Styrene–Water Mixtures—No Particles

Reaction in the aqueous phase can be significant in emulsion polymerization systems that contain one or more water-soluble monomers. Accurate prediction of the partition of monomers between the aqueous, particle, and droplet phases is necessary for determining reaction rates, copolymer compositions, and surface properties of the latex particles. A model for predicting the partition of monomers between the various phases has been developed for an emulsion copolymer system.¹⁵ The model was limited to unneutralized systems where only two species, undissociated acid and styrene are present. Therefore, further study was needed to understand the effects of partially neutralizing the acid on its partition behavior.

The effect of degree of neutralization (DN) on the acid partition was investigated by adding different levels of sodium hydroxide solution to acid–styrene–water mixtures. Figure 3 reveals that the

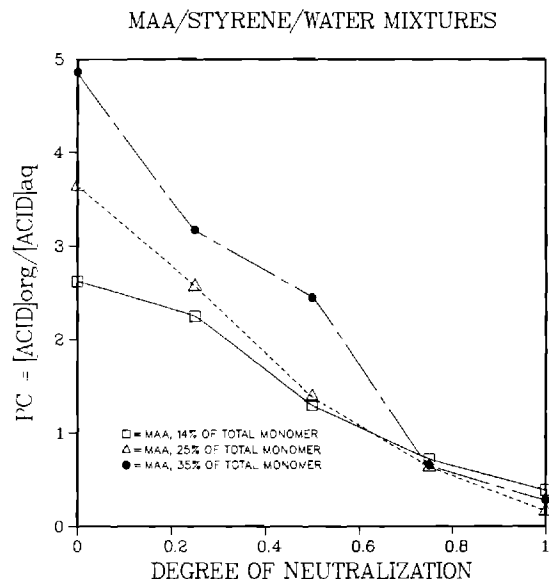


Figure 3 Effect of degree of neutralization on the partition coefficient for MAA in an MAA–styrene–water mixture at various acid levels (25°C).

partition coefficient of MAA decreases significantly with increasing DN. The dissociated (anionic) form of the acid monomer exhibits a negative charge making it more polar than the undissociated form. The increased polarity of the dissociated monomer causes it to be more attracted to the polar water molecules in the aqueous phase as opposed to the relatively nonpolar styrene molecules in the organic phase. Thus as the fraction of dissociated monomer increases, the overall fraction of monomer, which partitions into the organic phase, decreases. The partition coefficient for MAA is also dependent on acid level at low DN, but it becomes relatively independent of acid level as DN approaches 1.0.

Addition of sodium hydroxide to increase DN changes the overall ionic strength of the solution. A simple experiment was performed to examine the effects of increasing DN without changing the overall ionic strength. Mixtures of acid, styrene, water, and sodium hydroxide were made as previously described over a range of DN from 0 to 1. The aqueous phase was separated, and titrations were performed to determine the concentration of acid in each phase. However, sodium chloride was also added in an amount that would yield an ionic strength in solution equivalent to that obtained at a DN of 1. [Example: If 1.0 mole of acid is used, then to obtain a DN of 0.25 while maintaining a constant ionic strength equivalent to that obtained at a DN of 1, 0.25 mol of sodium hydroxide (NaOH) and 0.75 mol of sodium chloride (NaCl) are added to the mixture.]

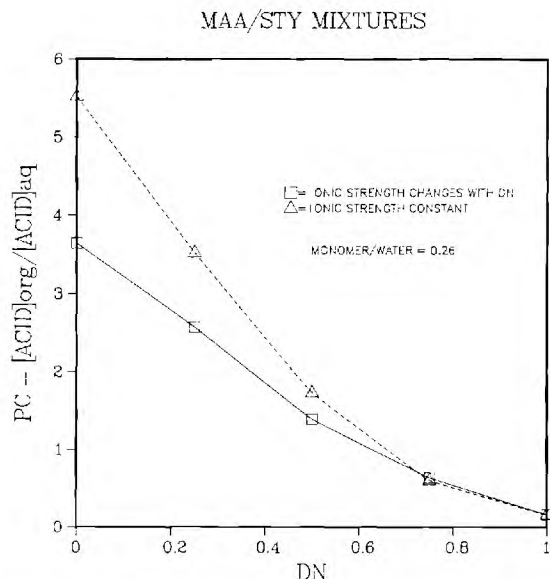


Figure 4 Comparison of the partition coefficient of MAA between water and styrene for increasing ionic strength and constant ionic strength at DN between 0 and 1. The monomer/water ratio is 0.26, and MAA represents 25% of the total monomer. ($T = 25^{\circ}\text{C}$).

Results for MAA at constant ionic strength (Fig. 4) revealed that the partition coefficient is higher for the case where the ionic strength is maintained constant than the case when the ionic strength decreases with decreasing DN. The difference in the partition coefficients measured for the two curves reflects the relative difference in the ionic strengths of the solutions over the full range of DN. The difference is large at a DN of 0, while there is no difference at a DN of 1. MAA monomer forms aggregates in solution due to hydrogen bonding between the monomer molecules.¹⁶ Increasing the ionic strength may tend to disrupt these hydrogen-bonded aggregates thus forming a greater number of single molecules that more easily partition into the organic phase.

These preliminary studies show that the DN, the acid level, and the ionic strength of the solution all significantly affect the partition of MAA between styrene and water at various DN. Therefore, the addition of bases and/or buffers to regulate pH or other desired product properties in a multiphase reaction system such as an emulsion can significantly change the partitioning of carboxylic acids between the organic and aqueous phases.

Solution Polymerization Studies

Solution polymerizations of MAA were carried out under each of the conditions listed in Table II.

Table II Conditions Used for Solution Polymerizations of Both MAA and AA ($[I]_0 = 0.001M$).

Concentration Acid (wt %)	DN	Temperature ($^{\circ}\text{C}$)
2.0	0.0	85
4.0	0.0	85
7.0	0.0	85
10.0	0.0	85
7.0	0.25	85
7.0	0.50	85
7.0	0.75	85
7.0	1.00	85
7.0	0.0	70
7.0	0.0	80
7.0	0.0	90
7.0	0.0	96-98

Conversion-time curves for the natural pH (DN = 0) reactions of MAA at 85°C over a range of concentrations from 2.0 to 10.0 wt % are shown in Figure 5. The basic free-radical solution polymerization equation, which has been shown to apply to many simple solution systems, was used to examine the experimental data.

$$R_p = -\frac{dM}{dt} = k_p \frac{(2fk_d[I])^{1/2}}{(2k_t)^{1/2}} [M] \quad (50)$$

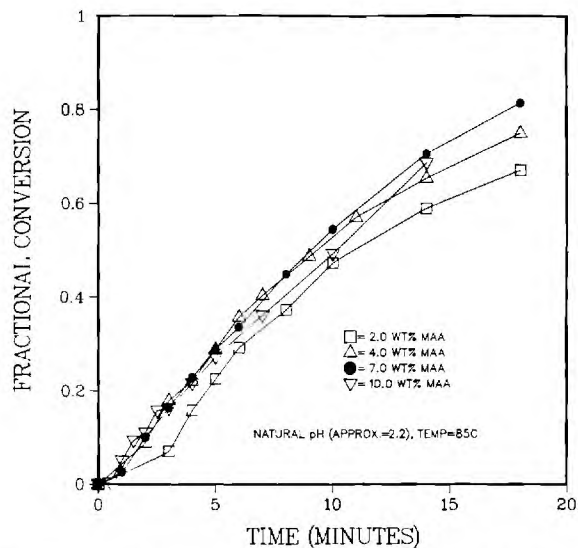


Figure 5 Conversion-time curves for the MAA solution polymerization at various initial monomer concentrations (85°C).

Integration of eq. (50), assuming that only $[M]$ varies, results in

$$\ln \frac{[M]_0}{[M]} = k_p \frac{(2fk_d[I])^{1/2}}{(2k_t)^{1/2}} t = Kt \quad (51)$$

Reaction samples were obtained over time, and monomer conversions were measured gravimetrically. $[I]$ can be calculated as a function of time through

$$[I] = [I]_0 \exp(-k_d t) \quad (52)$$

It remained essentially constant over the short reaction period (< 20 min) required for nearly completely conversion of MAA and AA. (i.e. $[I] = 0.92[I]_0$ after 20 min). A value of k_d of 6.89×10^{-5} was obtained from the literature.¹⁷ A value of 1.0 was used for the initiator efficiency factor f .

Gromov et al.⁷ assumed that the reaction rate given by eq. (50) applied to both AA and MAA solution polymerizations. (Chapiro and Dulieu¹⁶ and Shoaf,¹³ however, showed that the mechanism for reaction of AA is more complicated than the simple solution polymerization scheme.) The value of k_p should then be independent of monomer concentration. Gromov does not specifically state the actual monomer concentrations utilized in their experiments. However, similar work performed with Galperina et al.⁶ involved reactions of AA at concentrations of 3.0–4.0 wt %. The values for k_p based on the Gromov et al. data were obtained by fitting an Arrhenius expression to the data (which were given for temperature ranges of 0–60°C) and extrapolating to 85°C, the temperature of the reactions performed in this work. These experiments as well as the Gromov et al. were performed at natural pH (approximately 2.2–2.4).

Plots of $\ln[M]_0/[M]$ versus time should be linear with a slope K based on the relationship given by eq. (51). Values of $k_p/k_t^{1/2}$ can be obtained from this slope. Gromov et al.⁷ reported values of k_t for MAA (0.12×10^8 L/mol s) from experiments utilizing the method of alternating illumination. The

values were relatively constant over a range of temperatures from 0 to 60°C, and these values were assumed to apply also at 85°C so that propagation constants could be calculated directly from $k_p/k_t^{1/2}$ ratios. Values of $k_p/k_t^{1/2}$ and k_p (L/mol s) obtained from the experimental data as well as those predicted from the Gromov's et al. data are listed in Table III for the range of monomer concentrations investigated.

The $\ln[M]_0/[M]$ versus time plots for MAA are shown in Figure 6. Plots of the MAA data results in relatively straight lines as predicted by the assumed first-order kinetic model given by eq. (51). Figure 7 plots k_p values as a function of initial monomer weight percent for MAA. The data for MAA agree fairly well (within experimental error) with the k_p values predicted from the Gromov's et al. data.

Solution Polymerizations: Experimental and Model Results with $DN > 0$

The initial rates of MAA polymerizations in solution were measured over a range of DN from 0 to 1 to check the reproducibility of the results reported by Kabanov et al.⁴ The results are shown in Figure 8 for MAA. The rates of reaction decreased with increasing DN as expected.

Additional unseeded solution polymerizations of MAA at DN between 0 and 1 were conducted to determine to what extent the DN of the unreacted monomer changed over the conversion period. The pH of these reactions was measured throughout the reaction period by inserting a pH probe and temperature probe into the reactor. The DN of the unreacted monomer could then be calculated with eq. (53) and the concentration of hydrogen ions as determined from the pH measurements.

$$DN = \frac{K_a/[H^+]}{1 + K_a/[H^+]} = \frac{10^{-pK_a}/10^{-pH}}{1 + 10^{-pK_a}/10^{-pH}} \quad (53)$$

Equation (12) is based on the assumption that a single value of K_{a2} may be used. The value of K_{a2}

Table III $k_p/k_t^{1/2}$ and k_p Values for MAA and AA at 85°C

wt %	$k_p/k_t^{1/2}$ (L/mol s) ^{1/2}	$k_{p\text{exper}}$ (L/mol s)	$k_{p\text{Gromov}}$ (L/mol s)
2.0	4.37	15,200	15,900
4.0	5.24	18,200	15,900
7.0	4.89	16,900	15,900
10.0	4.34	15,000	15,900

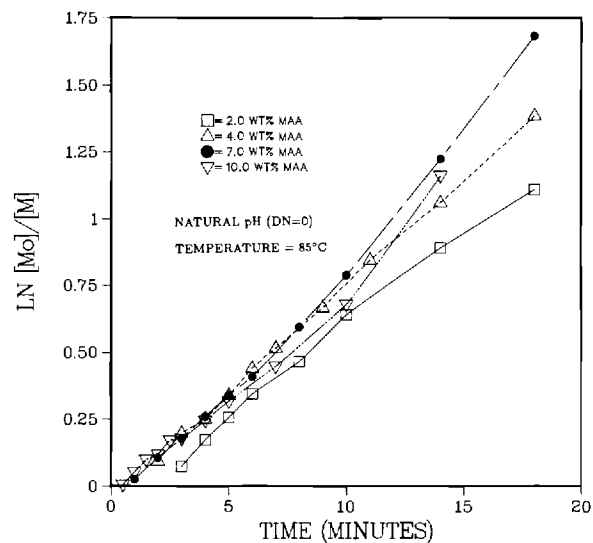


Figure 6 $\ln[M_0]/[M]$ -time relationship for 2.0, 4.0, 7.0, and 10.0 wt % MAA solution polymerizations at 85°C and natural pH.

has a large effect on the value of DN predicted from eq. (11) as revealed by Figure 9. The actual DN of the unreacted monomer does increase with conversion as expected (Fig. 10), but the best fit of the experimental DN-conversion data required some modification of K_{a2} from the average value of 1.0×10^{-7} as reported by Molyneux.¹² The correct value of K_{a2} for the polymer is uncertain since there are actually many values depending on the lengths and

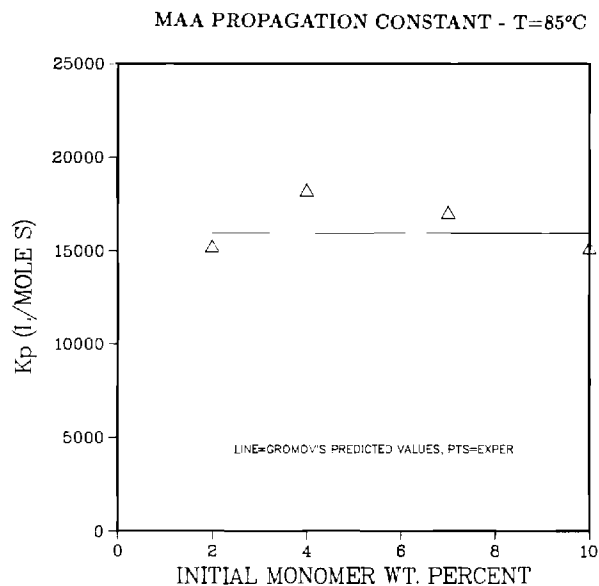


Figure 7 Dependence of k_p on initial monomer weight percent for MAA solution polymerization at 85°C.

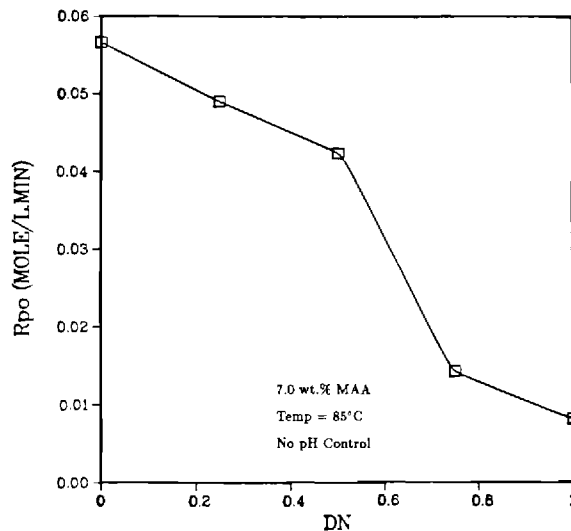


Figure 8 Initial rates of reaction as a function of DN for 7.0 wt % MAA in solution at 85°C.

conformations of the polymer chains. Therefore, K_{a2} was adjusted in the model to give the best fit of the data. A single value of 3.5×10^{-6} resulted in consistent fits of the DN versus conversion plots for the full range of initial DN values examined.

The next step was to predict the reaction rate of MAA at various DN accounting for the fact that the DN of the unreacted monomer does change with conversion. Kabanov et al.⁴ report a value of 670 L/mol s for the propagation constant (k_{pCC}) of the MAA anion and 2.1E8 L/mol s for the termination

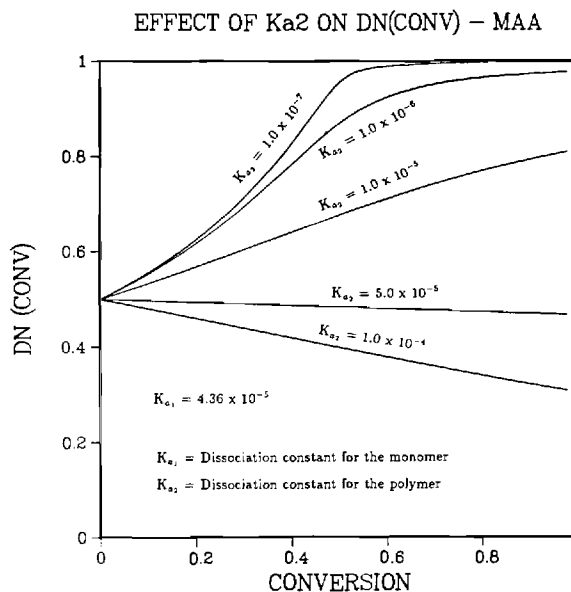


Figure 9 Effect of K_{a2} on the predicted DN as a function of conversion with an overall DN of 0.5.

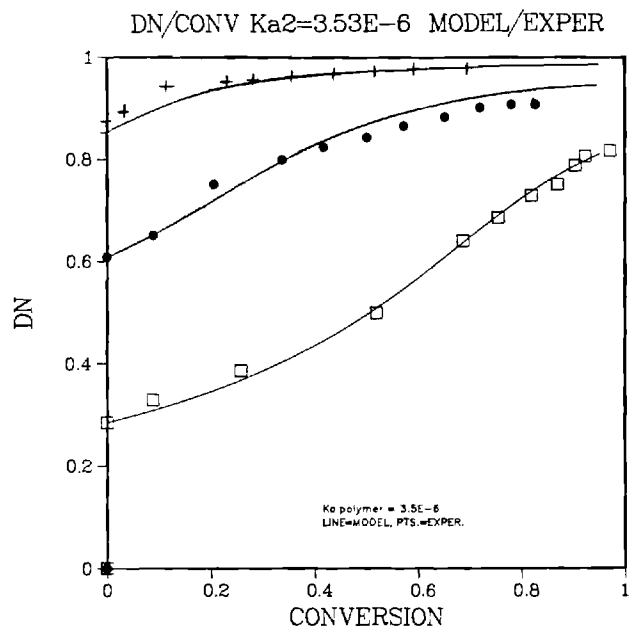


Figure 10 Comparison of predicted DN as a function of conversion with experimental values (K_{a2} of 3.5×10^{-6}).

constant at 23°C. A value for k_{pCC} at 85°C was obtained by fitting experimental conversion data of MAA obtained at a DN of 1.0 using the basic solution polymerization equation since at a DN of 1.0, only one reaction species, the anions, will be present in the system. The best fit was obtained with a k_{pCC} of 5000 L/mol s (Fig. 11). (The k_t value was assumed not to change significantly with temperature. Values

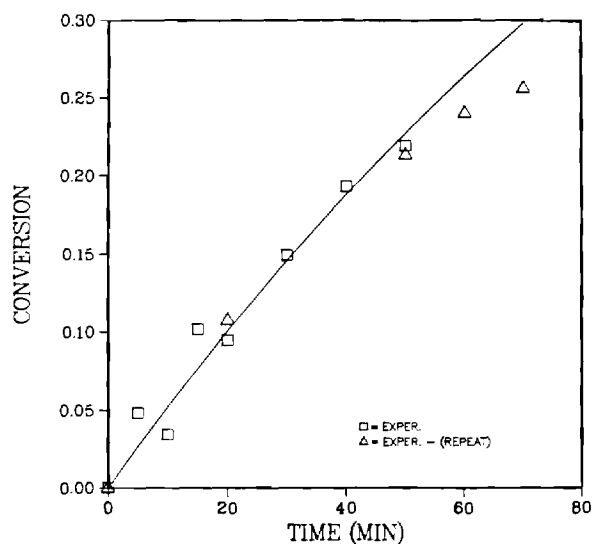


Figure 11 Fit of conversion-time data for the MAA anion at 85°C using the solution polymerization equation, a value of k_t of 2.1×10^8 (L/mol s) as reported by Plochocka⁹ and an adjustable propagation constant, k_{pCC} . The best fit was obtained with a k_{pCC} of 5000 (L/mol s).

of k_t reported by Kabanov et al.⁴ for the unneutralized MAA polymerization were constant over a temperature range of 20–60°C.)

The copolymer model was modified to account for the changing DN with conversion by using eq. (12). The results of the model using a K_{a2} value of 3.5×10^{-6} are shown in Figure 12. The predicted conversion-time results slightly underestimate the experimental data for all initial DN values.

A further adjustment of K_{a2} was then made in order to obtain a better fit to the conversion-time data. Figure 13 shows that a good fit of the reaction data is obtained for all initial DN values if a value of K_{a2} of 8.0×10^{-6} is used. The predicted DN was recalculated using the adjusted K_{a2} value and compared to the measured values as exhibited in Figure 14. The predicted values are close to the observed values, but in each case the observed values are slightly underestimated.

Therefore, good fits of both DN-conversion data and conversion-time data can be obtained using a solution copolymerization model that accounts for the change in DN of the unreacted monomer with conversion for a wide range of initial DN values. However, some discrepancy between the values of K_{a2} that give consistent fits of both types of data, simultaneously, still remains.

Acid-Styrene Emulsion Copolymerization: Experimental and Model Results with DN > 0

One objective of this study was to determine if partially neutralizing the acid exhibited the same effects

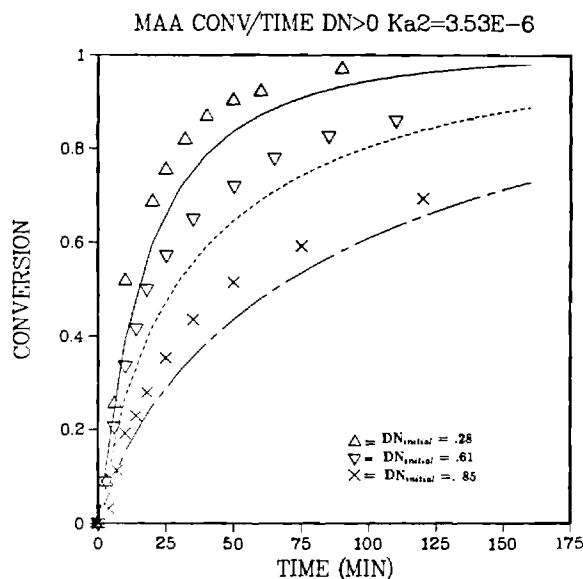


Figure 12 Comparison of solution copolymerization reaction model results to experimental data for MAA at various DN ($K_{a2} = 3.5 \times 10^{-6}$).

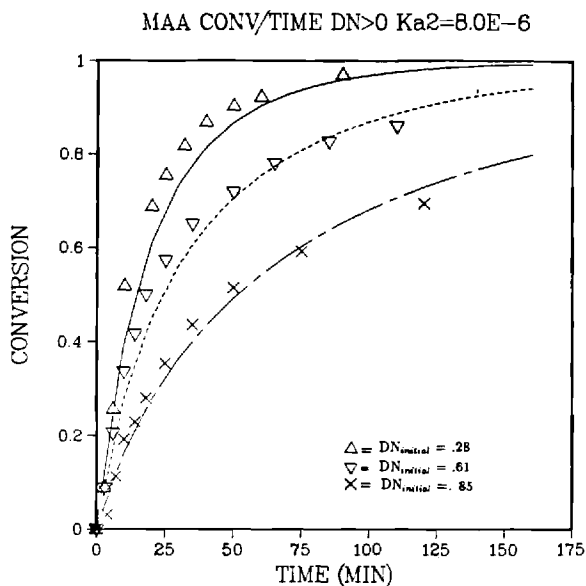


Figure 13 Comparison of solution copolymerization reaction model results to experimental data for MAA at various DN ($K_{a2} = 8.0 \times 10^{-6}$).

on the reaction rate in an emulsion “terpolymerization” between the acid, anion, and styrene as observed with the solution polymerizations. Experimental methods were developed to address this issue. Initial MAA-styrene emulsion polymerizations were performed at a DN of 0.25. The experimental conversion profiles for both acid (including the undissociated and dissociated species) and styrene at a DN of 0.25 are contrasted to conversion profiles at

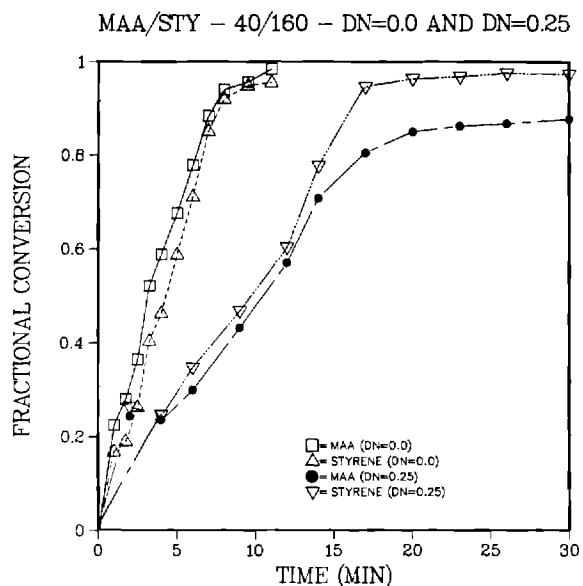


Figure 15 Experimental conversion profiles for MAA-styrene at overall DN values of 0.0 and 0.25 ($T = 85^\circ\text{C}$).

a DN of 0.0 in Figure 15. The rate of reaction of MAA was slower at a DN of 0.25 as expected due to the slower rate of reaction of the anions as a result of their increased electrostatic repulsion. However, the rate of reaction of styrene was also slower in both cases for the run at elevated DN.

Figure 16 shows that as the DN increases, the fraction of monomer that partitions into the organic phase decreases. Since the aqueous-phase oligomeric

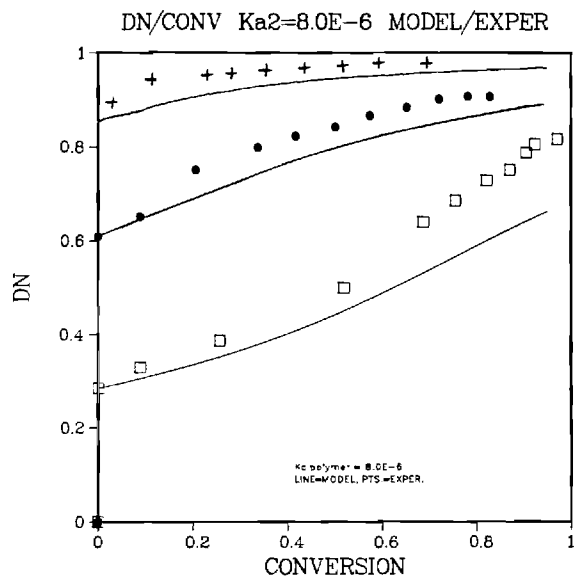


Figure 14 Comparison of predicted DN as a function of conversion with experimental values (K_{a2} of 8.0×10^{-6}).

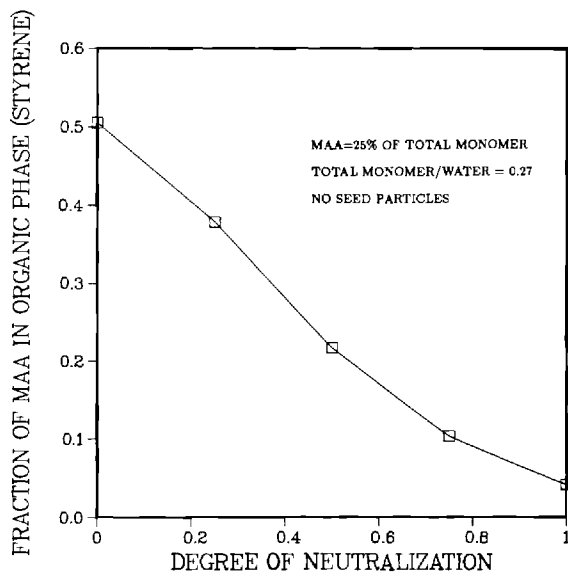


Figure 16 Partition of MAA into the aqueous and styrene phase as a function of DN.

radicals are comprised to a large extent of acid and anion molecules, the rate of entry of these radicals may be slower than when the acid is partially neutralized. The increased polarity due to the negative charge of the anion increases the attraction of the neutralized acid to the polar water molecules in the aqueous phase. The anionic species, therefore, are less likely to partition into the organic phase than the undissociated species. This result suggests that the concentration of free radicals inside the polymer particles (\bar{n}) is lower at a DN of 0.25 than at a DN of 0.0 perhaps due to a slower entry rate into the particles of oligomers that contain anionic species. Consequently, a lower concentration of free radicals in the particles (lower \bar{n}) will result in a slower rate of reaction of styrene in the particles as observed.

Another factor contributing to the decrease in reaction rate of styrene is that the cross-propagation constant for reaction of styrene with the acid anion is lower than the cross-propagation constant for reaction with the undissociated acid for the MAA-styrene system. The values of the cross-propagation constants for reaction with the anion were calculated from reactivity ratios for styrene and the anion based on Q - e values reported for the MAA-styrene system.¹¹ The concentration of anions in the organic phase, however, is relatively small based on the partition data obtained at high DN values.

The emulsion copolymerization model was modified to account for the formation and reaction of the dissociated acid, a third reacting monomeric species, due to partial neutralization of the acid with sodium hydroxide. The formation of a third reacting species complicates the reaction mechanism. Modifications of the equations in the kinetic model to account for reaction of all three species, styrene, acid, and the anion, were developed earlier.

Application of the model depends on several parameters that are directly affected by the presence of the dissociated acid. These parameters include the partition coefficients, radical capture and desorption coefficients, termination and propagation constants, and the DN of each phase. Accurate prediction of the values for these parameters cannot be made without a long series of experimental studies to determine the effects of overall DN over a range of monomer/water ratios for each monomer system. Nevertheless, initial estimates can be made for each of these parameters based on previous work performed in this study.

The degree of neutralization changes with conversion due to the changing equilibrium between the monomer and polymer, and also due to the varying partition of monomer into the particles depending

on the relative concentrations of styrene, acid, and anions. Some progress on predicting the changing DN with conversion was discussed earlier for the solution polymerization of MAA. However, the addition of polymer particles and partition of monomers between the various phases greatly complicates the equilibrium between undissociated and dissociated species. Fortunately, this complication can be circumvented by measuring the pH of the reaction mixture over the conversion period and calculating the DN of the unreacted aqueous-phase monomer directly from the pH measurement using the equilibrium expression given by eq. (53).

This approach limits the predictive capabilities of the model because the DN-conversion profile must be known a priori. However, it allows the other aspects of the model to be investigated without having to quantitatively predict the DN of the unreacted monomer in a complex system containing particles with monomer and polymer present in both aqueous and particle phases. Results of calculated DN as determined from pH measurements over the conversion period are presented in Figures 17 and 18 for runs with an overall DN of 0.25 and 0.50 based on the ratio of sodium hydroxide and acid monomer initially added to the system. The initial DN values at zero conversion exceed the overall DN values of 0.25 and 0.50 in part due to disproportional partition of the monomer and sodium hydroxide into the organic phase. As much as 30–40% of the MAA par-

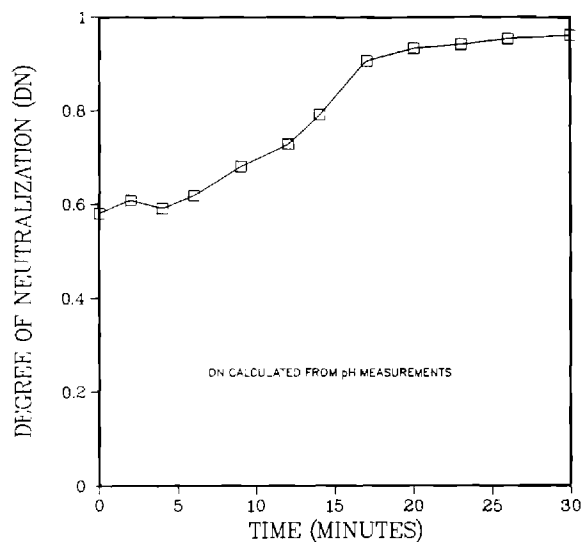


Figure 17 Change in DN over the conversion period as determined from pH measurements for the reaction of MAA-styrene at an acid (including neutralized acid)/styrene ratio of 40/160 with an initial DN of 0.25 based on total moles base/total moles acid ($T = 85^{\circ}\text{C}$).

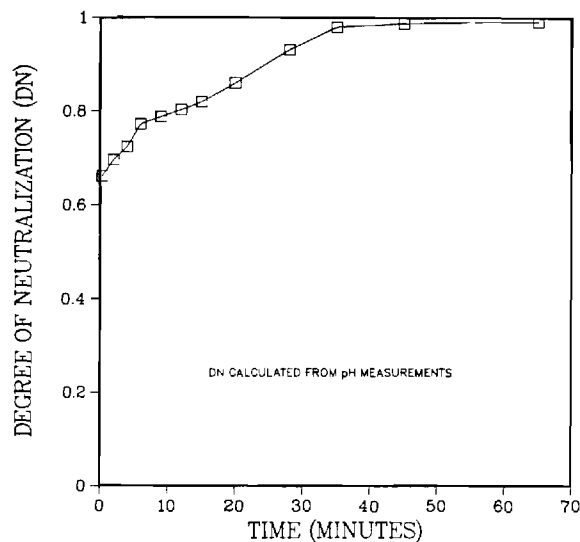


Figure 18 Change in DN over the conversion period as determined from pH measurements for the reaction of MAA-styrene at an acid (including neutralized acid)/styrene ratio of 40/160 with an initial DN of 0.50 based on total moles base/total moles acid ($T = 85^{\circ}\text{C}$).

titions into the particles and droplets. But when styrene, water, and sodium hydroxide were mixed and allowed to separate in a separatory funnel for about 2 h, only about 2.0% of the sodium hydroxide was found to distribute into the styrene phase. Therefore, a significant amount of MAA partitions into the organic phase whereas almost all of the sodium hydroxide remains in the aqueous phase. Thus

the initial measured DN values are higher than if all the acid and base were in the same phase.

A thermodynamic partition model¹⁵ was utilized in making initial estimates of the concentrations of the acid and styrene in each phase. The fraction of acid in the organic phase was then determined as a function of DN from experimental data reported in Figure 16. This organic fraction was distributed evenly between the particles and droplets in the model. Then adjustments in the amount of styrene in the particles were made to compensate for the difference in the original amount of acid estimated to be in the organic phase based on the partition model calculations and the amount based on the experimental partition data in Figure 16 at various DN. This approach provided a method for accounting for the dependence of acid partition on DN.

An estimate for the average desorption coefficient, \bar{k}_{des} , was made based on the typical range of values calculated for the unneutralized MAA-styrene system. Though the actual value changed as the relative amounts of each monomer changed, typical values were about 2.0 (1/s) for this system. The addition of the anion as a third reacting species made calculation of \bar{k}_{des} difficult, especially since values for chain transfer and cross-transfer constants are unknown for the anion or any similar dissociated monomeric acid. Therefore, a constant value of 2.0 (1/s) was utilized in the model of the partially neutralized MAA-styrene system.

An estimate of the average capture coefficient, \bar{k}_c , was also made based on the typical range of val-

Table IV Values for Parameters Used in Seeded Emulsion Copolymerization Simulation of MAA and Styrene with $\text{DN} > 0$ ($T = 85^{\circ}\text{C}$)

Parameter	Monomer	Value	Source
k_p (L/mol s)	MAA	15900	Experiment, 5
k_p (L/mol s)	Anion	670	9
k_p (L/mol s)	Styrene	900	17
k_t (L/mol s)	MAA	0.1×10^8	7, 18
k_t (L/mol s)	Anion	2.1×10^8	9
k_t (L/mol s)	Styrene	2.5×10^8	17
Γ_{AB}	MAA-Styrene	0.55	19, 20
Γ_{BA}	Styrene-MAA	0.25	19, 20
Γ_{AC}	MAA-Anion	0.68	11 (Q-e scheme)
Γ_{CA}	Anion-MAA	0.08	11 (Q-e scheme)
Γ_{BC}	Styrene-Anion	1.30	11 (Q-e scheme)
Γ_{CB}	Anion-Styrene	1.10	11 (Q-e scheme)
\bar{k}_{des} (1/s)	Assumed constant	2.0	
\bar{k}_c (cm ³ /s)	Assumed constant	2.0×10^{-14}	DN = 0.25
\bar{k}_c (cm ³ /s)	Assumed constant	5.0×10^{-15}	DN = 0.50
N_p (part/L _{reactor})	Assumed constant	3.0×10^{18}	$\approx 4.0 \times 10^{18}$ (part/L _{aq})

ues calculated for the unneutralized MAA-styrene system. A value of 2.0×10^{-14} (cm^3/s) was used for the simulation with DN of 0.25. However, a value of 5.0×10^{-15} (cm^3/s) produced a better fit of the data for the run with a DN of 0.50. This lower value of \bar{k}_c for the run at DN of 0.50 is consistent with the expected decrease in rate of radical entry into the particles with increased concentration of anions.

Reactivity ratios were estimated using Q and e values reported by Alfrey et al.¹¹ for the acid and anion and by Brandrup and Immergut¹⁷ for styrene. The reactivity ratios for MAA and styrene were adjusted to correspond to the same values used in the model at a DN of 0.0.

An average termination constant for both the particle and aqueous phases was calculated based on the fraction of each monomer in each phase. Propagation constants were based on values reported in the literature. An overall listing of the kinetic parameters used in the model with DN greater than zero is displayed in Table IV.

Simulations with the initial version of the model, which assumed the DN to be the same in all three phases, resulted in predicted reaction rates of MAA that were too high relative to styrene. The model predicted that at a 40/160 acid (including neutralized acid)/styrene ratio the MAA reached high conversions before the styrene for both the DN of 0.25 and 0.50 cases. However, the data in Figures 19 and

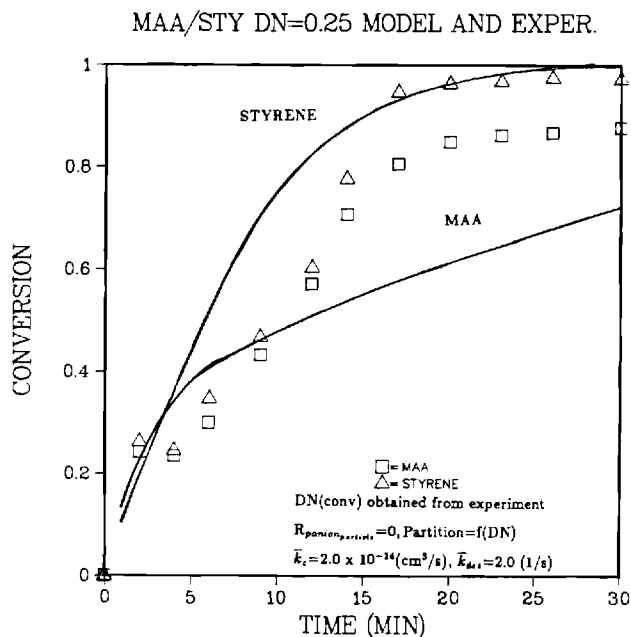


Figure 19 Comparison of experimental data and model predictions for the conversion profiles of MAA and styrene at an acid (including neutralized acid)/styrene ratio of 40/160 and an initial DN of 0.25 ($T = 85^\circ\text{C}$).

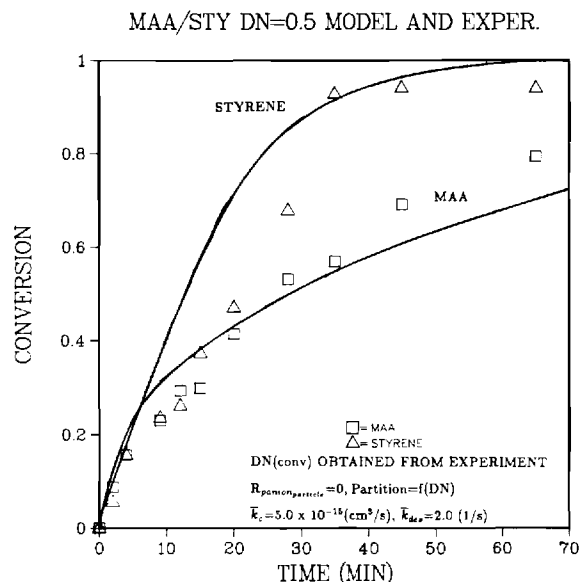


Figure 20 Comparison of experimental data and model predictions for the conversion profiles of MAA and styrene at an acid (including neutralized acid)/styrene ratio of 40/160 and an initial DN of 0.50 ($T = 85^\circ\text{C}$).

20 reveal that for overall DN values of 0.25 and 0.50, styrene reaches high conversions before MAA. The model was then modified so that only copolymerizations of the undissociated acid and styrene occurred inside the particles, and terpolymerization of all three species occurred only in the aqueous phase (i.e., it was assumed that the concentration of anions inside the particles was negligible). Results from these simulations also shown in Figures 19 and 20 reveal that the model predicts not only the proper trends for the acid and styrene conversion profiles, but the fits of the data are also reasonably good, especially for the case with a DN of 0.50.

The accuracy of the reaction model for partially neutralized systems is limited by the assumptions that must be made in accounting for the many effects of the dissociated species on a large number of important parameters. Much additional work is needed in order to quantitatively determine the effects of these anions on the kinetics of the reaction system. Nevertheless, this portion of the study establishes some important directions for further work related to kinetic modeling of partially neutralized acid-styrene emulsion polymer systems.

CONCLUSIONS

Simple first-order solution polymerization kinetics may be used to describe the reaction of MAA in

water. Partially neutralizing the acid slows the reaction rate in both solution and emulsion systems. The slower rates are attributed to the increased electrostatic repulsion of the dissociated acid (anions). The degree of neutralization of unreacted monomer increases in a solution polymerization throughout the course of a batch reaction due to the different acid strengths of acid monomer and acid polymer.

Partial neutralization of these acids also results in a decreased partitioning of acid into the organic phase. This decreased tendency of partially neutralized acid species to enter the organic phase probably leads to a lower rate of capture of oligomeric radicals and thus a lower average number of radicals per particle resulting in the decreased rate of reaction of styrene, which was observed experimentally.

A model has been developed to predict both the change in degree of neutralization and polymerization rates throughout the course of a partially neutralized MAA solution polymerization. An emulsion copolymerization model developed for acid-styrene systems was extended to the case where the acid is partially neutralized. Comparison of model and experimental results suggests that very little of the dissociated acid reacts inside the particles.

Funding for this work was provided by Dow Chemical, Midland, Michigan and the National Science Foundation under Grant No. CBT-8717926.

NOMENCLATURE

A	parameter relating the relative reactivities of monomer i and monomer j
CMC	critical micelle concentration (mol/L _{aq})
DN	degree of neutralization (moles base/moles acid)
f	initiator efficiency factor
F_i	instantaneous fraction monomer i in copolymer
$[I]$	initiator concentration (mol/L)
\bar{k}_c	average radical capture coefficient (cm ³ /s)
k_d	initiator decomposition rate coefficient (1/s)
\bar{k}_{des}	average radical desorption coefficient (1/s)
k'_{des}	volume independent desorption coefficient (cm ² /s)
k_{mij}	chain transfer to monomer (L/mol s)
k_p	propagation constant (L/mol s)

k_{pji}	propagation constant of monomer i with monomer j (L/mol s)
k_t	termination constant (L/mol s)
\bar{k}_{tij}	average termination constant of radical i with radical j (L/mol s)
k_{tw}	termination constant in the aqueous phase (L/mol s)
K_{a1}	acid dissociation constant (monomer)
K_{a2}	acid dissociation constant (polymer)
$[M]$	concentration of monomer (mol/L)
\bar{n}	average number of free radicals per particle
N_A	Avogadro's number (6.02×10^{23} /mol)
N_p	concentration of polymer particles (no./L _{aq})
r_i	reactivity ratio = k_{pii}/k_{pji}
R_i	rate of initiation (mol/L _{aq} s)
R_p	rate of polymerization (mol/L _{aq} s)
SDS	sodium dodecyl sulfate (anionic surfactant)
T	temperature (°C)
t	time (s)
x	moles of dissociated acid monomer
y	moles of reacted acid monomer
z	moles of dissociated acid polymer

Greek Symbols

α	fraction of dissociated acid monomer
β	fraction of dissociated radicals
ϕ	cross-termination coefficient = $k_{ij}/(k_{ii}k_{jj})$

Subscripts

aq	aqueous phase
A	monomer A (acid)
B	monomer B (styrene)
C	monomer C (anion)
d	droplet phase
I	initiator
m	monomer
o	initial condition
p	polymer or particle phase
P	polymer or copolymer
T or tot	total
w	water or aqueous phase
1	monomeric species
2	polymeric species

REFERENCES

1. G. L. Shoaf and G. W. Poehlein, *J. Appl. Poly. Sci.*, to appear.

2. A. Katchalsky and G. Blauer, *Faraday Soc. Trans.*, **47**, 1360 (1951).
3. S. H. Pinner, *J. Poly. Sci.*, **9**, 282 (1952).
4. V. A. Kabanov, D. A. Topchiev, and T. M. Karaputadze, *J. Polym. Sci., Polym. Symp.*, **4**, 173 (1973).
5. G. Blauer, *J. Poly. Sci.*, **11**, 189 (1953).
6. N. I. Galperina, T. A. Gugunaua, V. F. Gromov, K. I. Khomokovskii, and A. D. Abkin, *Vysokomol. Soyed*, **A17**, 1455 (1975).
7. V. F. Gromov, N. I. Galperina, T. O. Osmanov, P. M. Khomikovskii, and A. D. Abkin, *Eur. Polym. J.*, **16**, 529 (1980).
8. M. K. Mishra and S. N. Bhadani, *Makromol. Chem.*, **184**, 955 (1983).
9. K. Plochocka, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C20**(1), 67 (1981).
10. J. M. Atherton and A. M. North, *Trans. Faraday Soc.*, **58**, 2049 (1962).
11. T. Alfrey, C. G. Overberger, and S. H. Pinner, *J. Am. Chem. Soc.*, **75**, 4221 (1953).
12. P. Molyneaux, *Soluble Synthetic Polymers: Properties and Behavior*, CRC Press, Cleveland, OH, 1983, Vol. I.
13. G. L. Shoaf, Ph.D. Thesis, School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA (1989).
14. M. Nomura, K. Yamamota, I. Horie, and K. Fujita, *J. Appl. Poly. Sci.*, **27**, 2483 (1982).
15. G. L. Shoaf and G. W. Poehlein, *I.E. and C.-Fund.*, to appear.
16. A. Chapiro and J. Dulieu, *Eur. Polym. J.*, **13**, 563 (1977).
17. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, 2nd ed., Wiley, New York, 1975.
18. V. G. Popov, D. A. Topchiev, V. A. Kabanov, and V. A. Kargin, (dec) *Vysokomol. soyed.*, **A14**(1), 117 (1972).
19. R. Z. Greenley, *J. Macromol. Sci.-Chem.*, **A14**(4), 427 (1980).
20. F. V. Loncar, Ph.D. Thesis, Emulsion Poly. Inst., Lehigh University, Bethlehem, PA (1985).

Received March 6, 1990

Accepted May 14, 1990

Kinetic Analysis of Seeded Emulsion Polymerization of Vinyl Acetate

DAVID M. LANGE, GARY W. POEHLEIN,^{1*} SADAO HAYASHI,² AKIHIKO KOMATSU,²
and TOSHIHIRO HIRAI²

¹School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100, ²Faculty of Textile Science and Technology, Shinshu University, Ueda, Japan

SYNOPSIS

Particle number and size data from a series of seeded, emulsifier-free, vinyl acetate emulsion polymerization experiments have been analyzed with the aid of polymerization and particle growth models. A secondary population of particles, with a significantly greater number concentration than the seed, was nucleated in all experiments. The two populations (seed and new) had rather narrow size distributions and large diameters. Hence the reactions were in the area normally associated with Smith-Ewart Case III kinetics. Water-phase termination reactions can be important in this reaction region but radical desorption from such large particles does not significantly influence the kinetics. The results of the analysis were used to evaluate the magnitude of water-phase termination; to estimate radical capture coefficients; and to evaluate competitive particle growth.

INTRODUCTION

Hayashi and co-workers¹ published a considerable amount of data on the seeded emulsion polymerization of vinyl acetate in the absence of emulsifier. The results show that new particles are formed if the concentration of seed particles is not adequate to capture all the free-radical oligomers initiated in the aqueous phase. One series of experiments involved measuring particle concentrations and sizes as a function of time and conversion for the same recipe.

The purpose of this article is to present a kinetic analysis of this data. The data obtained were from a seeded batch system in which significant secondary nucleation occurred early in the reaction. This provided a second relatively monodisperse population of particles in addition to the latex seed. An additional feature is the large sizes of both particle populations. If the theory of Ugelstad et al.² is applied, this system would possess large values of the dimensionless parameter, α' , which is defined by

$$\frac{\rho_i v_p N_A^2}{N k_{tp}}$$
 ρ_i is the rate of radical generation in the aqueous phase (mole/L_{H₂O} s), v_p is the volume of the monomer-swollen polymer particles (L), N_A is Avogadro's number, N is the number of particles (particles/L_{H₂O}), and k_{tp} is the termination rate constant in the particles (L/mol s).

The unusual features of this system provide additional information on vinyl acetate emulsion polymerization. First, the data obtained at high α' values allows estimation of a radical capture constant k_c ($k_c = k_a/N$) for vinyl acetate. Secondly, the initial formation of a second population of particles yields conditions used for competitive growth experiments. Thus competitive growth of particles may also be examined with these data.

EXPERIMENTAL

Experimental details are given by Hayashi et al.¹ The recipe used for the experiments considered in this paper was as follows.

Deionized water: 24.0 g
KPS (initiator): 0.144 g

* To whom correspondence should be addressed.

Distilled VAC: 8.0 g
 Seed particles (number): 7.4×10^{13}
 particles/ L_{H_2O}
 Seed particles (mass): 0.0706 g
 Seed diameter: 0.4 μm
 Temperature: 70°C

Seven parallel experiments were carried out with this recipe. These reactions were stopped at different times and the reaction mixture analyzed for monomer conversion and particle concentrations and sizes. The results are shown in Table I. The number concentrations of the two particle populations do not change after the early part of the reactions. The number of particles formed by secondary nucleation was more than an order of magnitude greater than the number of seed particles. Hence the new particles represent a majority of the particle surface area (approximately 85%).

UGELSTAD THEORY ANALYSIS

The kinetics of emulsion polymerization with a monodisperse particle population involves radical balances on the particles and the aqueous phase.

A balance on the radicals inside particles provides the following recursion relation³

$$\frac{dN_n}{dt} = N_{n-1}(\rho_A/N) + N_{n+1}k_d(n+1) + N_{n+2}k_{tp} \times (n+2)(n+1)/v_p - N_n[(\rho_A/N) + k_d n + k_{tp}n(n-1)/v_p] \quad (1)$$

with solution^{4,5}

$$\bar{n} = \frac{a}{4} \left(\frac{I_m(a)}{I_{m-1}(a)} \right) \quad (2)$$

Table I. Data from Vinyl Acetate Seeded Polymerization

Time* (min)	Overall Conversion	D_{seed} (nm)	N_{seed} ($\times 10^{13}$ particles/L H_2O)	D_{new} (nm)	N_{new} ($\times 10^{15}$ particles/L H_2O)
0	0.0	400	7.4	0	0
10	18.8	780	7.4	400	1.32
20	39.1	950	7.4	490	1.29
30	71.4	1010	7.4	590	1.34
40	90.2	1180	7.4	650	1.34
50	99.2	1190	7.4	670	1.38

* The time data which were not part of the original publication were provided by Hayashi via private communication.

where

$$a = (8\alpha)^{1/2}$$

$$\alpha = \frac{\rho_A v_p N_A^2}{N k_{tp}}$$

$$m = \frac{k_d v_p N_A}{k_{tp}}$$

$I_m(a)$ and $I_{m-1}(a)$ are Bessel functions, N is the number of particles (particles/ L_{H_2O}), N_n is the number of particles containing n radicals, \bar{n} is the average number of radicals in a particle, ρ_A is the total rate of radical absorption by particles (mol/ L_{H_2O} s), k_d is a radical desorption constant (1/s), k_{tp} is the termination rate constant in particles (L/mol s), and v_p is the volume of a monomer swollen particle (L).

An overall balance on radicals in the aqueous phase provides²

$$\rho_A = \rho_i + \sum_{n=1}^{\infty} k_d n N_n - 2k_{tw} [R\cdot]_{\text{aq}}^2 \quad (3)$$

ρ_i is the rate of radical production in the aqueous phase (mole/ L_{H_2O} s), k_{tw} is the termination rate constant in the water phase (L/mol s), and $[R\cdot]_{\text{aq}}$ is the radical concentration in the aqueous phase (mol/ L_{H_2O}).

Assuming $\rho_A = k_a [R\cdot]_{\text{aq}}$, the radical flux into the seed particles can be written as:

$$\rho_A = \rho_i + \sum_{n=1}^{\infty} k_d n N_n - 2k_{tw} \left(\frac{\rho_A}{k_a} \right)^2 \quad (4)$$

where k_a is the radical absorption constant (1/s).

Multiplying each term by v_p/Nk_{tp} produces the following dimensionless relation:

$$\alpha = \alpha' + m\bar{n} - Y\alpha^2 \quad (5)$$

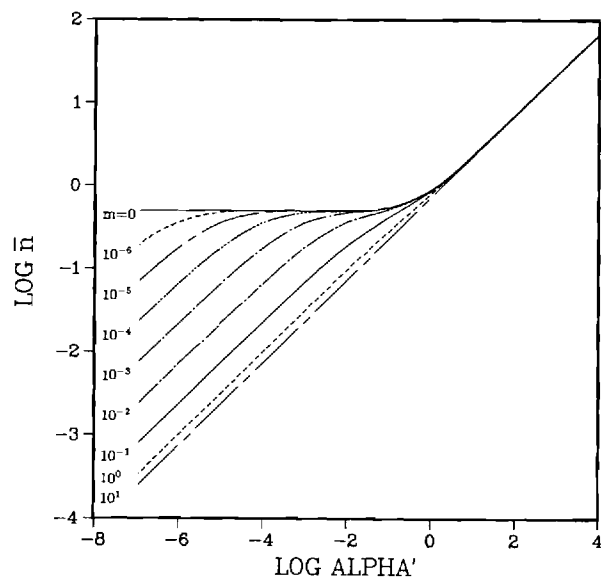


Figure 1. Solution plot for emulsion polymerization, m varied and Y held constant.

where

$$\alpha' = \frac{\rho_i v_p N_A^2}{N k_{tp}}$$

$$Y = \frac{2k_{tw} k_{tp} N}{v_p k_a^2 N_A^2}$$

and

$$k_c = \frac{k_a}{N}$$

Equations (2) and (5), which constitute the Ugelstad theory, can be plotted as shown in Figure 1 where Y is held constant and m varied, or as in Figure 2 where m is constant and Y varied.² A point on these plots would represent a specific instant in time during a batch reaction. Thus if values of \bar{n} and α' can be calculated from kinetic data one can use these plots to estimate a value of either m or Y , if one of these parameters is known.

An important observation related to these solution plots is that at low α' values radical desorption effects are significant and aqueous-phase termination effects are negligible for typical reaction conditions. At high α' values, aqueous-phase termination effects are significant and radical desorption effects are negligible. Thus if experimental runs are carried out under high α' conditions, \bar{n} and α' values from the experiments can be superimposed on Figure

2 to estimate Y for the system (assuming negligible radical desorption effects). The radical capture constant, k_c , can then be calculated from this value of Y if k_{tw} , k_{tp} , v_p , and N are known. A system with low α' values may be used to estimate m (and k_d) in a similar manner.

The vinyl acetate system considered in this paper contains a small number of large particles. This provides conditions necessary for high α' . Secondary nucleation occurs at the start of the batch reaction producing two populations of different size particles; the conditions necessary for competitive growth studies.

Conversion, particle number, and particle size data (shown in Table I) were obtained at each sample time and individual polymerization rates for each particle population were calculated. These rate data were then used to calculate values of \bar{n} for each particle population at each sample time.

The two different particle populations present a problem in estimating Y . The emulsion polymerization kinetic analysis presented earlier considers only a single monodisperse particle population. An initial estimate of Y can be obtained by considering this system to be monodisperse and calculating α' and various dimensionless parameters using average values of particle volume and \bar{n} . With these assumptions, the $\bar{n} - \alpha'$ data is superimposed on a solution plot in Figure 3. Two points are shown for data obtained at lower conversions in interval III, i.e., the data at 20 and 30 min. Higher conversions

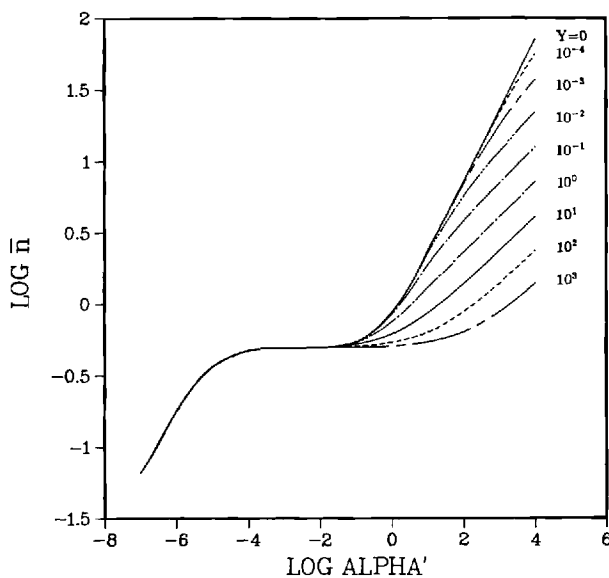


Figure 2. Solution plot for emulsion polymerization, Y varied and m held constant.

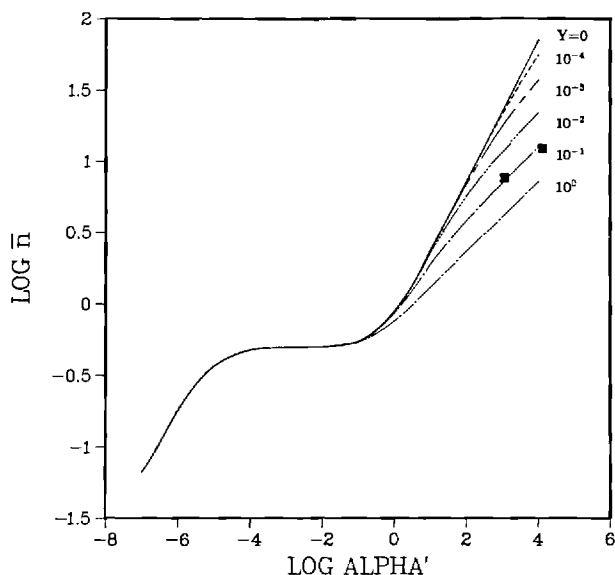


Figure 3. Estimation of Y for system assuming particles are monodisperse.

were not considered due to gel-effect uncertainties. The termination constant used in the calculations was adjusted for the gel-effect as indicated below. Both data points fall on a line representing a constant $Y_{\text{monodisperse}}$ value of approximately 10^{-1} . With this value of Y , the radical capture rate constant k_c was found to be $2.46 \times 10^{-12} \text{ cm}^3/\text{s}$. This estimate of k_c is influenced to a large extent by the nucleated particles due to their large number and surface area.

The gel-effect was accounted for by using an empirical treatment of bulk polymerization of vinyl acetate presented by Friis and Hamielec.⁶ The relation used is:

$$\frac{k_t}{k_{t_0}} = \exp(-0.4407X - 6.7530X^2 - 0.3495X^3) \quad (6)$$

where k_{t_0} is the termination rate constant at low conversions (without gel-effect), and X is the polymerization conversion. This empirical relation was fitted from bulk vinyl acetate polymerization data obtained at 50°C . We assumed that this same equation would be approximately correct at 70°C with the value of k_{t_0} selected to reflect the higher temperature. The water-phase termination constant, k_{tw} , is assumed equal to k_{t_0} and was estimated as $3.8 \times 10^8 \text{ L/mol s}$ from an Arrhenius plot of data obtained in the literature.⁷

A second proposed method for dealing with the two particle populations is to assume the radical absorption rate into each particle population is either

proportional to surface area (as in the case of collisional entry of radicals proposed by Gardon⁸) or can be modeled on the basis of continuum diffusion theories. Both cases were examined in this study. The population of particles formed by secondary nucleation are referred to as "new" particles in the nomenclature.

Considering seed particles, the radical absorption rate into the seed particles can be expressed as:

$$X_{\text{seed}} \rho_{A_{\text{total}}} \quad (7)$$

where

$$X_{\text{seed}} = \frac{N_{\text{seed}} D_{\text{seed}}^2}{N_{\text{seed}} D_{\text{seed}}^2 + N_{\text{new}} D_{\text{new}}^2}$$

for radical absorption proportional to surface area, or

$$X_{\text{seed}} = \frac{N_{\text{seed}} D_{\text{seed}}}{N_{\text{seed}} D_{\text{seed}} + N_{\text{new}} D_{\text{new}}}$$

for radical absorption modeled on the basis of continuum diffusion theory.

A balance on the radicals inside seed particles provides the following recursion relation

$$\begin{aligned} \frac{dN_{n_{\text{seed}}}}{dt} = & N_{n-1_{\text{seed}}} (\rho_{A_{\text{seed}}}/N_{\text{seed}}) \\ & + N_{n+1_{\text{seed}}} k_{d_{\text{seed}}} (n+1) + N_{n+2_{\text{seed}}} k_{tp} (n+2) \\ & \times (n+1)/v_{p_{\text{seed}}} - N_{n_{\text{seed}}} [(\rho_{A_{\text{seed}}}/N_{\text{seed}}) \\ & + k_{d_{\text{seed}}} n + k_{tp} n(n-1)/v_{p_{\text{seed}}}] \quad (8) \end{aligned}$$

with solution

$$\bar{n}_{\text{seed}} = \frac{a_{\text{seed}}}{4} \left(\frac{I_{m_{\text{seed}}}(a_{\text{seed}})}{I_{m_{\text{seed}}} - 1(a_{\text{seed}})} \right) \quad (9)$$

where

$$a_{\text{seed}} = (8\alpha_{\text{seed}})^{1/2}$$

$$\alpha_{\text{seed}} = \frac{X_{\text{seed}} \rho_{A_{\text{total}}} v_{p_{\text{seed}}} N_A^2}{N_{\text{seed}} k_{tp}}$$

$$m_{\text{seed}} = \frac{k_{d_{\text{seed}}} v_{p_{\text{seed}}} N_A^2}{k_{tp}}$$

An overall balance on radicals in the aqueous phase provides:

$$\rho_{A_{\text{total}}} = \rho_i + \sum_{n=1}^{\infty} k_{d_{\text{seed}}} n N_{n_{\text{seed}}} + \sum_{n=1}^{\infty} k_{d_{\text{new}}} n N_{n_{\text{new}}} - 2k_{tw} [R \cdot]_{\text{aq}}^2 \quad (10)$$

Assuming radical desorption has a negligible net effect on the resulting kinetics in the range of α' values considered (this is not to imply radical desorption does not occur) and $\rho_{A_{\text{seed}}} = k_{a_{\text{seed}}} [R \cdot]_{\text{aq}}$, the radical flux into the seed particles can be written as:

$$\begin{aligned} \rho_{A_{\text{seed}}} &= X_{\text{seed}} \rho_{A_{\text{total}}} \\ &= X_{\text{seed}} \rho_i - X_{\text{seed}} 2k_{tw} \left(\frac{\rho_{A_{\text{seed}}}}{k_{d_{\text{seed}}}} \right)^2 \end{aligned} \quad (11)$$

Multiplying each term by $v_{p_{\text{seed}}} / N_{\text{seed}} k_{tp}$ produces the following dimensionless relation:

$$\alpha'_{\text{seed}} = \alpha'_{\text{seed}} - Y_{\text{seed}} \alpha'^2_{\text{seed}} \quad (12)$$

where

$$\begin{aligned} \alpha'_{\text{seed}} &= \frac{X_{\text{seed}} \rho_i v_{p_{\text{seed}}} N_A^2}{N_{\text{seed}} k_{tp}} \\ Y_{\text{seed}} &= \frac{2 X_{\text{seed}} k_{tw} k_{tp} N_{\text{seed}}}{v_{p_{\text{seed}}} k_{d_{\text{seed}}}^2 N_A^2} \end{aligned}$$

Analysis of the new particle population will be similar except using $X_{\text{new}} = (1 - X_{\text{seed}})$.

A solution for the seed particles can be obtained using eqs. (9) and (12). This solution would produce a plot identical to Figure 2 for the monodisperse system. Thus the two particle populations may be considered individually with the redefined parameters.

Plotting individual $\bar{n} - \alpha'$ data on the solution plot with constant m_{seed} (radical desorption is assumed to have negligible effects on kinetics and m_{seed} is set to zero) and varying Y_{seed} allows estimation of the defined Y . This allows determination of k_a and k_c based on the seed growth ($k_a = N k_c$). A similar method is used for the new particle population. It should be noted that the Y 's in these individual cases are different since they are based on individual populations. The individual Y values would not be the same as $Y_{\text{monodisperse}}$ determined earlier with the "monodisperse" assumption.

Results are shown on Figure 4 for the two samples obtained at 20 and 30 min. The data points for the two different absorption theories overlap. Hence these data cannot help to resolve the question con-

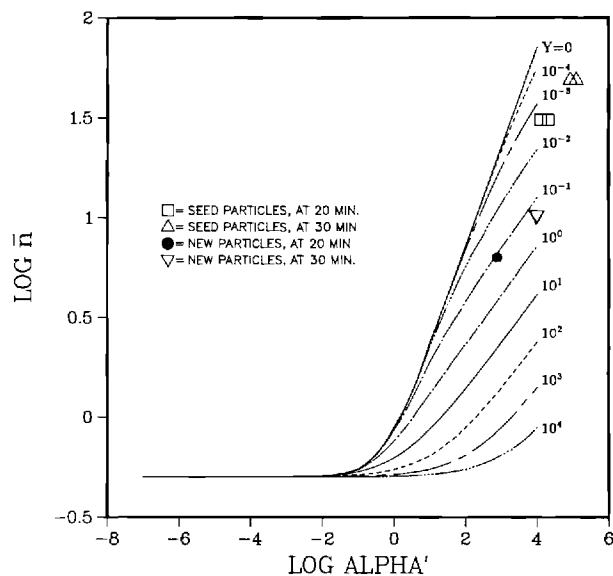


Figure 4. Estimation of Y_{seed} and Y_{new} . Data based on radical absorption proportional to surface area and radical absorption modeled on continuum mechanics are both plotted.

cerning models for radical absorption. The results shown in Figure 4 are used with data from the sample obtained at 20 min to calculate the values of k_c displayed in Table II. Calculation of k_c with data from the sample obtained at 30 min produced similar results. Values of k_c estimated for styrene are also shown in Table II for comparison. Penboss et al.⁹ estimated values of k_c for styrene by analysis of seeded styrene emulsion polymerization data. In an analysis of particle nucleation in emulsifier-free styrene systems, Hansen and Ugelstad^{10,11} considered the effects of electrostatic repulsion and irreversible absorption of radicals on k_c . From their analysis Hansen and Ugelstad proposed a value for an effective diffusion parameter \bar{D} (discussed below) which provides the values of k_c stated.

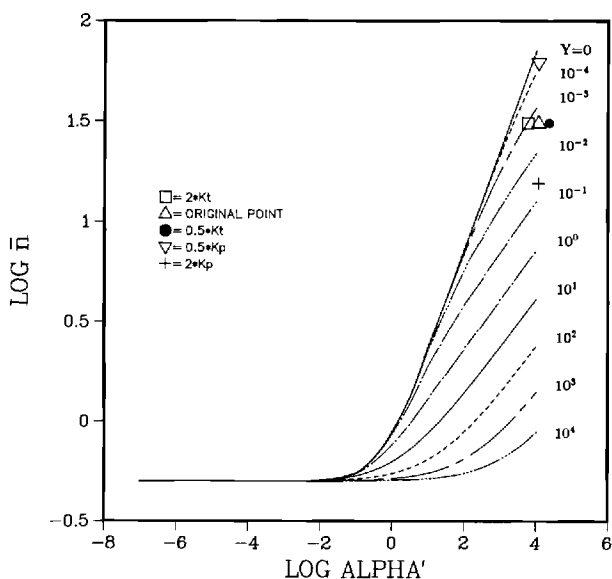
The estimates of k_c are dependent on accurate values of k_{tp} and k_p used to calculate \bar{n} and α' . Values of k_{tp} and k_p used in the calculations ($k_{t_0} = 3.8 \times 10^8$ L/mol s, $k_p = 13000$ L/mol s) are the estimates we obtained from Arrhenius plots of literature data. However variations of k_{t_0} and k_p about a linear least squares fit of literature data on the Arrhenius plots suggest some uncertainty in their values. Accounting for gel-effects with eq. (6) obtained from bulk polymerization data) also causes uncertainty in the value of k_{tp} for vinyl acetate emulsion polymerization. From consideration of the k_{tp} and k_p data, it appears reasonable to assume the true values of k_{tp} and k_p would not deviate from the values used by

Table II. k_c Estimates

System	k_c (cm^3/s)
Monodisperse assumption	2.5×10^{-12}
Based on seed particles	7.1×10^{-12}
Based on new particles	2.8×10^{-12}
Styrene polymerization (Penboss ⁹) (emulsifier present, $r_{\text{unswollen}} = 47 \text{ nm}$)	$6.6 \times 10^{-15} - 5.0 \times 10^{-16}$
Styrene polymerization (Hansen ^{10,11}) (emulsifier-free, $r_{\text{swollen}} = 50 - 500 \text{ nm}$)	$3.1 \times 10^{-10} - 3.1 \times 10^{-9}$

more than a factor of two. In order to obtain a reference as to the precision of the k_c estimates, the independent effects of changes in k_{tp} and k_p were examined. Figure 5 shows the effects of changing the values of k_{tp} or k_p by a factor of two on the estimate of Y . Table III displays the resulting effects on the values of k_c . Changing k_{tp} or k_p by a factor of two in both directions produces a range of k_c values covering approximately an order of magnitude.

The value of k_c estimated for the seed particles is approximately twice the estimate of k_c for the nucleated particles. If radical entrance into particles occurs by a diffusive mechanism, k_c would be expected to be proportional to the radius of the swollen particle. Since the seed particles have a radius approximately double that of the nucleated particles, $k_{c_{\text{seed}}}$ would be expected to be double the size of $k_{c_{\text{new}}}$ for a diffusive mechanism. Thus the estimates

**Figure 5.** Sensitivity of Y estimates to values of the rate constants k_{tp} and k_p .

obtained are in agreement with the diffusive mechanism for radical entrance.

Two factors must be considered regarding the estimates of k_c for this system. First is the size of particles used in this system. The value of k_c for a system will depend on the size of the swollen particles. The swollen particles considered in this vinyl acetate system have diameters in the 670–1330 nm range. These particles are relatively large in comparison with the particles in most emulsion polymerization systems. Thus the estimates of k_c obtained would be expected to be large compared to many typical emulsion polymerization systems.

A second factor to be considered is the absence of emulsifier. Emulsifier on the surface of particles would be expected to retard radical entrance into particles by acting as a physical barrier and electrostatic repulsion. This would tend to decrease the resulting value of k_c . Thus the absence of emulsifier in this study may produce larger estimates of k_c than would be expected with typical emulsion polymerization systems containing emulsifier.

If radicals are irreversibly absorbed into particles by a diffusive mechanism, then k_c may be expressed as:

$$k_c = 4\pi D_{\text{aq}} r_p \quad (13)$$

Table III. Sensitivity of k_c Estimates to Rate Constant Values

System	k_c (cm^3/s)
Original Estimate	7.1×10^{-12}
$2.0 * k_p$	2.3×10^{-12}
$0.5 * k_p$	4.5×10^{-11}
$2.0 * k_{tp}$	2.9×10^{-11}
$0.5 * k_{tp}$	3.2×10^{-12}

where D_{aq} is the diffusion coefficient of radicals in the aqueous phase and r_p is the switch radius. Since reversible absorption of radicals and electrostatic repulsion occur, these effects will lower k_c . Hansen and Ugelstad¹⁰ proposed expressing k_c as:

$$k_c = 4\pi\bar{D}r_p \quad (14)$$

where \bar{D} is the effective diffusion coefficient defined as

$$\bar{D} = \sum_{j=1}^{j_{cr}-1} \frac{F_j D_{aq,j} [R_j \cdot]}{[R \cdot]_{tot}} \quad (15)$$

with j representing the number of monomer groups polymerized on the oligomer radical, and j_{cr} the critical length of oligomer precipitation. Equation (15) accounts for reversible absorption and electrostatic effects through the term F_j . \bar{D} , the effective diffusion coefficient, should not be confused with the diffusion coefficient for oligomer radicals in water. The effects of reversible absorption and electrostatic effects are grouped with diffusion in \bar{D} . Hansen and Ugelstad¹¹ proposed a value of $\bar{D} = 5 \times 10^{-8} \text{ dm}^2/\text{s}$ for the emulsifier-free styrene system they studied. The particles used in Hansen and Ugelstad's study are in the same size range as the particles in this study.

The k_c values obtained from the respective Y 's in this study can be used, along with eq. (14) and the size data, to estimate the effective radical diffusion coefficient, \bar{D} . The values obtained were $\bar{D}_{seed} = 8.5 \times 10^{-11} \text{ dm}^2/\text{s}$ and $\bar{D}_{new} = 6.6 \times 10^{-11} \text{ dm}^2/\text{s}$. These values are smaller than the value suggested by Hansen and Ugelstad¹¹ for emulsifier-free styrene systems. The higher water solubility and larger propagation rate constant of vinyl acetate, in comparison to styrene, would lead to larger pre-capture sizes of the radical oligomers and hence a smaller diffusion coefficient. The more polar structure of vinyl acetate, in comparison to styrene, should also increase the electrostatic repulsion of oligomer radicals. These effects would be expected to produce smaller \bar{D} values for the vinyl acetate system.

COMPETITIVE GROWTH

Vanderhoff et al.,¹² based on extensive work with polystyrene latexes comprised of relatively small particles, considered the tendency of the particle size distribution of a polydisperse latex to become narrower during polymerization. This phenomena was modeled by expressing the particle growth rate in

terms of the unswollen diameter in the particles in the form of a power law.

$$\frac{dv_{P_{unswollen}}}{dt} = kD_{P_{unswollen}}^c \quad (16)$$

where $v_{P_{unswollen}}$ is the unswollen particle polymer volume, $D_{P_{unswollen}}$ is the unswollen particle diameter, and k and c are adjustable parameters.

Styrene emulsion polymerizations with two different size seed particle populations initially present were carried out to examine competitive growth effects. Conditions were adjusted to prevent secondary particle nucleation and the different size particles were allowed to compete for resources (monomer, radicals, etc.) during the polymerization. At the end of reaction the resulting average diameters of both seed populations were obtained. The vinyl acetate data reported by Hayashi et al.¹ fit these same conditions; hence, the Vanderhoff treatment was used to analyze the competitive growth results.

The theory presented in the remainder of this section was originally published by Vanderhoff and co-workers.¹² One can debate the validity of eq. (16) because the parameters k and c could be a function of particle size as well as other reaction parameters: ρ_i , N , T , etc.

Poehlein and Vanderhoff¹³ have shown, however, that k should be relatively independent of size and c should have specific values for the following limiting cases:

Case	\bar{n}	c
Smith-Ewart Case II	0.5	0.0
Smith-Ewart Case III	variable	2.5
Large particles with oil-soluble initiator	variable	3.0

Further development of the competitive growth model involves the integration of eq. (12), with c assumed constant to yield

$$\begin{aligned} D_b^{3-c} - D_{b_0}^{3-c} &= D_a^{3-c} - D_{a_0}^{3-c} \\ &= \frac{2(3-c)}{\pi} \int_0^t k(t) dt \quad (17) \end{aligned}$$

with a and b representing two different size populations of particles initially at D_{a_0} and D_{b_0} . Rearranging this relation and assuming that the $k(t)$ integrals cancel when ratios are calculated gives eq. (18),

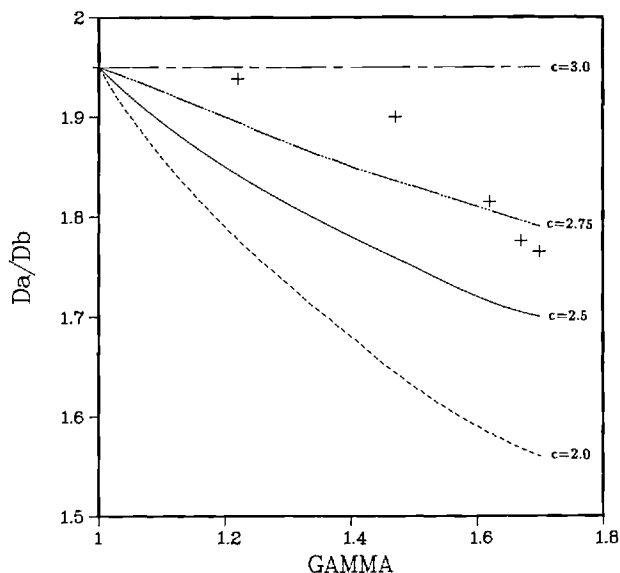


Figure 6. Variation of D_b/D_a with γ .

$$\frac{D_b}{D_a} = \frac{1}{\gamma} [\gamma^{3-c} + \beta^{3-c} - 1]^{1/3-c} \quad (18)$$

with

$$\beta = \frac{D_{b0}}{D_{a0}}$$

$$\gamma = \frac{D_a}{D_{a0}}$$

The various curves in Figure 6 demonstrate the effect of different values of c on the particle size ratio. If $c < 3$ then smaller particles will grow at a faster rate than larger particles and the particle size distribution will become narrower during reaction. If $c > 3$ the opposite effect will occur and the particle size distribution will broaden. Data from competitive growth experiments may be plotted on Figure 6 to estimate the value of c . Styrene emulsion polymerization was found to produce values of c in the range of 0 to 1 for smaller particles. A value of $c = 2.5$ was found to apply to large particles ($> 150 \text{ nm}$)¹² when water-soluble initiator was used.

In this seeded study of vinyl acetate, a second relatively monodisperse population of particles is nucleated shortly after the start of the polymerization (as observed by SEM). Thus, unintentionally, the particle size-time data for both particle popu-

lations allows competitive growth analysis of this vinyl acetate system. The particle size data were smoothed and corresponding diameter ratio values plotted on Figure 6. The data indicate the value of c is in the range of 2.75–3.0 for this system. This is the expected result for latexes comprised of relatively small numbers of larger particles.

SUMMARY

Kinetic analysis of data from the emulsifier-free, seeded emulsion polymerization experiments demonstrate that this system is in the high α' or Smith-Ewart Case III reaction region. Hence the data are useful for evaluation of water-phase termination phenomena and for estimation of radical absorption coefficients.

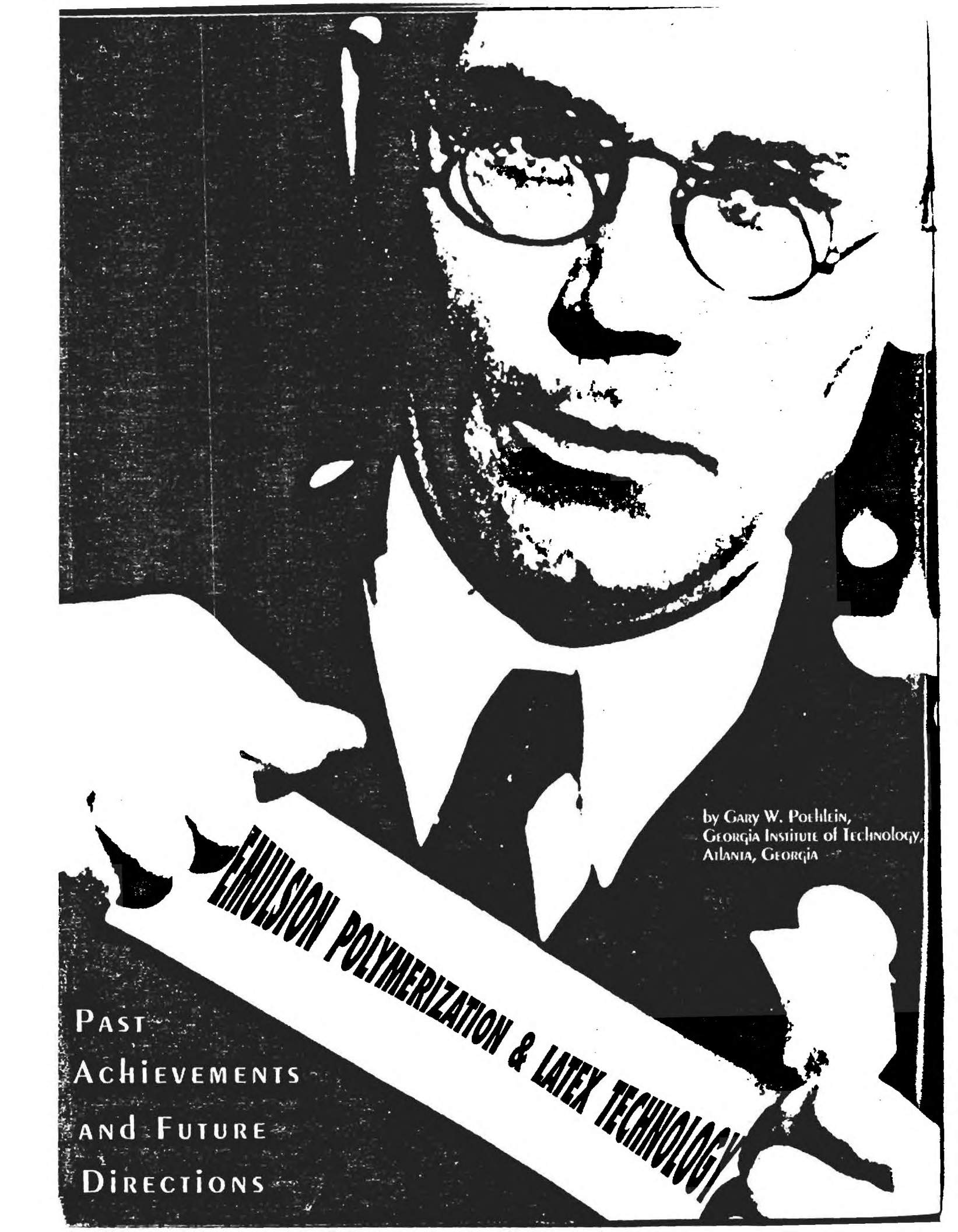
The authors acknowledge the support of the National Science Foundation under Grant No. CBT 8717926.

REFERENCES AND NOTES

1. S. Hayashi, A. Komatsu, and T. Hirai, *J. Polym. Sci. Part A: Polym. Chem.*, **27**, 157 (1989).
2. J. Ugelstad, P. C. Mork, and J. O. Aasen, *J. Polym. Sci. A-1*, **5**, 2281 (1967).
3. W. V. Smith and R. W. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).
4. W. H. Stockmayer, *J. Polym. Sci.*, **24**, 314 (1957).
5. J. T. O'Toole, *J. Appl. Polym. Sci.*, **9**, 1291 (1965).
6. N. Friis, and A. E. Hamielec, *Emulsion Polymerization*, ACS Symposium Series **24**, American Chemical Society, Washington, DC, 1976, p. 82.
7. J. Brandrup and E. M. Immergut, Eds., *Polymer Handbook*, 2nd ed., Interscience, New York, 1975.
8. J. L. Gardon, *J. Polym. Sci. A-1*, **6**, 643 (1968).
9. I. A. Penboss, R. G. Gilbert, and D. H. Napper, *J. Chem. Soc., Faraday Trans. 1*, **82**, 2247 (1986).
10. F. K. Hansen, and J. Ugelstad, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 1953 (1978).
11. F. K. Hansen, and J. Ugelstad, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 3033 (1979).
12. J. W. Vanderhoff, J. F. Vitkuske, E. B. Bradford, and T. Alfrey, *J. Polym. Sci.*, **20**, 225 (1956).
13. G. W. Poehlein and J. W. Vanderhoff, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 447 (1973).

Received December 8, 1989

Accepted November 9, 1990



by Gary W. Poehlein,
Georgia Institute of Technology,
Atlanta, Georgia

EMULSION POLYMERIZATION & LATEX TECHNOLOGY

PAST
ACHIEVEMENTS
AND FUTURE
DIRECTIONS



Everyone comes in contact with the products of emulsion polymerization daily—the synthetic rubber in our automobile tires, the latex paints inside and outside of our homes, the glue that holds our furniture together, and the key ingredient in some medical diagnostic tests.

Photo: DOW

Emulsion polymerization is an important commercial process for manufacturing such products as synthetic elastomers, surface coatings, adhesives, engineering plastics, model colloids, and process or product additives. Everyone comes in contact with the products of emulsion polymerization daily—the synthetic rubber in our automobile tires, the latex paints inside and outside of our homes, the glue that holds our furniture together, and the key ingredient in some medical diagnostic tests.

Classical emulsion polymerization involves the dispersion of organic monomers in water with an oil-in-water emulsifier, followed by polymerization with a water-soluble initiator. The course of a batch reaction is sometimes described in terms of three intervals. Interval I comprises particle nucleation in

the presence of a dissolved or micellar emulsifier. This interval ends early in the reaction (≈ 5 percent monomer conversion) when the surface of the particles becomes sufficient to adsorb all of the emulsifier. Interval II is the particle growth phase, with monomer being supplied by diffusion from the droplets through the water phase to the monomer-swollen particles. Interval III begins when the monomer droplets disappear and continues to the end of the reaction.

As with many commercial chemical processes, emulsion polymerization has progressed from an experience-based art to a reasonably well understood process. The purpose of this article is to provide a brief history of the process, followed by a review of some of the major milestones in establishing a more fundamental knowledge base.

Applications first, understanding second

A process for the polymerization of oily monomers in aqueous suspension or emulsion was first reported in the early 1900s. Commercial scale production apparently started in Germany in the 1930s, with the polymerization of vinyl acetate using polyvinyl alcohol as the emulsifier. (1)

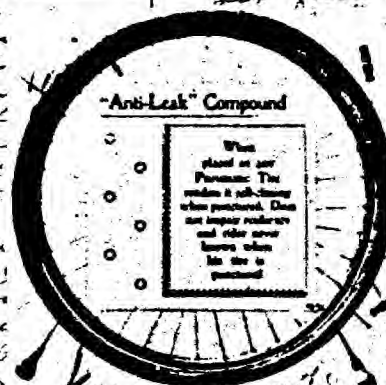
Early efforts to understand and commercialize the process in this country were clearly associated with the Rubber Reserve Program of World War II. Initiated to fill the country's rubber needs when supplies of natural rubber from Southeast Asia were cut off, the Rubber Reserve Company was created by the Reconstruction Finance Corporation on June 28, 1940. Though the company's original task was to locate

DOW AND RUBBER

Some interesting facts on Herbert Dow (a former director of the Institute) and the company he founded that would help to change the materials that make the world.



Herbert Dow in 1888



Dec. 16, 1889
To make the material of your own principle
only first in 9 days
 Left: One of Herbert Dow's earliest ventures. This company made and sold a compound to be poured into bicycle tires to seal punctures from the inside. The venture collapsed when tire manufacturers removed their guarantee from any tire showing signs of having been filled with the stuff. The company was born and died in the spring of 1896.

Right, top: A 1950 shot of the Latex production plant at Dow in Midland, Michigan.

Right, bottom: "Durable, Beautiful and Economical" Dow Latex paint in 1955.

photo: DOW

new sources of natural rubber and build stockpiles of the material, after Pearl Harbor its activities were primarily concerned with the development of a synthetic rubber industry in this country. (2)

The Rubber Reserve Program was one of the first successful collaborations between industry, universities and government. Indeed the synthetic rubber industry, which was up and running in the span of only two years, is considered one of the greatest chemical engineering feats of all time, earning it the top spot on the "Ten Greatest Achievements of Chemical Engineering," list compiled during AIChE's 75th Anniversary in 1983.

Out of these efforts came the "mutual recipe" (see table 1) for commercial production of styrene butadiene rubber (SBR). The reaction was slow using this recipe—only about 6 percent conversion per hour—and was stopped at about 60 to 75 percent conversion to avoid excessive crosslinking. Modern SBR recipes would be more carefully defined, would involve a higher monomer to water ratio, and would utilize redox initiators at lower temperatures.

During the early 1940s, a great deal was learned about the detailed reaction mechanisms and kinetics of the process. Experimental work with the monomer emulsions, and the resulting latexes, clearly demonstrated that the number of particles in the product were

significantly greater than the initial number of monomer droplets.

The first comprehensive picture of particle nucleation, published in 1947, suggested that particles were formed when water-borne free radicals entered emulsifier micelles containing solubil-

where R_p is the rate of polymerization per unit volume of water phase, $[M]_p$ is the monomer concentration in the particles, k_p is the propagation constant, N is the number of particles per volume of water phase and N_A is the Avogadro number. Please note that this equation is based on the assumption that no significant conversion of monomer to polymer occurs in the water phase.

Early workers who studied other monomers, such as vinyl acetate⁽⁵⁾ and vinyl chloride,⁽⁶⁾ found that the Smith-Ewart Case 2 theory did not fit the particle number or polymerization rate data. These workers proposed that nucleation occurred in the aqueous phase. Such a mechanism would be favored, they argued, by the higher water solubility of the monomers and larger propagation rate constants. Under these conditions the radicals in the aqueous phase would grow until they reached their solubility limit. The massive amount of work with the Rubber Reserve Program was aimed at styrene and styrene-butadiene systems. Hence, the concepts associated with more water-soluble monomers were not examined in more detail until the 1960s.

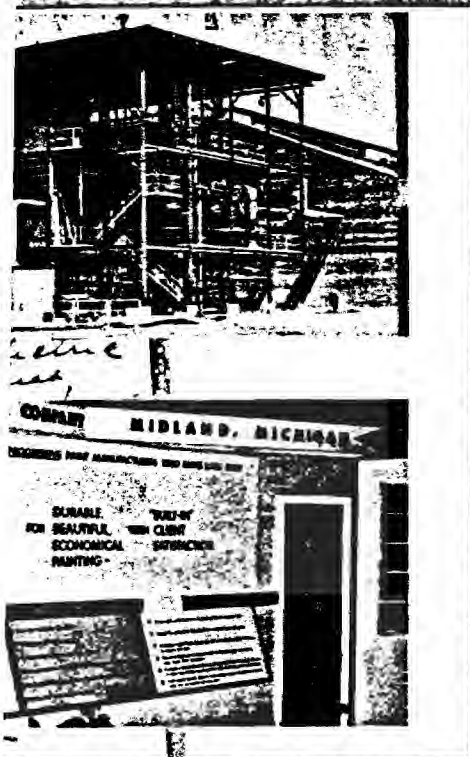
The common textbook and lecture statement that "emulsion polymerization has an advantage over bulk, solution and suspension processes because one can achieve both high rates and high molecular weight," is based on the Smith-Ewart Case 2 model. This is not

Table 1: "Mutual Recipe" for SBR Rubber Production

Ingredient	Parts by Weight
Butadiene	75
Styrene	25
Commercial Dodecyl Mercaptan	0.5
Potassium Persulfate	0.3
Soap Flakes	5
Water	180
Polymerization Temperature	50°C

ized monomer. (3) These "radical-stung" micelles would then grow by polymerization, with monomer being supplied via diffusion from the droplets. Emulsifier would adsorb on the new surface of the particles until the micelles disappear, at which time the nucleation process would stop. A quantitative kinetic model, known as the Smith-Ewart Case 2 Theory, appeared the following year. (4) Successfully applied in many studies of styrene emulsion polymerization, the key assumption of this theory is that the average number of free radicals per particle, \bar{n} , in the following rate expression is 0.5:

$$R_p = k_p [M]_p (\bar{n} N / N_A)$$

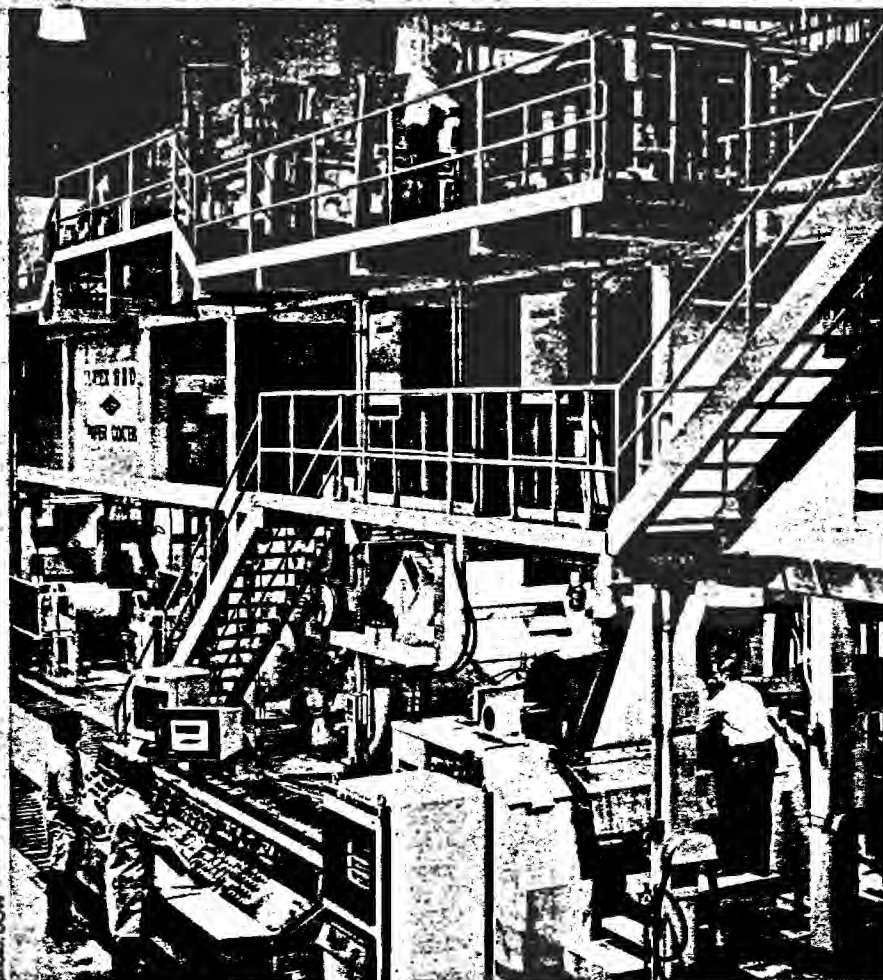


a valid concept for vinyl acetate or vinyl chloride emulsion polymerization because of the significant rate of chain transfer to monomer—a molecular weight controlling phenomenon. In addition, we now know that the small monomer-unit radicals formed in such a reaction can diffuse back into the aqueous phase. This so-called "radical desorption" leads to \bar{n} values considerably less than 0.5 for vinyl acetate, vinyl chloride, and even for styrene if a significant amount of appropriate chain transfer agent is used.

Advancing by accident

The development of emulsion polymerization processes continued into the 1950s, but most of the work was carried out in industrial laboratories and publication of fundamental papers in journals slowed. One of the most important contributions occurred by accident in 1948. R.C. Williams and R.C. Backus of the University of Michigan requested a latex sample from the Dow Chemical Company for use in electron microscope studies. They were sent, presumably by random selection, one gallon of Dow latex 580-G, Lot 3584, which they discovered was monodisperse with a diameter of 254 ± 1.5 nm—with the ± 1.5 due more to measurement uncertainty than particle polydispersity.

The Williams-Backus publication caused considerable interest in the Dow latex among academic scientists working in areas such as particle measurement, microscope calibration and



Paper coater at the Dow Research and Development Center

other scale-measurement techniques. The Dow latex was distributed, in small samples, to many workers and the supply was soon exhausted. Other Dow latexes were not found to be monodisperse and numerous attempts to reproduce 580-G Lot 3584 were unsuccessful.

Toward the end of this period (1950-52), Turner Alfrey asked a young chemist in his group at Dow, John W. Vanderhoff, to begin learning about emulsion polymerization. With true beginner's luck, Vanderhoff was able to reproduce the 580-G monodisperse latex on his first try, and was later able to show that these latexes could be routinely produced if one had short nucleation periods, followed by long growth periods.

The development of techniques for producing monodisperse latexes was important for several reasons. First, such particles could be used for a variety of fundamental research applications. Later advances, which permitted the characterization and control of the surface chemistry of these latexes, made them even more useful for the scientific community. Second, these particles allowed researchers to study emulsion polymerization kinetics. The

rate expression presented earlier contains three unknown terms— $[M]_p$, \bar{n} and N . The interpretation of data from experiments that involve both nucleation and growth is made more complicated because both \bar{n} and N can vary. Seeded experiments, in which N is known and no new particles are formed, have proven to be very valuable for kinetic studies of particle growth.

A third development to come out of this work was the use of seed latexes for commercial production. The particle nucleation component of emulsion polymerization is the least well understood, in a quantitative sense, and the least reproducible in industrial practice. The use of seed particles, produced in a separate reaction, can help to increase batch-to-batch uniformity of a finished product. The final product recipe is reformulated based on starting and target particle sizes and number concentrations for each batch of seed. Reaction kinetic studies in the 1950s and early 1960s focused on determining the influence of recipe and reactor variables on the rate equation variables.

LATEX TECHNOLOGY AT LEHIGH

Interest in emulsion polymerization and latex technology increased significantly in the late 1960s and 1970s, when it became clear that latexes would replace many solvent-based polymer systems, especially in the coating and adhesives area. Around the same time, I began conducting research in this area at Lehigh University in Bethlehem, Pennsylvania.

Emulsion polymerization research at Lehigh began in the late 1960s, when graduate student Andrew DeGraff investigated the emulsion polymerization of styrene in a continuous stirred-tank reactor (CSTR). His results, published in 1971, used Smith-Ewart Case 2 kinetics to model the CSTR for prediction of R_p , N , particle size distribution and molecular weight. (9)

In June of 1970, the school offered its first short course on this topic, entitled "Advances in Emulsion Polymerization and Latex Technology." Among the speakers were W.V. Smith (of the Smith-Ewart theories), C.P. Roe of Uniroyal, and Vanderhoff, the Dow researcher who had just joined the faculty of Lehigh's Chemistry Department. The course was an instant success, with 35 industrial registrants in its first year.

Vanderhoff and I began working together that year to form what was to become the school's Emulsion Polymer Institute (EPI). An industrial affiliates program, the Emulsion Polymers Industrial Liaison Program, was formed in the early 1970s and already had a membership of about 12 companies when EPI was officially chartered by Lehigh in 1975.

Since its rather modest start, EPI has made numerous contributions to the field in three general areas:

Education: The educational and instructional component of EPI serves both full-time students and those working in the field. The number of students participating in undergraduate and graduate research has increased from one in 1968, to nearly 50 in 1990. Most of the present 40-plus graduate students are pursuing degrees in chemistry or chemical engineering.

These students are involved in a very broad range of research projects, including preparation of latexes, measurement of important characteristics, such as particle size distributions and surface chemical group concentrations, and determination of performance in specific applications. The desired end goal of this research is to generate the knowledge base which could be used to establish the chemical recipes and

processing procedures necessary to manufacture high-quality latexes for a variety of important applications. A similar program at Georgia Institute of Technology is strongly focused on reaction kinetics, process modeling and control.

Registration in the annual emulsion polymers short course at Lehigh has grown rapidly, with nearly 150 enrolled in the June 1991 course. A similar course has also been offered every year since 1978 in Davos, Swit-



zerland. Approximately 3,000 people have taken the courses at Lehigh and Davos since they were started. Many of the organizations that send scientists and engineers to these courses also support emulsion polymers research at Lehigh and/or at Georgia Institute of Technology, where I have been employed since 1978.

Service: Service activities for industry have been offered through the Emulsion Polymers Industrial Liaison Program (EPIIP) at Lehigh, and now through a similar program, the Polymer Program Associates, at Georgia Tech in Atlanta. The EPIIP at Lehigh has grown from 5 companies in the early 1970s to 44 in 1990, with member companies drawn from many countries. Georgia Tech's Polymer Program Associates currently has 16 members, with 4 supporting emulsion polymerization activities. Companies in these affiliate programs interact extensively with faculty and students. They are kept informed about specific research projects and have early access to results.

Lehigh's program was one of the early affiliate programs in the U.S. and clearly is very successful. Membership

fees have helped educate many students in this important area of polymer science and engineering, and produced research results useful to industry. Member companies monitor the research results closely and offer recommendations for new research directions, in addition to providing financial support. In some cases part of the research is conducted in the laboratories of affiliate companies.

Research: Lehigh's research program is very broad and has, since the mid-1970s, involved contributions from a number of other faculty members. The range of areas studied include:

- ▶ Latex characterization
- ▶ Kinetics and reaction engineering
- ▶ Application problems
- ▶ Stabilization phenomena

Some of the more significant areas of work in the program's early days were:

Characterization—Many of the advances in reaction engineering and application performance have been made possible by enhanced analysis techniques. Some areas in which the Lehigh group have contributed include surface cleaning through ion exchange and serum replacement, surface group titration and modification, chromatography methods for particle size measurement, and surface tension/structure determination. The ability to remove dissolved and adsorbed species from the latex serum and particle surfaces, and to modify surface groups and/or ionic charges has permitted the preparation of a wide range of model colloids for fundamental scientific research. Using these same techniques to determine the end location of recipe ingredients has also helped to develop a more complete understanding of the reaction process.

Kinetics/Reaction Engineering—Studies in the areas of latex preparation, kinetics, and reactor problems have involved a number of graduate students and faculty. Two very different areas of study will serve to illustrate the breadth of these contributions: continuous reactor systems, and preparations involving mixed stabilizing species. My group at Lehigh initiated emulsion polymerization studies in continuous reactors at a time when very little had been published on such systems. Steady-state well-mixed CSTRs offer the advantage of direct rate measurement and a broad particle size distribution (PSD) in the latex effluent. Simulation of PSDs are a good test for particle growth models and early experimental results were very useful

In eliminating some proposed model forms.

Achieving steady-state operation in a CSTR is not always easy, however, since the coupled nucleation-growth kinetics often lead to sustained conversion and particle number oscillations. This problem was solved by placing a plug-flow tubular reactor upstream of the CSTR. The nucleation takes place in the tube and the reactor operates at a stable steady-state.

The tube-CSTR combination was then employed at Georgia Tech to study radical transport from particles. Polymerization rate and the effluent PSD measurements are quite useful in quantifying radical desorption rates. More recent work has involved copolymerization with monomers having different water solubilities in tube-CSTR systems. A second area of interesting work within the Lehigh group was initiated when John Ugelstad of the University of Trondheim was a visiting scientist in the early 1970s. This effort involved using mixed emulsifier systems to achieve very small monomer droplets that could compete effectively for free radicals during the particle nucleation stage of the reaction. These emulsifier mixtures, comprised of an ionic emulsifier and a long-chain fatty alcohol, were used at a level of 1-3 wt percent based on monomer, and one could form bimodal latexes from such recipes.⁽¹⁰⁾

This work has been followed in two directions. First, the combination of monomer-droplet and continuous-phase nucleation was used to yield bimodal or broadened particle size distributions. Such PSDs can help in the production of high solids dispersions for coatings, PVC plastisols, etc.

A second application was to prepare latexes from polymer solutions by direct emulsification to yield small droplets followed by solvent stripping. This technology permits the production of latexes from polymers that are not formed by free radical mechanisms.

Work with recipes involving mixed stabilizer systems also led to the concept of using swelling agents to greatly enhance the swelling of polymer particles by monomer. These agents can also be used to stabilize monomer emulsions against diffusive degradation.

SUMMARY

Emulsion polymerization and latex technology has progressed from a "practiced art" to a reasonably well-understood complex process. Workers from industry, government laboratories, and universities have contributed to the progress that has been

made since the first major commercial utilization of the process in the 1930s and 1940s. The field is still progressing, however, and a number of problems need future work.

The problems being explored in depth today are generally focused at special applications that require very specific properties and/or particle structures. Examples include latexes for property modification of engineering plastics, controlled non-spherical shapes, hollow particles to enhance light scattering in coatings, particles with bioactivity for medical applications, large monodisperse particles—solid and porous—for chromatography columns, colored particles, synthetic pigments, etc. Most of these applications require the control of the structure of individual particles, an exciting area for present and future research contributions.

ACKNOWLEDGMENTS

I wish to acknowledge my former colleagues at Lehigh University for sharing the excitement of discovery and the building of an interdisciplinary program. A particular debt is due to John Vanderhoff, a friend who made the importance of creative chemistry clear to a chemical engineer. Support from the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, Lehigh, Georgia Tech and numerous industrial organizations is also acknowledged. Last, but not least, I thank the students who did most of the work and were a pleasure to be with for a few years. ▼

LITERATURE CITED

1. El-Aasser, M.S. and J.W. Vanderhoff, *Emulsion Polymerization of Vinyl Acetate*, Applied Science Publishers, New York, 1981.
2. Bovey, F.A., I.M. Koethoff, A.I. Medalia and E.J. Meehan, *Emulsion Polymerization*, Interscience Publishers, New York, 1955.
3. Harkins, W.D., *Journal of the American Chemical Society*, 69, 1428, 1947.
4. Smith, W.V. and R.H. Ewart, *Journal of Chemical Physics*, 16, 592, 1948.
5. Priest, W.J., *Journal of Physical Chemistry*, 56, 1077, 1952.
6. Jacobi, B., *Angew. Chem.*, 64, 539, 1952.
7. Backus, R.C. and R.C. Williams, *Journal of Applied Physics*, 19, 1186, 1948.
8. *Ibid*, 20, 224, 1949.
9. DeGraff, A.W. and G.W. Poehlein, *Journal of Polymer Science A-2*, 9, 1955, 1971.
10. Ugelstad, J., M.S. El-Aasser, and J.W. Vanderhoff, *Journal of Polymer Science, Polymer Lett. Edition*, 11, 505, 1973.

RECOMMENDED READING

- Hohenstein, W.P. and H. Mark, *Journal of Polymer Science*, 1, 127, 1946.
- Piirma, I. and J.L. Gordon, editors, *Emulsion Polymerization*, ACS Symposium Series 14, Washington, DC, 1976.
- Bassett, D.R. and A.E. Hamilec, editors, *Emulsion Polymers and Emulsion Polymerization*, ACS Symposium Series, 165, Washington, DC, 1981.
- Piirma, I., editor, *Emulsion Polymerization*, Academic Press, New York, 1982.
- Eliseeva, V.I., S.S. Ivanchev, S.I. Kuchanov, A.V. Lebedev, *Emulsion Polymerization and its Applications in Industry*, translation from Russian by S.J. Teague, Consultants Bureau, New York, 1981.
- Poehlein, G.W., R.H. Ottewill, and J.W. Goodwin, editors, *Science and Technology of Polymer Colloids*, NATO ASI Series E - No. 67, Martinus Nijhoff Publishing, The Hague, 1983.
- Candau, F. and R.H. Ottewill, editors, *Scientific Methods for the Study of Polymer Colloids and their Applications*, NATO ASI Series C - Vol 303, Kluwer Academic Publishing, Dordrecht, 1990.
- El-Aasser, M.S. and R.M. Fitch, editors, *Future Directions in Polymer Colloids*, NATO ASI Series E - No. 138, Martinus Nijhoff Publishing, Dordrecht, 1987.
- Morton, M., S. Kaisermann and M.W. Altier, *Journal of Colloid Science*, 9, 300, 1954.
- Stockmayer, W.H., *Journal of Polymer Science*, 24, 314, 1957.
- O'Toole, J.T., *Journal of Applied Polymer Science*, 9, 1291, 1965; *Journal of Polymer Science Part C*, 27, 171, 1969.
- Napper, D.H. and A.E. Alexander, *Journal of Polymer Science*, 61, 127, 1962.
- Stannett, V.T., M. Litt and R. Patsiga, *Journal of Physical Chemistry*, 64, 801, 1960.
- Dunn, A.S. and P.A. Taylor, *Makromol. Chem.*, 83, 207, 1965.
- Fitch, R.M., *Official Digest of the Journal of Paint Technology Engineering*, 37, 489, Pt. 2, 32, 1965.
- Fitch, R.M., M.B. Prenosil and K.J. Sprick, *Journal of Polymer Science, Part C*, 27, 95, 1969.
-
- This paper was originally presented at a symposium organized by AIChE's History of Chemical Engineering Subcommittee at the 1990 Annual AIChE Meeting in Chicago. It was revised by the author in June of 1991.*

ANNUAL PROGRESS REPORT

(January 1993)

NATIONAL SCIENCE FOUNDATION GRANT NO. CTS-9023240

GEORGIA TECH PROJECT NO. E-19-645

PROJECT TITLE: Emulsion and Dispersion Polymerization

PROJECT DIRECTOR: Gary W. Poehlein

SUBMITTED TO: Dr. Maria Burka, Program Director
Process and Reaction Engineering Division of
Chemical, Biochemical and Thermal Engineering
National Science Foundation

INTRODUCTION

Research has been primarily focussed on reactions in the continuous phase of heterogeneous free radical process. These reactions include initiation, propagation, absorption into particles and chain transfer to water-soluble polymer. These reactions are especially important in the early, particle nucleation parts of emulsion and dispersion polymerization processes.

RESEARCH SUMMARIES

Water-Phase Reactions in Emulsion Polymerization: The overall conversion of monomer to polymer in most emulsion polymerization reactions takes place in the submicron monomer-swollen polymer particles. Water soluble initiators, however, produce hydrophilic free radicals which must add some monomer units in the water phase in order to be able to enter the monomer-polymer particles. These water-phase reactions have not received much attention in the literature even though they are an important part of the reaction sequence.

We have carried out experiments in which the low molecular weight, water soluble materials which are left after inhibition have been characterized. Inhibition was accomplished by two methods: the addition of a water soluble inhibitor and the use of latex seed particles contain inhibiting SH groups on the surface. These experiments were made with co-monomers which has vastly different solubilities in the water--e.g., styrene and acrylic acid. Both compositions and molecular weights of the isolated materials were measured. The results show that water-soluble oligomers have as many as 13-15 monomer units before they enter latex particles.

Dispersion Polymerization Kinetics: Batch dispersion polymerization reactions start as homogeneous solutions of monomer, solvent, initiator and a polymeric stabilizer. The polymer formed is not soluble in the continuous phase. The polymeric precipitate is stabilized in particle form by the polymeric stabilizer. In contrast to emulsion polymerization dispersion systems are more complex because:

- The nature of the continuous phase (solvency) changes during the course of the reaction.
- A significant amount of polymerization can take place in both the continuous and particle phases.

We have developed a reaction model which can be used to predict reaction rates in both phases and transport between the phases. Preliminary work has involved the use of this model for analysis of literature batch data. Future work will involve competitive growth experiments with bimodal seeds and seed-fed runs in continuous stirred tank reactors. Reactions have been carried out to produce seeds. The experiments with these seeds will be conducted so that no new particles will be formed. This will permit a detailed evaluation of reaction rates and transport phenomena.

PAPERS AND PRESENTATION

PUBLISHED (ATTACHED):

"Characterization of Styrene-Carboxylic Acid Monomer Emulsion Copolymerization," with David Lange, *Polym. React. Eng.*, 1:1, 1-39 (1992).

"Modeling of Styrene-Carboxylic Acid Monomer Emulsion Copolymerization in a Series of Seed-Fed Continuous Stirred-Tank Reactors," with David Lange, *Polym. React. Eng.*, 1:1, 41-73 (1992).

"Emulsion Polymerization and Copolymerization in Continuous Reactor Systems," *Polymer International*, 30, 243-251 (1993).

IN PRESS:

"Modelling Poly(Vinyl Alcohol)-Stabilized Vinyl Acetate Emulsion Polymerization, Part I: Theory," with Cheryl M. Gilmore and F. Joseph Schork, *J. Appl. Polym. Sci.*

"Modelling Poly(Vinyl Alcohol) - Stabilized Vinyl Acetate Emulsion Polymerization, Part II: Comparison with Experiment," with Cheryl M. Gilmore and F. Joseph Schork, *J. Appl. Polym. Sci.*

ACCEPTED:

"Investigation of the Sequence Distribution of Bulk and Emulsion Styrene - Acrylic Acid Copolymers by ^1H - and ^{13}C -NMR," with S. Wang, *J. Appl. Polym. Sci.*

PRESENTATIONS:

"Emulsion Polymerization Mechanisms and Kinetics," Short courses at Lehigh University (June 1992) and Davos, Switzerland (August 1992).

"Emulsion Polymerization Reaction Engineering," Short course at Lehigh University (June 1992) and Davos, Switzerland (August 1992).

"Influence of Reactor Design and Operation on Latex Characteristics," National Starch and Chemical Company (New Jersey).

"Emulsion Polymerization Kinetics and the Use of Seeds in Commercial Production," Eastman Chemical Company (Tennessee).

RESEARCH PLANS

Future research will focus in three areas.

- Dispersion polymerization with seeds in semi-batch and continuous stirred-tank reactors. This work will help develop a more complete understanding of particle growth phenomena.
- Preliminary work will be carried out on grafting reactions in free radical polymerization. Such reactions can be very important in multiple phase disperation and emulsion particles.
- Studies of water-phase reactions and blocky copolymers formed in emulsion polymerization reactions with comonomers having significantly different water solubilities will be continued.

These studies will continue to enhance our understanding of heterogeneous free radical polymerization processes. The end goal of being able to design a reaction process to achieve specific product properties will be closer to reality.

STAFF

Dr. Gary W. Poehlein, Principal Investigator
Dr. Shouting Wang, Postdoctoral Fellow

Mr. Pei-Hua Yang, Ph.D. Candidate (ChE)
Mr. Syed Ahmed, Ph.D. Candidate (ChE)
Mr. Ravindia Kshirsogan, M. S. Candidate (ChE)
Mr. Jeffery Cross, Undergraduate (ChE)
Mr. Ryosuki Nishida, Visiting Industrial Scientist

Additional support from Georgia Institute of Technology, J. Exlan Co. and Dow Chemical has helped to expand this NSF-funded program.

NATIONAL SCIENCE FOUNDATION
 4201 Wilson Blvd.,
 Arlington, VA 22230

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

PI/PD Name and Address

Gary W. Poehlein
 School of Chemical Engineering
 GA Tech Res Corp - GIT
 Atlanta GA 30332-0100

NATIONAL SCIENCE FOUNDATION FINAL PROJECT REPORT

PART I - PROJECT IDENTIFICATION INFORMATION

1. Program Official/Org.	Maria Burka - CTS	
2. Program Name	CHEMICAL REACTION PROCESSES PROGRAM	
3. Award Dates (MM/YY)	From: 05/91	To: 10/94
4. Institution and Address	GA Tech Res Corp - GIT Administration Building Atlanta GA 30332	
5. Award Number	9023240	
6. Project Title	Emulsion and Dispersion Polymerization	

This Packet Contains
 NSF Form 98A
 And 1 Return Envelope

F Grant Conditions (Article 17, GC-1, and Article 9, FDP-11) require submission of a Final Project report (NSF Form 98A) to the NSF program officer no later than 90 days after the expiration of the award. Final Project Reports for expired awards must be received before new awards can be made (NSF Grants Policy Manual Section 677).

Now, or on a separate page attached to this form, provide a summary of the completed projects and technical information. Be sure to include your name and award number on each separate page. See below for more instructions.

PART II - SUMMARY OF COMPLETED PROJECT (for public use)

The summary (about 200 words) must be self-contained and intelligible to a scientifically literate reader. Without restating the project title, it should begin with a topic sentence stating the project's major thesis. The summary should include, if pertinent to the project being described, the following items:

- The primary objectives and scope of the project
- The techniques or approaches used only to the degree necessary for comprehension
- The findings and implications stated as concisely and informatively as possible

See Attachment 1.

PART III - TECHNICAL INFORMATION (for program management use)

List references to publications resulting from this award and briefly describe primary data, samples, physical collections, inventions, software, etc. created or gathered in the course of the research and, if appropriate, how they are being made available to the research community. Provide the NSF Invention Disclosure number for any invention.

See Attachment 2.

I certify to the best of my knowledge (1) the statements herein (excluding scientific hypotheses and scientific opinion) are true and complete, and (2) the text and graphics in this report as well as any accompanying publications or other documents, unless otherwise indicated, are the original work of the signatories or of individuals working under their supervision. I understand that willfully making a false statement or concealing a material fact in this report or any other communication submitted to NSF is a criminal offense (U.S. Code, Title 18, Section 1001).

	Nov. 7, 1994
Principal Investigator/Project Director Signature	Date

**IMPORTANT:
MAILING INSTRUCTIONS**
Return this *entire* packet plus all attachments in the envelope attached to the back of this form. Please copy the information from Part I, Block I to the *Attention block* on the envelope.

PART II

SUMMARY OF COMPLETED PROJECT / AWARD # CTS-9023240

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

Project Title: Emulsion and Dispersion Polymerization

Heterogeneous free radical polymerization processes such as suspension, dispersion and emulsion are used to manufacture a wide variety of important commercial products. Environmental issues have been a major driving force for increased research and utilization of water-based coatings and adhesives produced by emulsion polymerization. These products are often copolymers of monomers which have significantly different solubilities in the continuous aqueous phase. The primary focus of the research completed under this grant has been to develop a more complete fundamental understanding of reactions with such monomer mixtures.

Water soluble monomers which contain functional groups such as carboxyl, sulfate or sulfonate can influence polymerization kinetics by increasing the number of latex particles formed and/or by changing the average number of growing free radicals per particle. Our research has focussed on determining the mechanisms that are responsible for these observations. Measurements of polymerization rates have been coupled with determinations of the distribution of the monomer between the organic and aqueous phases. This has permitted the development of a reasonably complete understanding of the kinetics of such systems.

Other work has focussed on the growth of oligomeric radicals in the water phase prior to entry into the monomer-swollen polymer particles. The length and composition of these oligomers have been experimentally determined for a number of comonomer pairs. This has enhanced our ability to design reaction conditions and procedures to achieve desired product characteristics.

PART III

TECHNICAL INFORMATION / GRANT # CST-9023240

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

Project Title: Emulsion and Dispersion Polymerization

The results of the research conducted under CTS-9023240 have been made available to the external community via a number of 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 areas are provided in the remainder of this section.

(1) Publications during Grant period:

1. "Kinetics of Emulsion Copolymerization with Acrylic Acids," with G. L. Shoaf, *J. Appl. Polym. Sci.*, 42:5, 1213-1238 (1991).
2. "Solution and Emulsion Polymerization with Partially Neutralized Methacrylic Acid," with G. L. Shoaf, *J. Appl. Polym. Sci.*, 42:5, 1239-1258 (1991).
3. "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).
4. "Emulsion Polymerization and Latex Technology: Past Achievements and Future Directions," *Chapter One*, 5(1), 22-28 (9/1991).
5. "Characterization of Styrene-Carboxylic Acid Monomer Emulsion Copolymerization," with David Lange, *Polym. React. Engr.*, 1:1, 1-39 (1992).
6. "Modeling of Styrene-Carboxylic Acid Monomer Emulsion Copolymerization in a Series of Seed-Fed Continuous Stirred-Tank Reactors," with David Lange, *Polym. React. Engr.*, 1:1, 41-73 (1992).
7. "Emulsion Polymerization and Copolymerization in Continuous Reactor Systems," *Polymer International*, 30, 243-251 (1993).
8. "Modeling Poly (Vinyl Alcohol)-Stabilized Vinyl Acetate Emulsion

- Polymerization. I. Theory," with C. M. Gilmore and F. J. Schork, *J. Appl. Polym. Sci.*, 48, 1149-1460 (1993).
9. "Modeling Poly (Vinyl Alcohol)-Stabilized Vinyl Acetate Emulsion Polymerization. II. Comparison with Experiment," *J. Appl. Polym. Sci.*, 48, 1461-1473 (1993).
 10. "Investigation of the Sequence Distribution of Bulk and Emulsion Styrene - Acrylic Acid Copolymers by ¹H- and ¹³C-NMR," with S. Wang, *J. Appl. Polym. Sci.*, 49, 991-1001 (1993).
 11. "Characterization of Water-Soluble Oligomer in Acrylic Acid-Styrene Emulsion Copolymerization," with S. Wang, *J. Appl. Polym. Sci.*, 50, 2173-2183 (1993).
 12. "Studies of Water-Soluble Oligomers Formed in Emulsion Copolymerization," with S. Wang, *J. Appl. Polym. Sci.*, 51, 593-604 (1994).
 13. "Radical Entry into Particles During Emulsion Polymerization of Vinyl Acetate," with R. S. Kshirsagar, *J. Appl. Polym. Sci.*, 54, 909-921 (1994).

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

- (i) 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.
- (ii) Seminars have been presented at universities and industrial laboratories including:
 - Beijing Institute of Technology
 - National Starch & Chemical Co.
 - University of Tennessee
 - Ameripol Synpol Co.
 - University of South Carolina
 - W. R. Grace & Co.
 - Xerox Research and Development
 - Washington State University
 - Henkel Corporation
 - Eastman Chemical Co.
 - 3M Polymer Products Division
- (iii) Papers have been presented by G. W. Poehlein and by graduate students at:
 - Gordon Conference session chair and discussion leader.
 - International Polymer Colloid Conference, Fukui, Japan (Invited Paper)

- Engineering Foundation Conference on Polymerization Reaction Engineering (Invited Paper)
- International Symposium on Emulsion Copolymerization, Lyon, France (Invited Paper)

(4) **Consulting**

Consulting on emulsion polymerization has included Eastman Chemical, Xerox-Canada, Ameripol Synpol, National Starch & Chemical, and Henkel

(5) **Students**

Students listed below worked in Dr. Poehlein's group during the grant period and most received some financial support from NSF

1. Cheryl Mathews-Gilmore (PhD 1991) - (Jointly directed by Dr. F. J. Schork)
Currently a part-time Post Doctoral student at Georgia Tech.
2. Ravindra S. Kshirsagar (MS ChE 1993) - Currently in graduate business school at Texas A&M University.
3. David M. Lange (PhD 1991) - Currently employed by Ameripol Synpol Co. in Port Neches, Texas.
4. P.-H. Yang (PhD Expected 1995).
5. S.-T. Wang (Post Doctoral Fellow 1992-93)
6. Syed Ahmed (PhD Expected 1995)

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									
B. Total, Permanent Residents			1							
U.S. Citizens or Permanent Residents ² :										
American Indian or Alaskan Native										
Asian			1							
Black, Not of Hispanic Origin										
Hispanic										
Pacific Islander										
White, Not of Hispanic Origin										
C. Total, Other Non-U.S. Citizens					2					
Specify Country										
1. Taiwan					1					
2. India					1					
3.										
D. Total, All participants (A + B + C)	1		1		2					
Disabled³										

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 to 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 maintains cultural identification through tribal affiliation or community recognition.

ASIAN: A person having origins in any of the original peoples of East Asia, Southeast Asia or 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, and the Northern Marianas; the U.S. Trust Territory of Palau; the islands of Micronesia and 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.

