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E- 19- X71
#1 (New)

ANNUAL PROGRESS REPORT

NATIONAL SCIENCE FOUNDATION GRANT NO. CTS-9417306

GEORGIA TECH PROJECT NO. E-19-X71

PROJECT TITLE: Copolymerization in Dispersed Systems

PROJECTOR DIRECTOR: Gary W. Poehlein

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PERIOD COVERED: Dec. 1994 to Dec. 1995

INTRODUCTION: Free radical polymerization in disperse systems continues to be of major commercial and scientific importance. Much of the commercial interest stems from increased pressures to reduce or eliminate volatile organic compounds from products such as coatings and adhesives and in the potential for manufacturing high-value, controlled-morphology submicron polymer particles. Scientific interest is driven by numerous phenomena at the interface between chemistry, polymer science and colloid science. Work supported by this grant is motivated by both fundamental and applied issues. Brief discussions of projects, research results and personnel comprise the remainder of this annual report.

RESEARCH SUMMARIES: Four areas of research have been pursued during 1995: Dispersion Polymerization Kinetics, Water-Phase Reactions in Emulsion Polymerization, Performance of Continuous Reactor Systems, and Miniemulsion Polymerization with Polymeric Stabilizers.

Dispersion Polymerization Kinetics: Dispersion polymerization involves a continuous phase which is a solvent for the monomer but not the polymer. Hence particle nucleation in the continuous phase

and polymerization in both continuous and disperse phases must be considered in reaction models. Our work has focussed on modeling the reaction kinetics for seeded batch and continuous stirred tank reactors. Experimental reaction rate and particle growth data from batch reactions has been successfully modeled and work with CSTR systems is underway. Preliminary results have been presented at the North American Research Conference on The Science & Technology of Emulsion Polymers/Polymer Colloids - Poster (11-95) and at the 1995 AIChE Annual Meeting (11-95).

Water-Phase Reactions in Emulsion Polymerization:

Reactions involving free radicals formed from water-soluble initiators and the small amounts of monomers in the water phase followed by the transport of the resulting free-radical oligomers to the major polymerization sites in the polymer particles has been an area of research for several years. Techniques have been developed for isolating and characterizing the oligomers that enter the monomer-swollen polymer particles. Current research involves preliminary evaluation of the effectiveness of phase-transfer catalysts in enhancing the transport of hydrophilic species from the aqueous phase into the polymer particles.

Continuous Reactor Systems: Continuous reactors have become more important as product demands have increased. Most products, however, have been developed in batch or semi-batch pilot plants. Hence, one of the thrusts of our research over the years has been the fundamental understanding of emulsion polymerization reactions in CSTR and Tubular Reactor Systems. Current research has involved the study of multi-monomer emulsion polymerization in a reactor system comprised of a tube followed by two or three CSTRs. The influence of using multiple feed points for different monomer mixtures and other ingredients on reaction kinetics and the latex product properties is being studied.

Miniemulsion Polymerization with Polymeric Stabilizers:

This research has been collaborative with Dr. F. J. Schork and has involved an exploratory study of using alkyd resin as a polymeric stabilizer to produce small monomer droplets for miniemulsion polymerization. Early results have demonstrated that such a process is feasible. Further research in this area is motivated by the

possibility of manufacturing hybrid latex coatings to replace solvent-based systems.

PAPERS AND PRESENTATIONS:

Published (copies attached):

"Radical Entry into Particles During Emulsion Polymerization of Vinyl Acetate," R. A. Kshirsagar and G. W. Poehlein, **J. Appl. Polym. Sci.**, **54**, 909-929 (1994).

"Polymerization of Acrylonitrile in Continuous Stirred-Tank Reactors," R. Nishida, G. W. Poehlein and F. J. Schork, **Polym. React. Engr.**, **3(4)**, 397-420 (1995).

"Emulsion Polymerization with Water Soluble Comonomers in Batch and Continous Reactors," G. W. Poehlein, **Macromol. Symp.**, **92**, 179-194 (1995).

Accepted:

"Emulsion and Miniemulsion Copolymerization of Acrylic Monomers in the Presence of Alkyd Resin," S. T. Wang, F. J. Schork and G. W. Poehlein, **J. Appl. Polym. Sci.**

"Continuous Processes for Emulsion Polymerization," G. W. Poehlein, Chapter in book **Emulsion Polymerization and Emulsion Polymers**, M. S. El-Aasser & P. A. Lovell (Eds.), John Wiley & Sons

"Surface Active Properties of Polyester Surfactants with Applications to Seeded Emulsion Polymerization," J. Dorsey, F. J. Schork, G. W. Poehlein and G. L. Shoaf, **Polym. React. Engr.**

"Modern Emulsion Polymerization Processes," L. F. Albright and G. W. Poehlein, **Polymer News** - a brief review paper.

PRESENTATIONS:

"Kinetic Modeling of Dispersion Polymerization in Organic Media," AICHE Annual Meeting, **Polym. and React. Engr. I**, Miami (11/95), presented by S. F. Ahmed (PhD Student).

"Emulsion Polymerization Mechanisms and Kinetics," Short courses at Lehigh University (June 1995) and Davos, Switzerland (August 1995).

"Emulsion Polymerization Reaction Engineering," Short courses at Lehigh University (June 1995) and Davis, Switzerland (August 1995).

"Emulsion Polymerization in Continuous Reactor Systems," Seminar at Union Carbide Corp., Cary, NC (April 1995).

RESEARCH PLANS: Research activities during 1996 will include completion of the work on modeling dispersion polymerization in a seed-fed CSTR; evaluation of the potential benefits of using phase-transfer catalysts in emulsion polymerization; continued study of the use of miniemulsion processes for manufacture of hybrid water-based coatings by copolymerization with polymers that are normally applied from solvent-based systems (e.g. alkyds and polyurethanes); and initiation of a fundamental study of mass transfer of highly water-insoluble ingredients in emulsion polymerization reactions. This last area of interest will span the area between emulsion and miniemulsion processes. The eventual goal will be to quantify the magnitude of monomer droplet polymerization and its influence on the properties of the polymer colloids produced.

PERSONNEL:

Dr. Gary Poehlein, Principle Investigator
Dr. F. Joseph Schork, Faculty Collaborator*
Dr. Shouting Wang, Postdoctoral Fellow
Mr. Pei-Hau Yang, PhD Candidate**
Mr. Syed F. Ahmed, PhD Candidate
Mr. Robert Racz, MS Candidate

* Dr. Schork does not receive financial support from this grant.

** Mr. Yang has had major surgery three times for brain tumor.
He is recovering at home in Tiawan and we hope that he will
be able to continue his research in 1996.

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Union Carbide Corp., Japan Exlan Co., Eastman Chemical Co. and
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program.

Radical Entry into Particles During Emulsion Polymerization of Vinyl Acetate

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SYNOPSIS

The entry of free radicals (formed in the aqueous phase) into polymer particles is the subject of the present work. A model has recently been developed based on the postulate that the aqueous-phase growth of the free radicals to a critical size is the rate-determining step for entry. An experimental strategy was devised to study this phenomena. Polystyrene latex with a water-insoluble inhibitor partitioned into the polymer particles was used as seed for secondary polymerization of vinyl acetate. This was done to form and isolate stable oligomers of the critical size. The presence of vinyl acetate oligomers was detected with Fourier transform infrared spectroscopy and thin-layer chromatography. Fast atom bombardment-mass spectroscopy (MS) was used to determine the molecular weights of the oligomers. Though it was not possible to determine the precise size of the vinyl acetate oligomers formed, the MS results show that the number of monomer units in the oligomers has an upper bound of 12–14. The number of units in the oligomer of critical size was estimated to be about 5–6. These experimental results are quite close to model predictions; thus this work helps in corroborating the model. Additional work is necessary to conclusively validate this model. The experimental strategy used in this work has made it possible to determine the approximate size of oligomers formed in the aqueous phase during emulsion polymerization. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Emulsion polymerization is a process for the production of polymer colloids. It consists of free radical reactions with vinyl monomers in a heterogeneous medium. Monomers are dispersed in a continuous phase, commonly water, with oil-in-water emulsifiers. The reaction is normally carried out by employing a water-soluble initiator. The end product is a polymer latex (colloid) which consists of polymer particles dispersed in the continuous aqueous phase. The particles are stabilized by the emulsifier. The latex can be dried to isolate the polymer, but in many cases it is used in the colloid form as a coating, adhesive, or other product.

A water-soluble initiator produces primary free radicals either by chemical reaction, as in the case

of redox initiators, or by thermal decomposition. After the particle formation stage (Interval 1) the main locus of polymerization shifts to the interior of the monomer-swollen polymer particles. Since the free radicals are generated in the aqueous phase, they must be transported to and enter the polymer particles. Though a very large number of free radicals are generated in the aqueous phase, not all of them can enter polymer particles and lead to propagation. It has been shown that radical capture efficiencies can be very low.^{1,6,15} Since the rate of entry cannot be equated with the rate of free radical generation, the process of entry of free radicals acquires fundamental importance.

The primary free radical is ionic (e.g., the persulfate ion) and hence is unlikely to enter the polymer particle directly. Instead it must add monomer units in the aqueous phase to become sufficiently hydrophobic to be absorbed in a polymer particle.¹³ Different theories have been suggested to explain the entry mechanism for these oligomeric free radicals into the polymer particles. The models include

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diffusion control, surfactant displacement, colloidal entry, and collisional entry. None of these models, however, has been found to be totally satisfactory. Maxwell et al. (1991)¹² have proposed a new model for the entry process, in which the aqueous-phase free radicals enter latex particles only when they attain a particular size. Hence it is the rate of growth of aqueous-phase free radicals to this size that is rate-determining for entry of radical species into latex particles. This model offers a better explanation for experimental observations when compared to previously suggested theories, however it must be validated.

This paper describes an attempt to validate this model by experimentally determining the critical size of the oligomeric radicals that enter particles. Information about the size of the entering oligomer will also help in evaluating the other theories of radical entry. An experimental strategy has been developed to isolate the oligomers and determine their molecular weight.

Aqueous-phase Growth Control Model

According to the model proposed by Maxwell et al.,¹² the rate-determining step for free radical capture by latex particles in aqueous-phase propagation to a critical degree of polymerization denoted by z . Mutual aqueous-phase termination of smaller species also occurs. However, when an oligomeric free radical attains the critical size, its capture by a latex particle is essentially instantaneous. This model has been shown to corroborate experimental observations of the entry-rate coefficient as a function of the concentrations of the initiator, surfactant, aqueous-phase monomer, and latex particles, as well as the effect of particle size and ionic strength. The aqueous-growth model considers the following kinetic events involving free radicals in the aqueous phase: initiator decomposition, propagation, bimolecular termination, and entry of free radicals into particles. The model assumes that all entering free radicals are of the same size. The following relationship for the pseudo-first-order entry-rate coefficient is obtained on the basis of this model.

$$\rho = (N_A/N_C)k_p[M_{aq}][M_{z-1}\cdot]$$

where N_A is the Avogadro number, N_C is the number of particles, k_p is the propagation rate constant, $[M_{aq}]$ is the concentration of the monomer in the aqueous phase and $[M_{z-1}\cdot]$ is the concentration of oligomeric free radicals having $(z - 1)$ monomer units.

Maxwell et al. have also sought to explain the values obtained for z on the basis of thermodynamics of free radical adsorption. The minimum requirement for a primary free radical generated in the aqueous phase to enter a polymer particle would be for the radical to add sufficient monomer molecules in the aqueous phase to render the resultant oligomeric species surface-active and hence less likely to desorb from the surface of a polymer particle. Surface activity refers to the ability of the oligomeric species to adsorb strongly onto the surface of a polymer latex particle. However at a large enough degree of polymerization the oligomeric species becomes essentially insoluble in water. Maxwell et al.¹² have proposed the following equation for the minimum value of z necessary for surface activity of the oligomeric species starting with a sulfate anion primary free radical.

$$z_{\min,\text{surf}} = 1 + \text{int}(-23 \text{ kJ mol}^{-1} / \{RT \ln [M_{\text{aq,sat}}]\})$$

Here int refers to the integer function which rounds off the quantity in brackets to the lower integer value. The concentration $[M_{\text{aq,sat}}]$ is in mol/l. The value of z required for incipient insolubility is given by

$$z_{\min,\text{insol}} = 1 + \text{int}(-55 \text{ kJ mol}^{-1} / \{RT \ln [M_{\text{aq,sat}}]\})$$

Values of $z_{\min,\text{surf}}$ and $z_{\min,\text{insol}}$ of oligomers of various monomers with persulfate initiator were estimated by Maxwell et al.¹²

Oligomeric Size

Qualitative and quantitative characterization of oligomers formed in emulsion polymerization have been carried out by a number of researchers. Goodall et al. (1977)⁵ report that oligomers of styrene consisted of about four to five units of the monomer. Fitch and Tsai (1971)⁴ have studied oligomer formation in the case of methyl methacrylate, using the technique of gel permeation chromatography to determine molecular weights. In the case where low monomer concentration was used in order to prevent particle formation, they found the maximum degree of polymerization to be 65 or 66. This, however, was the size of oligomer required for homogeneous nucleation (self-nucleation). In the case where particles were formed, the maximum degree of polymerization was about 166. Litt et al. (1970)¹⁰ found that the number of monomer units in the case of vinyl acetate was between 50 and 300. This, again, was in the case of self-nucleation. The degree of polymer-

ization is unlikely to be the same in the case of seeded emulsion polymerization without secondary particle formation. Ammerdorffer et al. (1990)² used the technique of isotachophoresis for molecular weight determination. They found that the oligomers in the case of surfactant free emulsion polymerization of butadiene consisted of 1–3 monomeric units. The monomer content and conversion were kept low to prevent particle formation.

Water-soluble oligomers produced in the emulsion copolymerization of styrene and acrylic acid have been studied by Wang and Poehlein (1993).¹⁴ They measured oligomer composition, molecular weight, and copolymer sequence distribution for seeded and unseeded systems at varying conversions. They found that the content of acrylic acid in the oligomer increased significantly as the amount of acrylic acid in the monomer feed was increased. The water-soluble oligomeric molecules formed during the preparation of 10/90 acrylic acid/styrene copolymer were found to consist of 6–9 monomer units. Those formed from 40/60 acrylic acid/styrene ratios were comprised of 13–16 monomer units. High concentration of acrylic acid in the monomer mixture leads to a higher number of acrylic acid units in the water-soluble oligomer.

EXPERIMENTAL

Experimental Strategy

A seeded emulsion polymerization without secondary particle formation was employed in this project. Thus the oligomer size obtained was not affected by the kinetics of particle nucleation. Thereby, it becomes possible to study the event of free radical capture by polymer particles in seclusion. It was necessary to devise an experimental strategy that would enable the isolation of oligomers formed during seeded emulsion polymerization. A necessary prerequisite was that the growth of the oligomers had to be curtailed to their critical size. In other words, the propagation of the oligomeric free radical was to be prevented as soon as it attained the critical size which enabled entry into polymer particles.

An experimental strategy, based on a water-insoluble inhibitor which would permit aqueous phase propagation but prevent polymer particle-phase propagation, was visualized. It was thought that if an inhibitor could be selectively located inside the polymer particles, growth of the oligomers within the particles would be prevented or limited. The

oligomeric free radical would instantaneously react with the inhibitor and form a low molecular weight species incapable of further propagation. This low molecular weight species could then be isolated and analyzed.

In order for the above strategy to succeed, a water-insoluble inhibitor had to be found. Such a compound would partition almost exclusively in the particle phase with negligible solubility in the aqueous phase. Blackley (1975)³ indicated that 2,5-di-*tert*-butylhydroquinone has very low water solubility and this species was employed as the water-insoluble inhibitor.

The second important step in this strategy was the isolation of the oligomers, i.e., separation of the oligomeric species from the seed polymer. Obviously, different monomers had to be used for the seed polymer and the secondary polymerization leading to the formation of oligomers. Since chemical separation of two polymeric species was desired, it was decided to use polystyrene for the seed polymer and vinyl acetate for the secondary polymerization. It is possible to separate polystyrene and poly(vinyl acetate) by selectively extracting poly(vinyl acetate) in methanol. Hence the vinyl acetate oligomers could be isolated and analyzed. Maxwell et al.¹² predicted the critical oligomer size for vinyl acetate, which could then be compared with the experimentally determined values.

The most important step in the analysis of the oligomer is the determination of its molecular weight. A technique capable of measuring molecular weights as low as a few hundred daltons was desired, since the predicted values indicate a critical oligomer size consisting of 7–8 monomer units. The common techniques used in the measurement of polymer molecular weights, such as viscometry, GPC, and light scattering, are unable to measure such low molecular weights. Mass spectroscopy measures the absolute molecular weights of compounds. Though originally developed to study low molecular weight compounds, it has been extensively used to measure molecular weights as high as 10000 daltons.¹¹ Mass spectroscopy has been used to measure the molecular weights of polymeric oligomers.^{8,9} Hence this method was chosen to measure the molecular weights of the vinyl acetate oligomers.

Materials

Acetone: CH₃COCH₃ (MW = 58.08); Certified ACS.; supplied by Fisher Scientific Company, Fair Lawn, NJ. Amberlite MB-3 monobed resin: mixture of Amberlite IR-120 cation exchange resin (hydro-

gen form) and Amberlite IRA-410 anion exchange resin (hydroxide form); supplied by Sigma Chemical Company, St. Louis, MO. 2,5-Di-*tert*-butyl hydroquinone: $C_{14}H_{22}O_2$ (MW = 222.33); purum grade; supplied by Fluka Chemika, Switzerland. Hydroquinone: $C_6H_4(OH)_2$ (MW = 110.11); purified; supplied by Fisher Scientific Company, Fair Lawn, NJ. Chloroform: $CHCl_3$ (MW = 119.38); HPLC grade; supplied by Aldrich Chemical Company, Milwaukee, WI. Methanol: CH_3OH (MW = 32.04); acetone free, absolute; supplied by Fisher Scientific Company, Fair Lawn, NJ. Precoated TLC sheets: silica gel on polyester; supplied by Aldrich Chemical Company, Milwaukee, WI. Potassium persulfate: $K_2S_2O_8$ (MW = 270.33); certified grade; supplied by Fisher Scientific Company, Fair Lawn, NJ. Sodium dodecyl sulfate: $CH_3(CH_2)_{10}CH_2OSO_3Na$ (MW = 288.38); specially pure; supplied by BDH Limited, Poole, England. Styrene: $C_6H_5CH=CH_2$ (MW = 104.15); inhibited with 10–15 ppm 4 *tert*-butylcatechol; Aldrich Chemical Company, Milwaukee, WI; vacuum distilled before use. Vinyl acetate: $CH_3COOCH=CH_2$ (MW = 86.09); inhibited with 3–5 ppm hydroquinone; supplied by Aldrich Chemical Company, Milwaukee, WI; vacuum distilled before use. Nitrogen: N_2 ; high purity; supplied by Holox Company, Atlanta, GA. Deionized water: Used as received from the deionization unit in the lab.

Operating Procedure

Emulsion polymerizations were carried out in a 1.0 L 3-neck glass reactor. A paddle agitator with a Teflon blade was used as a stirrer. The reaction temperature was maintained with a constant temperature water bath. The reaction mixture (before addition of monomer) was purged with nitrogen. The nitrogen purge line was pulled above the level of the emulsion after the monomer addition to prevent polymer from coagulating at the interface of the nitrogen bubbles. Tap water was constantly passed through the condenser to prevent the loss of monomer during the reaction.

Table I Recipe for Styrene Seed Polymerization

Recipe for Polystyrene Seed Latex	
Water	500 g
Styrene	194 g
Potassium persulfate	0.676 g
Sodium dodecyl sulfate	2.884 g
Temperature	Varied from 50°C to 60°C

Table II Recipe for Secondary (Vinyl Acetate) Polymerization

Recipe for Secondary Polymerization	
Seed latex	557 g
Solid content in seed latex	31 g
Vinyl acetate	7.76 g
2,5-di- <i>tert</i> butyl hydroquinone (inhibitor)	0.005 g
Potassium persulfate	0.7 g
Temperature	50°C

Preparation of Seed

Polystyrene seed latex was made using the recipe shown in Table I. Potassium persulfate was used as the initiator and sodium dodecyl sulfate as the emulsifier. The reaction was carried out to nearly 100% conversion. The reaction time was around 24 h. The unreacted styrene was stripped off by bubbling nitrogen through the latex.

Secondary Polymerization

The secondary polymerization involved swelling of the polystyrene seed with vinyl acetate, followed by reaction in the presence of the water-insoluble inhibitor (2,5-di-*tert* butylhydroquinone). The inhibitor is oil soluble and could dissolve in the monomer droplets. Hence it was necessary to prevent the formation of monomer droplets during secondary polymerization. This was achieved by limiting the amount of monomer used and by removing the soap from the seed latex. A monobed ion exchange resin (Amberlite MB-3) was used for this purpose. To aid the transfer of the inhibitor across the aqueous phase and into the polymer particles, it was dissolved in about 50 ml acetone. This solution was added to the seed latex with constant agitation. The reaction mixture was equilibrated for about 8 h. The acetone was then removed by a nitrogen purge. The second-stage monomer (i.e., vinyl acetate) was then added at a very slow rate with constant stirring to prevent the formation of droplets. The reaction mixture was again equilibrated for about 2 h. The initiator (potassium persulfate) was added as an aqueous solution at a slow rate with low stirring speeds to prevent "shocking" of the latex. The reaction was allowed to proceed for about 4 h. Finally the reaction was stopped by the addition of a small amount of hydroquinone.

The amount of vinyl acetate had to be such that it caused sufficient swelling of the seed particles but at the same time prevented the formation of mono-

mer droplets. The amount of vinyl acetate added was one-fourth the solid content of the polystyrene seed latex. Proper amounts of the initiator and inhibitor were determined by trial and error. If the inhibitor were added in excess, it could kill the reaction because of the minute amount partitioned into the aqueous phase. The correct quantities of these compounds were determined by carrying out the reaction and subsequently detecting the presence of oligomers. A successful recipe for the secondary polymerization is shown in Table II.

Analysis of Oligomers

After the completion of the reaction the polymer latex was dried. The oligomeric poly(vinyl acetate) was extracted from the dry polymer using methanol. A Soxhlet extractor was employed for this purpose.

Fourier transform infrared (FTIR) spectroscopy was used to detect the presence of vinyl acetate oligomers in the methanol solution. A Nicolet 520 FTIR single-beam spectrometer and a Perkin-Elmer 1600 series FTIR double-beam spectrometer were used for this purpose. The results obtained by FTIR spectroscopy were confirmed by the use of thin-layer chromatography (TLC). TLC is a very sensitive method and can be used to detect the presence of individual polymers in a mixture. Precoated TLC sheets, which consisted of silica gel supported on polyester, were used. These sheets were pretreated with a mixture of equal parts of chloroform and methanol. The sample solution (the methanol extract) was applied at one end of the plate. The plate was then developed using an appropriate solvent, either methanol or chloroform. Inagaki and Tanaka⁷ indicate that poly(vinyl acetate) can be developed with methanol and polystyrene with chloroform. Development was continued until the solvent front traversed two-thirds of the plate. The mobile phase was removed from the plate by drying in an oven for about 5 minutes. The plates were then placed in a box containing iodine crystals in order to stain the component zones. The various zones were marked after staining, since iodine staining lasts for only a short time.

The final step in the analysis of oligomers consisted of mass spectroscopy (MS). Fast atom bombardment (FAB) was used as the ionization method in the MS analysis. The bombarding beam in FAB consists of atoms of high translational energy. The compound of interest is ionized by this high-energy beam. In FAB the molecular ion $[M^+]$ is not usually seen, but adduct ions (such as $[M + H]^+$) are prominent, as are fragment ions. A VG Analytical 70-SE

mass spectrometer was used for analysis. The instrument specifications were: high resolution, 2-sector, forward geometry, 11-250J data system. The FAB analysis was done at resolutions of 1000 and 1500.

RESULTS AND DISCUSSIONS

A standard polystyrene IR spectrum shows very strong absorption peaks at 699 cm^{-1} and 758 cm^{-1} . These arise from the out-of-plane deformation modes of the hydrogen atoms attached to the aromatic ring. Another strong absorption peak at 1600 cm^{-1} corresponds to the aromatic "breathing" vibration. Five smaller bands at 1670 , 1740 , 1800 , 1870 , and 1940 cm^{-1} indicate monosubstituted aromatic rings. The strong peaks between 2800 and 3000 cm^{-1} indicate saturated C—H groups and those between 3000 and 3100 cm^{-1} denote =C—H groups. The polystyrene IR spectrum also shows strong peaks at 540 , 1028 , 1454 , and 1495 cm^{-1} .

A standard poly(vinyl acetate) spectrum shows very strong bands at 1237 and 1737 cm^{-1} . The latter peak is the C=O stretching mode of a carbonyl compound. The peak at 1237 cm^{-1} is indicative of an acetate group. The spectrum also shows strong absorption at 1373 and 1022 cm^{-1} .

Figure 1 shows the IR spectrum of a dry polymer sample before extraction with methanol. Thus this sample is likely to contain a large quantity of polystyrene. This spectrum shows strong peaks at 699 , 1452 , 1493 , 2922 , and 3025 cm^{-1} . It also shows smaller peaks between 1600 and 1900 cm^{-1} . There is no peak at 1237 and 1737 cm^{-1} . This indicates either that this sample consists solely of polystyrene or that the poly(vinyl acetate) content is very small. This sample was obtained during the trial-and-error runs carried out to determine proper amounts of initiator and inhibitor to be used for favorable results. The dry polymer in this case was extracted with methanol and the methanol solution was dried. The residue was dissolved in benzene and a film was formed on a KBr disc using the benzene solution. The spectrum for this film is shown in Figure 2. This spectrum shows the characteristic peaks for polystyrene only and indicates that some polystyrene was also extracted into the methanol.

Figures 3 and 4 show the IR spectra of films made from methanol extract solution. Figure 3 shows the peaks distinctive of polystyrene. In addition to these peaks it shows moderately strong peaks at 1217 , 1365 , and 1736 cm^{-1} . These peaks indicate the presence of poly(vinyl acetate). However the amount

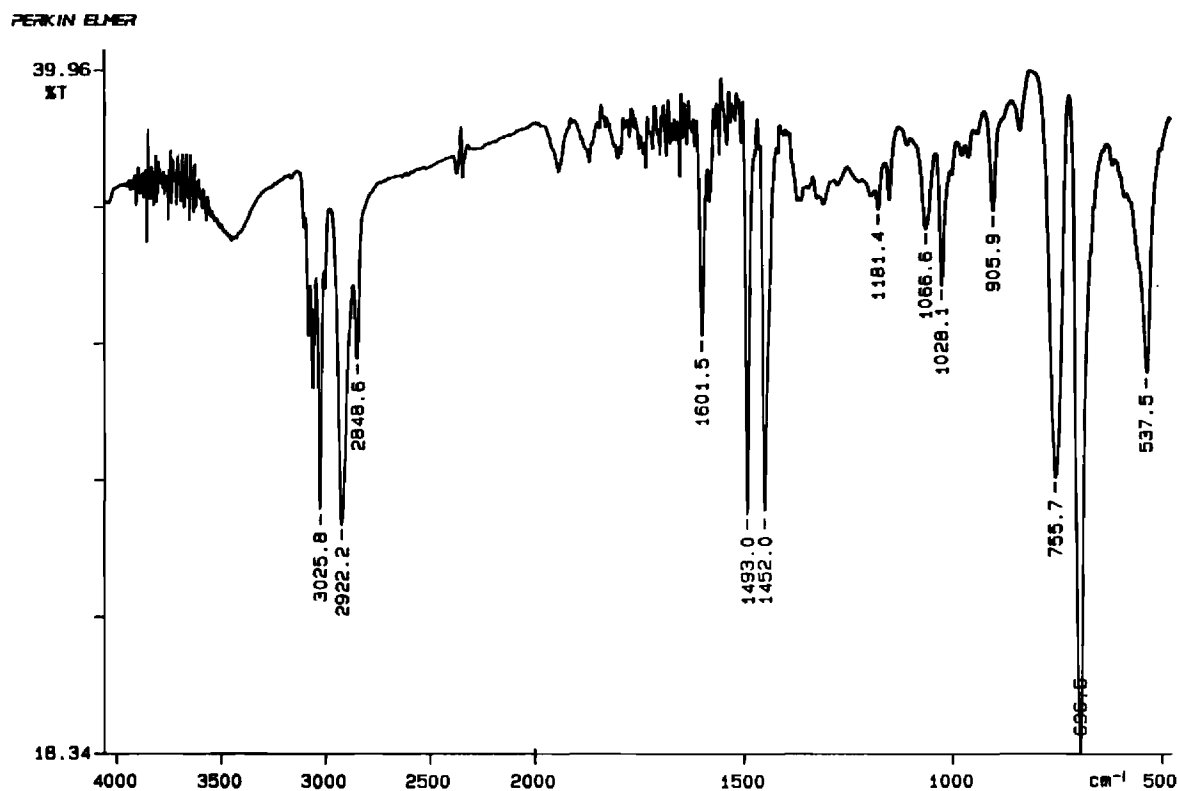


Figure 1 Infrared spectrum of dry polymer sample before extraction.

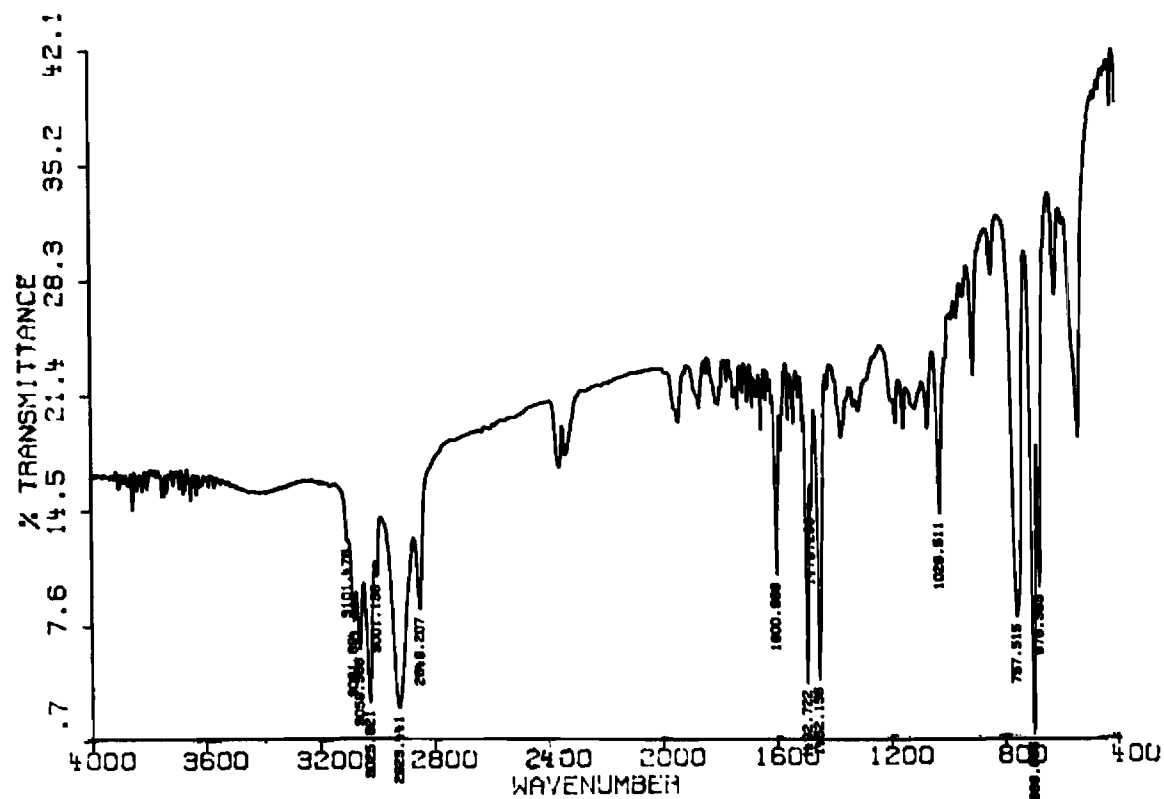


Figure 2 Infrared spectrum of film of methanol extract on KBr disc.

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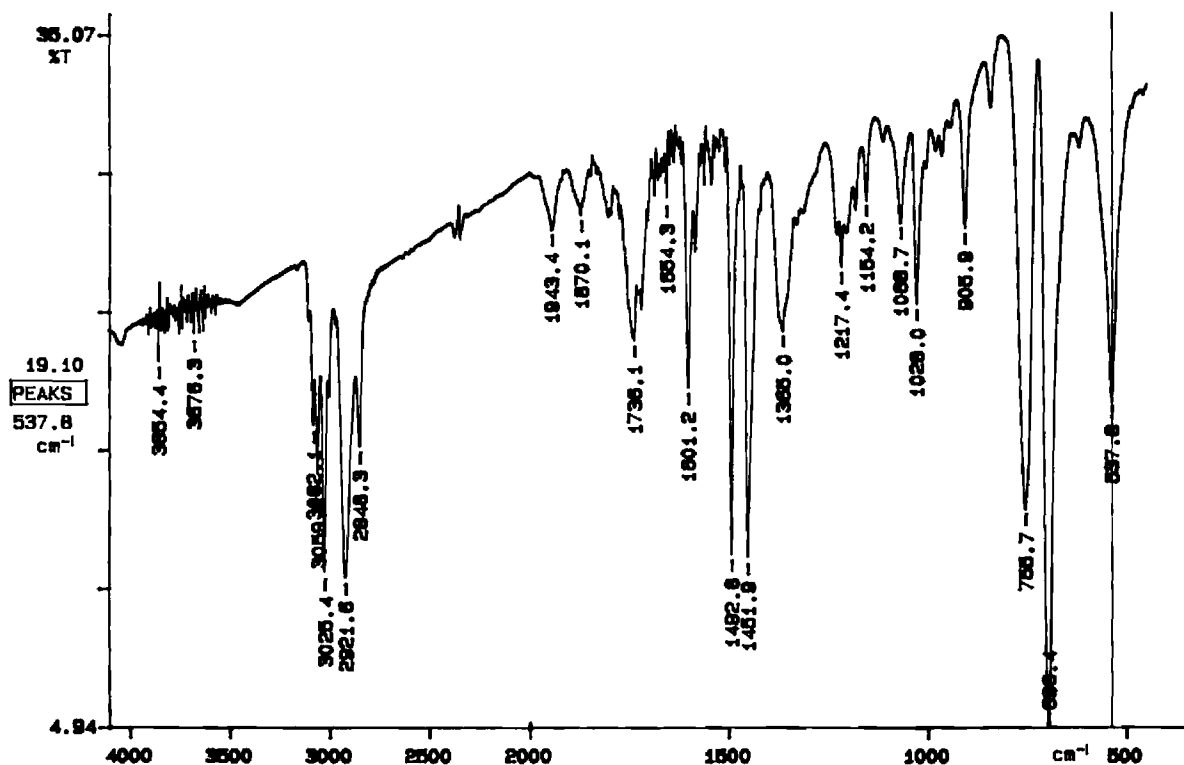


Figure 3 Infrared spectrum of film of methanol extract showing presence of poly(vinyl acetate).

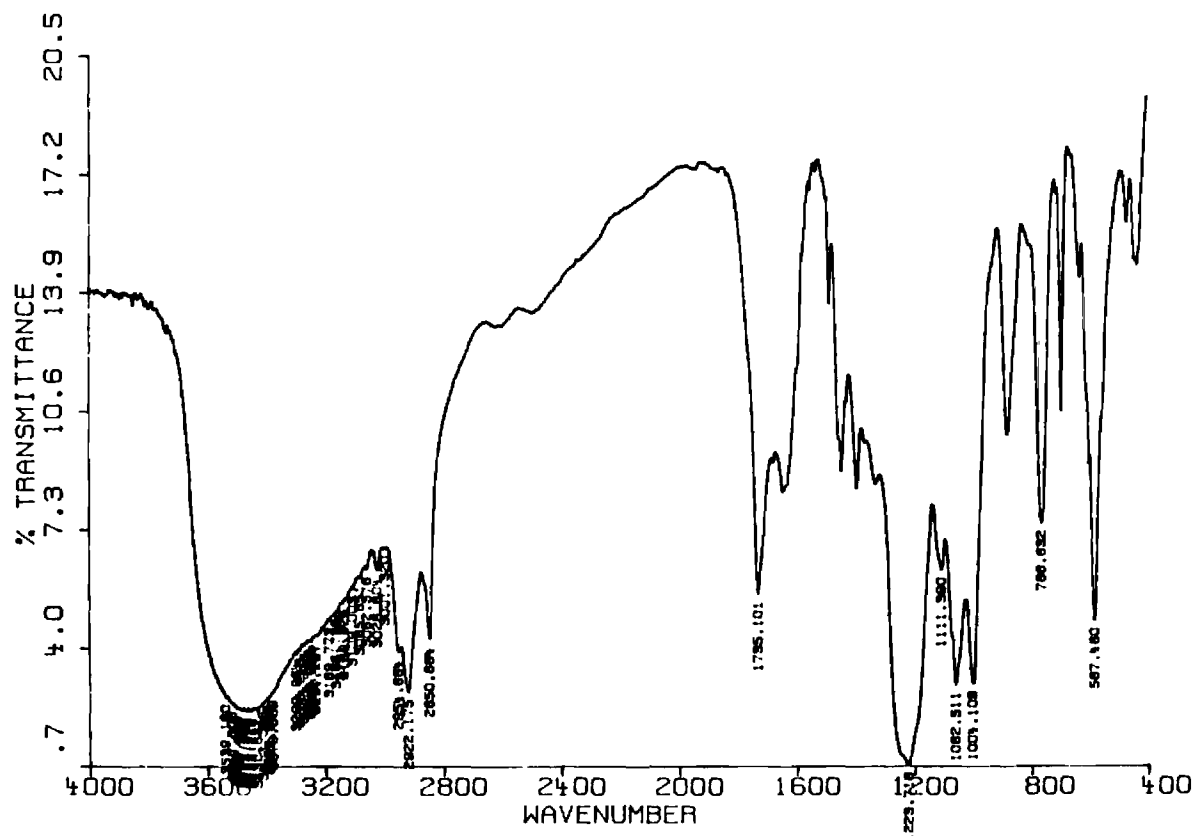


Figure 4 Infrared spectrum of film of methanol extract showing strong presence of poly(vinyl acetate).

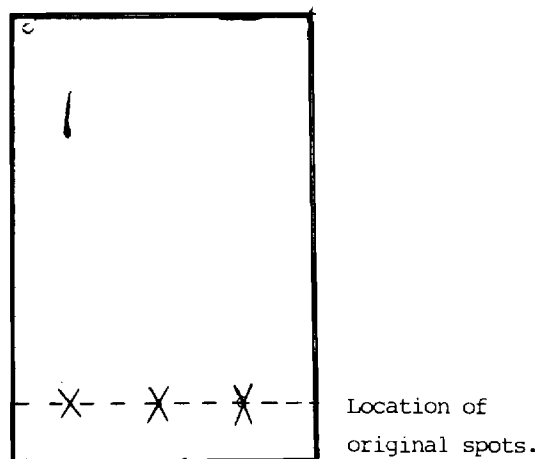


Figure 5 TLC plate spotted with pure poly(vinyl acetate) solution in methanol, methanol extract, and pure polystyrene solution in chloroform (from left to right), and developed with methanol.

of poly(vinyl acetate) is small compared to the amount of polystyrene. Figure 4 shows the peaks indicative of styrene (587, 768, 1450, 1490, 2850, 2922, and 2954 cm^{-1}). However the spectrum also shows very strong peaks at 1229 and 1735 cm^{-1} . These peaks also indicate the presence of poly(vinyl acetate). Since the peaks relating to poly(vinyl acetate) are very strong compared to the other peaks, poly(vinyl acetate) is present in relatively larger proportion. The large hump noticed at around 3400 cm^{-1} could indicate either poly(vinyl alcohol) or 2,5 di-*tert*-butylhydroquinone. It is possible that some poly(vinyl acetate) reacts with methanol and forms poly(vinyl alcohol). It is also likely that the water-insoluble inhibitor forms the vinyl acetate oligomer chain-end segments. The samples represented by the above two spectra were obtained by using the successful recipe shown in Table II.

TLC results corresponding to the sample results shown in the previous section are described below. Figure 5 shows a TLC plate which had been spotted with pure poly(vinyl acetate) solution in methanol, the methanol extract, and pure polystyrene solution in chloroform (from left to right). The plate showed that the pure poly(vinyl acetate) moved to the top of the solvent front. The other spots did not move. This indicates that the methanol extract does not contain any poly(vinyl acetate). This result thus confirms the FTIR result. Figure 6 shows a plate which had been spotted in a similar manner. However in this case the pure poly(vinyl acetate) as well as the methanol extract have shifted to the top of the solvent front. (In this case the order of spotting

was: pure poly(vinyl acetate), pure polystyrene, and methanol extract, from left to right). Thus this shows the presence of poly(vinyl acetate) in the methanol extract.

The results obtained from the TLC experiments corroborate those obtained from the FTIR spectra. The above analysis indicates the success of the experimental strategy. A small amount of poly(vinyl acetate) oligomer has been produced in the secondary polymerization stage. The FTIR and TLC experiments also demonstrate the importance of the recipe in the experimental strategy. The formation of poly(vinyl acetate) oligomers, in the presence of water-insoluble inhibitor located within the polymer particles, was achieved by manipulating the amounts of the inhibitor and the initiator used in the secondary polymerization. The experimental results also showed that some polystyrene was extracted into methanol along with the poly(vinyl acetate). It is quite likely that some low molecular weight polystyrene molecules partitioned into methanol at the high temperature (slightly below the boiling temperature of methanol) during extraction. Thus a "clean" separation of the two components was not achieved. This is likely to have an effect on the mass spectra of the oligomeric sample.

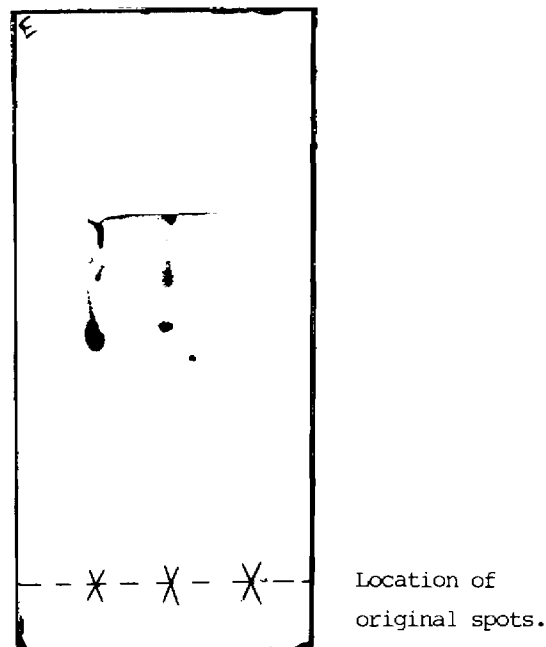


Figure 6 TLC plate spotted with pure poly(vinyl acetate) solution in methanol, methanol extract, and pure polystyrene solution in chloroform (from left to right), and developed with methanol. The TLC plate shows the presence of poly(vinyl acetate) in the methanol extract.

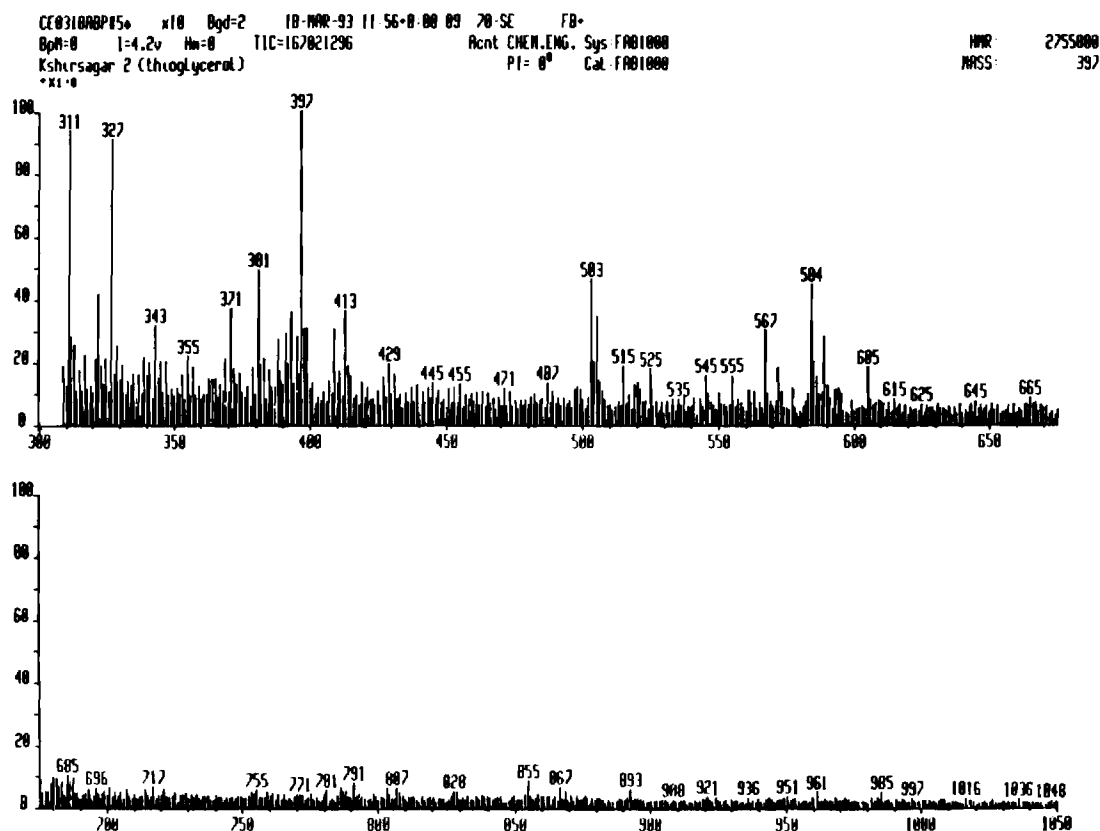


Figure 7 Mass spectrum of oligomer solution at a resolution of 1000.

The successful recipe [which lead to the formation of poly(vinyl acetate) during the secondary polymerization] was used to prepare samples whose mass spectra were then determined. Figure 7 shows one such spectrum. The sample in this case consisted of a solution of oligomers in methanol. The presence of oligomers had been established through FTIR and TLC. The FAB resolution in this case was 1000. The spectrum is cluttered with a large number of peaks. The molecular weights of the components in the sample range between ca. 300 to 1100. Figure 8 shows a mass spectrum of the same sample as in Figure 7 at a resolution of 1500. In this case it is seen that the spectrum is quite cluttered below an m/e value of about 950. The molecular weights in this case range from 400 to 1400.

Figure 9 shows the mass spectrum of another sample at a resolution of 1000. The spectrum, again, is very cluttered, with m/e values ranging from 300 to 1300. Figure 10 shows the mass spectrum for the same sample at a resolution of 1500. The spectrum in this case is not as cluttered with peaks as the previous three spectra, especially at an m/e value greater than 500. The range of m/e values is from 400 to 1300.

Interpretation of MS Results

Interpretation of MS results mainly involves identification of a compound through its molecular weight. The mass spectra of even a single compound may not appear simple, due to the presence of extensive fragmentation during ionization and the presence of various isotopes of elements. In the case of a sample consisting of a mixture of compounds, it is quite natural for the mass spectrum to appear cluttered with peaks. The oligomeric samples analyzed are mixtures of several compounds. In addition to the poly(vinyl acetate) oligomers, the sample contains 2,5-di-*tert*-butylhydroquinone, potassium persulfate, and sodium dodecyl sulfate. Further, each *x*-mer is, chemically, a different compound. Also, termination of oligomeric free radicals in the aqueous phase leads to the formation of many more chemical species. Moreover, FTIR and TLC experiments indicate that the separation of the two polymers [polystyrene and poly(vinyl acetate)] during extraction has not been total. Thus some polystyrene molecules find their way into the methanol solution. These polystyrene molecules constitute another set of chemical species, further increasing the number

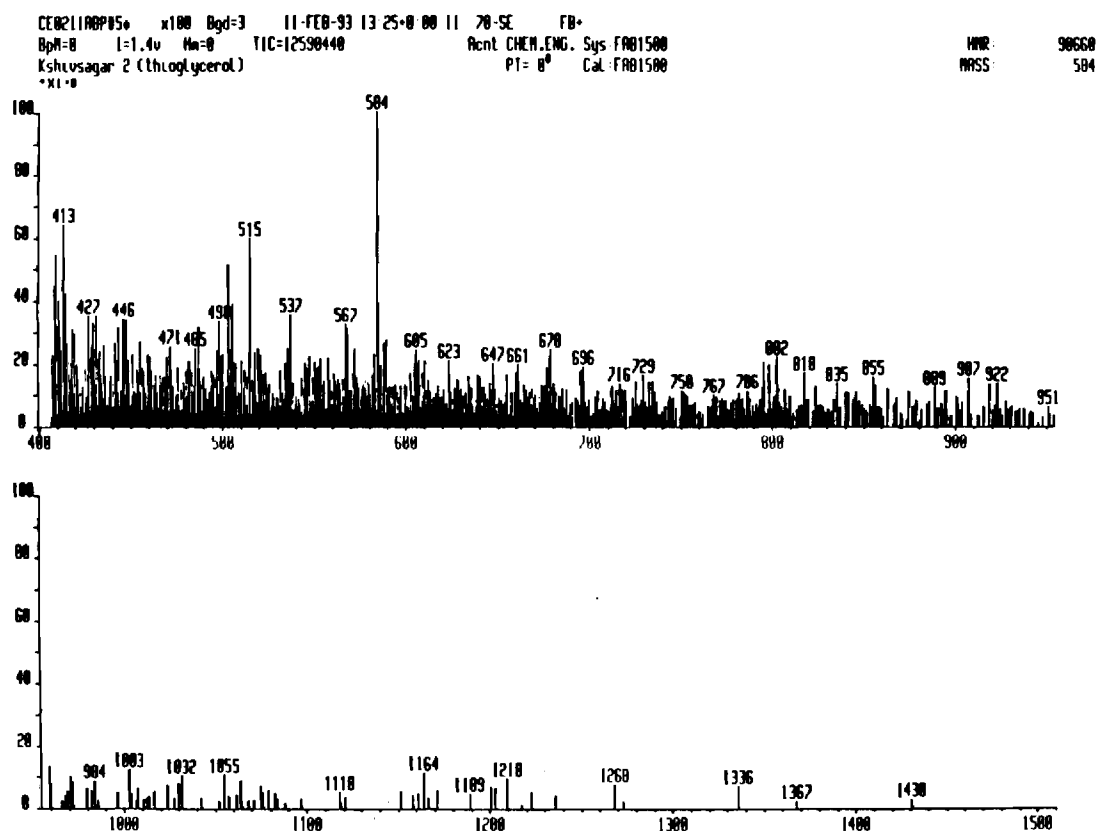


Figure 8 Mass spectrum of same sample as in Fig. 7, at a resolution of 1500.

of peaks. The net effect of all these factors is the formation of a spectrum cluttered with peaks. Interpretation of such a spectrum is difficult.

A necessary prerequisite for compound identification through mass spectra is the knowledge of the chemical formula of the species. In the case of poly(vinyl acetate) the structure of the body of the chain is known to consist of vinyl acetate molecules. However the identity of the terminal groups is not known beyond doubt. The mechanism of initiation by the persulfate radical and the mechanism of inhibition in the case of 2,5-di-*tert*-butylhydroquinone are not completely understood. In effect, the exact chemical structure of the poly(vinyl acetate) oligomers is not known.

The above discussion shows that it is extremely difficult to identify the individual components in the mass spectra of the poly(vinyl acetate) oligomers. This inhibits the identification of the exact oligomeric size capable of entering free radicals. However, it is still possible to draw significant conclusions regarding the poly(vinyl acetate) oligomers.

In all the mass spectra (Figs. 7 through 10) the range of molecular weights does not extend beyond 1400. Assuming that the primary initiating radical

is the $\text{SO}_4\cdot$ radical and that 2,5-di-*tert*-butylhydroquinone forms a quinonoid structure before attaching to the oligomer, it is possible to arrive at a rough estimate for the molecular weight of the poly(vinyl acetate) oligomer as follows.

$$\begin{aligned} \left(\begin{array}{l} \text{Molecular weight of} \\ \text{the largest oligomer} \end{array} \right) &= \left(\begin{array}{l} \text{Upper limit of} \\ \text{the MS range} \end{array} \right) - \\ &\left(\begin{array}{l} \text{Molecular weight} \\ \text{of } \text{SO}_4\cdot \end{array} \right) - \left(\begin{array}{l} \text{Molecular weight of} \\ \text{the inhibitor segment} \end{array} \right) \\ \left(\begin{array}{l} \text{Molecular weight of} \\ \text{the largest oligomer} \end{array} \right) &= 1400 - 96 - 222 = 1082 \end{aligned}$$

Units of vinyl acetate monomer in the oligomer = $1082/86 \approx 12-13$.

This estimate would represent the upper bound for the size of oligomer. If the primary initiating free radical is assumed to be the hydroxyl radical, the number of vinyl acetate units in the upper bound for the oligomer size would be about 13-14. The largest oligomer in the system is definitely to be found in the aqueous phase and could be formed by the mutual termination of two aqueous-phase free

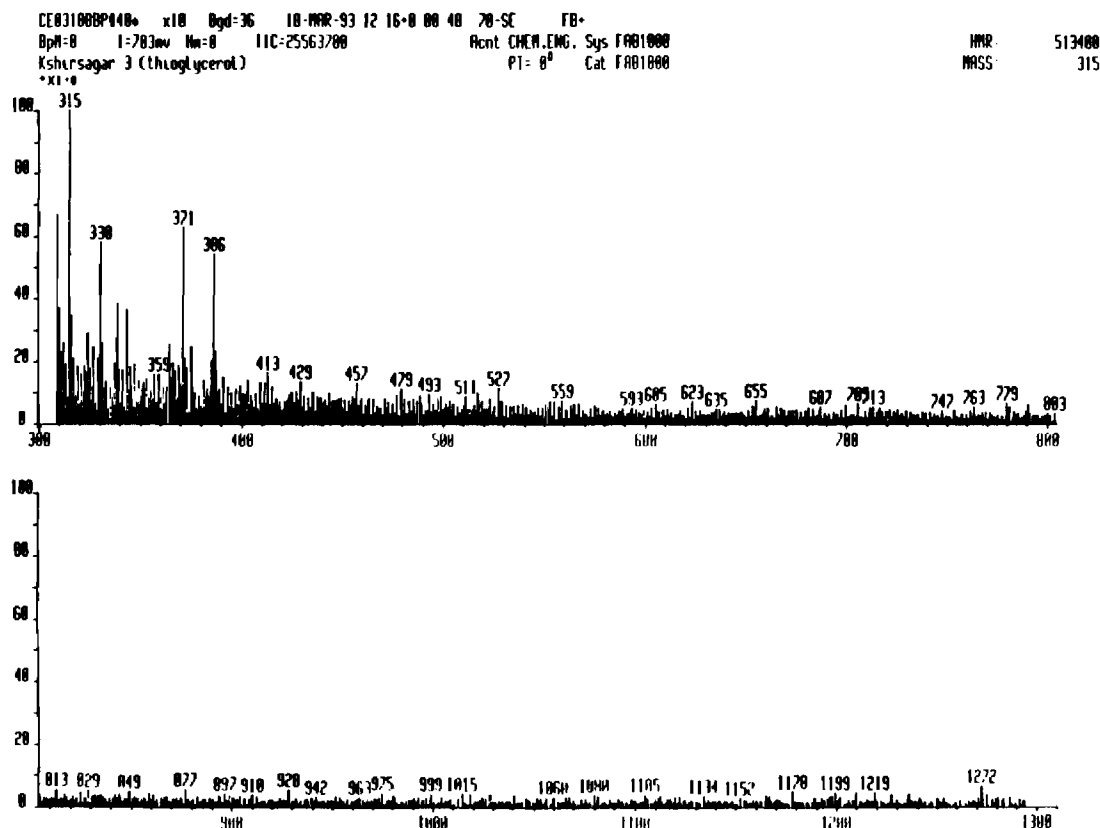


Figure 9 Mass spectrum of another oligomeric sample at a resolution of 1000.

radicals. Maxwell et al.¹² predicted from the thermodynamic point of view the value of z required for incipient insolubility to be 15–18 in the case of vinyl acetate. The approximate upper estimate obtained from the MS results is 12–14.

The mass spectra are not closely packed with peaks around 1400. It is reasonable to expect that more oligomers undergo entry as compared to aqueous-phase termination. Maxwell et al.¹² indicate that termination in water is not significant at low conversions. Thus many more oligomeric free radicals would enter polymer particles and react with the water-insoluble inhibitor than mutually terminate in the aqueous phase. Thus, higher concentration of oligomers of critical size (for entry) would lead to a larger number of fragmented ions. This would manifest itself in a more cluttered region of the spectrum. An enhanced peak density in the spectrum is seen to begin at around 800 daltons. With the same assumptions as used in the earlier case, the number of units of vinyl acetate in the oligomer of critical size is estimated to be $(800-96-222)/86 \approx 5-6$. Maxwell et al.¹² predict this value to be around 7–8.

The approximate estimates obtained from the mass spectra results are quite close to the predictions made by Maxwell et al.¹² on the basis of thermodynamics. Though the results from the mass spectra are certainly not definitive, they are helpful in gaining a better understanding of the sizes of oligomers formed in the seeded polymerization of vinyl acetate.

The approximate estimates of the critical oligomer size are important in more ways than one. As shown above, they do corroborate the thermodynamics of the entry mechanism. Moreover, they give an estimate of the size of oligomeric radicals in the case of polymerization of vinyl acetate. Previously, the oligomeric size in the case of homogeneous nucleation of vinyl acetate had been proposed to be in the range of 50–300 monomer units. The present estimates are much less than that. Thus an attempt in achieving the separation of entry and self-nucleation has been successfully made. The kinetic events involved in the two cases are vastly different and this has been brought out through the present work.

The estimates of the oligomeric size also help in better understanding the colloidal entry model. For the colloidal entry model to hold in the case of seeded

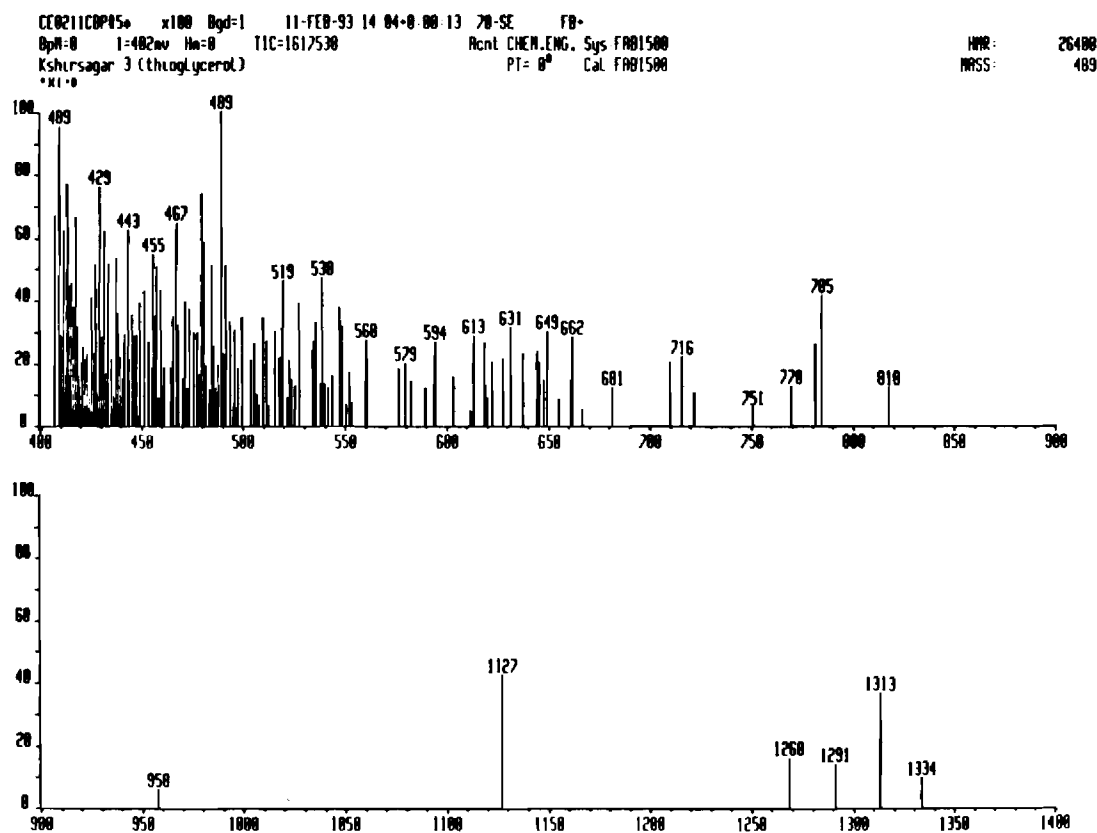


Figure 10 Mass spectrum of same sample as in Fig. 9, at a resolution of 1500.

emulsion polymerization, it is essential that the oligomeric sizes be quite large (large enough for the entering free radicals to attain a colloidal status). However the mass spectra of the oligomers show in clear terms that the oligomers are much smaller. Thus it is highly unlikely that the controlling mechanism for free radical entry could be colloidal coagulation. Since the oligomer sizes are much larger in the case of self-nucleation, the colloidal entry model could, perhaps, be valid in that case.

CONCLUSIONS

Though the experimental technique fails to give definitive values of the size of the vinyl acetate oligomers, approximate estimates have been obtained which closely match the predicted values—however, the results obtained from mass spectra are in no way conclusive. Also, merely showing that the critical oligomer sizes obtained experimentally are close to those predicted does not constitute proof for the model proposed. The predicted values were suggested by Maxwell et al.¹² as thermodynamic ratio-

nalization of their kinetic model. Thus the predicted values indirectly constitute support for their model. It is possible that the oligomers, after attaining a critical size, enter the polymer particles through a process of diffusional control. The thermodynamics remain the same in this case, too. Thus it is essential to test the model in terms of kinetics of free radical entry in the case of several monomers in order to determine its applicability. Without a proper experimental value of the critical oligomer size, however, the kinetic model alone cannot be considered to be adequate proof of the model's validity. The present work needs to be coupled with a kinetic model and tested with different monomers. Only then can the general applicability of the aqueous-phase growth model be fully validated.

The estimated oligomer sizes also help in bringing out the differences between seeded emulsion polymerization without secondary particle formation and unseeded emulsion polymerization accompanied by homogeneous nucleation. An attempt to achieve the separation of entry and self-nucleation has been successfully made. That the kinetic events involved in the two cases are vastly different has been brought

out through the present work. The size range estimate also helps in refuting the theory of colloidal entry as a possible mechanism for free radical capture by polymer particles.

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EMULSION POLYMERIZATION WITH WATER SOLUBLE
COMONOMERS IN BATCH AND CONTINUOUS REACTORS

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Abstract: Emulsion copolymerization reactions which include monomers that have significant solubility in the water phase are described and modeled. The reactions that take place in the aqueous phase are considered as is the influence of water-soluble comonomers on radical transport out of the monomer-swollen polymer particles. Experimental characterization of the oligomers formed in the aqueous phase is also a subject of this paper.

INTRODUCTION

Conventional emulsion polymerization involves the dispersion of a hydrophobic monomer(s) in water with an oil-in-water emulsifier followed by reaction with a water-soluble initiator. The reaction includes nucleation to form a large number of sub-micron particles leading to a polymer colloid product. The conversion of monomer to polymer occurs primarily in the numerous monomer-swollen polymer particles with transport of the monomers and the free radicals to the reaction sites from the monomer droplets and the water-phase respectively. Mass transfer is generally rapid and kinetic models are often based on the assumptions that the monomer compositions in the particles and droplets are the same and that very little monomer is in the water phase.

These assumptions are not valid, however, when one or more of the monomers have significant water solubility. In such cases the equilibrium distributions among the droplets, particles and the water will depend on the relative volumes of the phases as well as the partition coefficients. In addition, the reactions in the continuous phase will become more significant in the overall process. If ionic monomers are used the degree of ionization (of e.g., carboxylic acid groups) will also influence the reaction and the product formed.

This paper will focus on two aspects of emulsion copolymerization with more hydrophilic comonomers. First, the influence of the distribution of the reacting species on reaction mechanisms and kinetics will be considered. Second, the nature of the oligomeric free radicals that enter the monomer-swollen polymer particles from the aqueous phase will be examined. Research in both batch and continuous systems with a variety of monomer pairs will be reviewed.

RESULTS AND DISCUSSION

CSTR Experiments with S-MA and S-AN

Copolymerization experiments in continuous reactor systems comprised of a tubular reactor followed by one or two stirred-tank reactors (CSTR's) were carried with styrene-methyl acrylate and styrene-acrylonitrile recipes (Refs. 1&2). Seed particles were produced in the tubular pre-reactor or in a separate batch reactor. Experimental measurements included conversions of the individual monomers and particle size distributions in the effluent streams of the tube and the CSTR's as well as monomer partitioning among the phases.

A steady-state mathematical model was developed and fitted to the data by adjusting the coefficient for radical desorption from the particles. All other

parameters were based on literature values. Figs. 1 and 2 are three dimensional plots of the desorption coefficients for the two different monomer systems. As expected the magnitude of the desorption coefficient increases with concentration of the monomers in the particles and with the relative concentration of the monomer with the highest monomer chain transfer reaction rate constant.

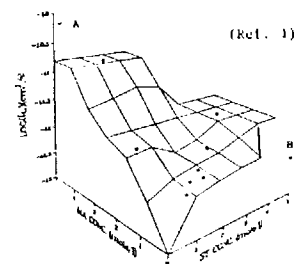


Figure 1 Experimentally fitted mean desorption constants for styrene-methyl acrylate emulsion copolymerizations. Point A, this work; point B, Lee (1985).

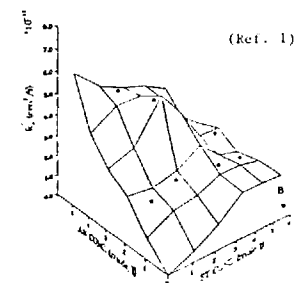


Figure 2 Experimentally fitted mean desorption constants for styrene-acrylonitrile emulsion copolymerizations. Point B, Lee (1985).

Emulsion copolymerizations reactions were carried out with styrene and the water soluble monomers, acrylic acid (AA) and methacrylic acid (MAA). Small amounts of these acid monomers are often used in commercial products to enhance product performance—e.g., to increase stability, promote adhesion and to provide reactive groups. The polymerization kinetics can be quite different because the acid monomers may increase particle nucleation and they are present to a significant extent in the aqueous phase. In addition, if the acid groups are partially neutralized the polymerization is, in some ways, similar to a terpolymerization with ionized and unionized monomers having different reactivities.

Experimental data from unseeded reaction systems can be difficult to analyze because the acid monomers can influence both the number of particles and the average number of free radicals per particle. Hence, most of the experimental work in this paper involves seeded systems in which the number of particles does not change, (Refs. 4-7). In addition, high water solubility of the monomer can lead to a significant amount of reaction in the continuous phase; especially late in the reaction after most of the hydrophobic monomer has polymerized. This is sometimes called Interval 4 of emulsion polymerization.

Figs. 3 and 4 show experimental data and model simulations for batch reactor conversions of the individual monomers in styrene-MAA and styrene-AA emulsion systems. The recipes included 30g of solid polymer in the form of 28 nm diameter seed particles, 5.0 mmol/Laq of $K_2S_2O_8$, 4.0 mmol of SDS, 200 gms of total monomers and water to yield a total mass of 1000 gms. The reaction temperature was 85°C.

The conversion-time profiles of styrene and MAA are similar and are predicted reasonably well by a model that accounts for polymerization in both the aqueous

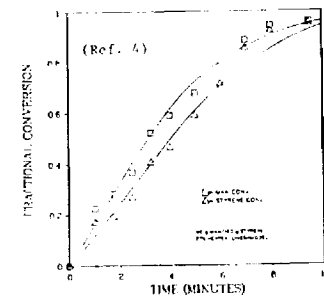


Figure 3. Comparison of predicted and experimental conversion-time data for the seeded batch emulsion copolymerization of MAA/styrene at a weight ratio of 40 g MAA/160 g styrene using a variable value of k_{ac} .

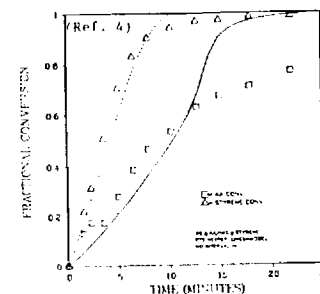


Figure 4. Experimental (points) and predicted (line) conversion-time data for the AA/styrene (40/160 g) seeded random copolymerization system at 85°C. The model assumes that reaction occurs in both the particle and aqueous phases throughout the conversion period (i.e., no interval IV).

and particle phases. Fig. 5 shows the model predictions for the reaction rates of each monomer in both phases. The rate of polymerization of MAA in the aqueous phase is more than an order-of-magnitude lower than in the particles but not insignificant. Styrene reaction in the water phase is very small and not shown on Fig. 5.

Acrylic acid is much more strongly partitioned in the aqueous phase and hence it reacts more slowly than styrene as shown in Fig. 4. The model predicts AA conversion reasonably well until the styrene conversion is high. AA conversion simulations after that point are inaccurate because the predicted reaction in the particles is much too high. The slower reaction rate in the particles apparently occurs because the water-borne free radicals are too hydrophilic to enter the particles. Figure 6 shows that the model prediction is much more accurate when only water-phase polymerization of AA is considered after the simulated styrene conversion exceeds 97+% (~10 min.).

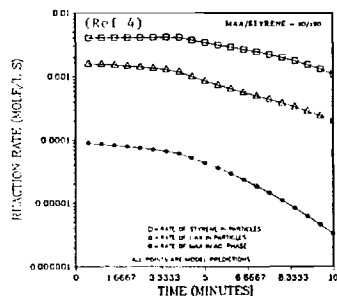


Figure 5 Predicted reaction rates of MAA and styrene as a function of time for an acid/styrene ratio of 40/160.

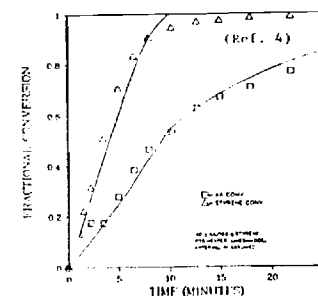


Figure 6 Model prediction of an AA/styrene (40/160) seeded copolymerization assuming that particle phase reaction rates are negligible during interval IV

The results presented above were from low pH reactions in which monomers were not ionized. The model was based on copolymerization concepts with the added consideration of partitioning into the aqueous phase. When the acid monomer is partially ionized, copolymerization involves three reactive monomers; acid, anion, and styrene. Several additional factors must also be considered. First, the partitioning of the acid monomer between the phases will be altered with the anion, favoring the aqueous phase. In this respect, partially neutralized monomers behave more like AA. Different dissociation constants for the acid and the acid units in the polymer chains is a second factor that will affect the course of the reaction. In some respects the reaction can be considered as a terpolymerization. Reaction modeling becomes more complex because an anion which is incorporated into a polymer chain can act as a unionized acid unit.

A series of copolymerizations (S-MAA) were carried out with varying MAA. Figure 7 shows conversion-time profiles for solution poly-

partially neutralized MAA. The reaction without pH control is relatively slow because of the lower reactivity of the anions. The dissociation constants are such that ionization of the monomer is favored over the polymer. When the pH is controlled the monomer mix (i.e. anions/acid) remains constant and the polymerization is more rapid. Fig. 8 illustrates how the DN of the unreacted monomer varies with overall MAA conversion when the pH is not controlled.

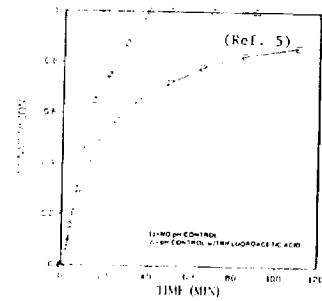


Figure 7. Comparison of reaction rates of 7.0 wt % MAA at initial DN of 0.50 with constant pH (pH control) and with naturally changing pH (no pH control).

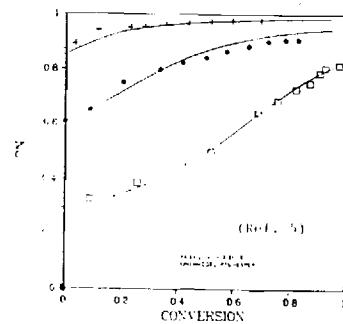


Figure 8. Comparison of predicted DN as a function of conversion with experimental values (K_a of 3.5×10^{-4}).

Lange (Ref. 8) studied S-MAA and S-AA seeded emulsion polymer batch and continuous reactor systems. Experiments were conducted with $K_2S_2O_8$ as the initiator and SDS as emulsifier. Seed and SDS concentration was adjusted to avoid additional nucleation and coagulation. Batch data were used to determine kinetic parameters, primarily radical desorption and coefficients, which were then used to model the steady-state behavior of continuous reactions.

Fig. 9 shows overall conversion transients for a seed-fed CSTR. The steady conversion was highest for the styrene homopolymerization, followed by the S-MAA copolymerization with the S-AA data being intermediate. Model simulations predict this observation. Lange (Ref. 8) found the effect of adding small amounts of carboxylic acid monomers to a seeded emulsion polymerization was to increase the transport of free radical particles to the aqueous phase. The radical desorption rates determined for the reactions were: $k'_{ds} = 3.3 \times 10^{-13}$, $k'_{ds-AA} = 8.0 \times 10^{-13}$ and $k'_{ds-MAA} = 3.0 \times 10^{-13}$. The higher value for the S-MAA results because MAA is partitioned to the particle phase than is AA.

Nomura et al. (Ref. 9) proposed defining the average desorption rate constant for an emulsion copolymerization as

$$k'_{dA-B} = (1/(1+L))k'_{dA} + (L/(1+L))k'_{dB}$$

$$\text{where } L = k_{pAA} r_H [B]_p / k_{pBH} r_A [A]_p$$

A and B represent monomers A and B, r_A and r_B the copolymer reactivity ratios, and k_{pA} the propagation rate constants. The batch measurements of k_{pA}

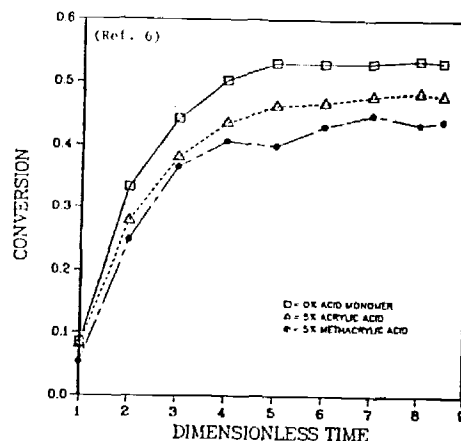


Figure 9 Effect of acid monomer addition on a seeded styrene emulsion polymerization in a CSTR with no particle nucleation or flocculation.

the following values for MAA and AA; $k'_{dMAA} = 9.4 \times 10^{-11}$ and $k'_{dAA} = 9.1 \times 10^{-10}$ cm²/s. Hence the AA desorption constant is higher than that of MAA but the small concentration of AA in the particles leads to a rate coefficient for the S-AA copolymerization which is less than that in the S-MAA system.

Species Formed in the Aqueous Phase During Emulsion Polymerization

The initiation process in most emulsion polymerization reactions begins with the formation of hydrophilic free radicals in the aqueous phase. These radicals are unlikely to enter an organic phase (monomer droplet, micelle or monomer-

swollen polymer particle) until sufficient monomer units are added to species with an appropriate hydrophilic - hydrophobic balance. Mo (Ref. 10) studied this phenomena for single monomer systems. They a theory based on thermodynamic considerations for predicting oligomer size needed for entry into the polymer particles. They p the rate of entry of free radicals was controlled by the rate of growth to a "critical" entry size. Then kinetic experiments and models w show that this critical length, "Z," for styrene was 2 or 3 monomer un

Wang and Poehlein (Refs. 11-13) applied some of the concepts of M. to copolymerization reactions and Kshirsagar (Ref. 14) studied species formed from vinyl acetate monomer. Wang studied copolymer reactions of styrene with MAA, AA and MMA. In all cases the species were isolated and their compositions and molecular w determined with FTIR, NMR and mass spectroscopy.

Three techniques were used to isolate the low molecular weight spe in the aqueous phase. The first, and simplest, was to remove sampl reaction mixture and inject them into cold hydroquinone solutions. technique involved the preparation of styrene-vinylbenzyl chloride which were post reacted with 2-aminoethanethiol hydrochloride presence of NaOH to form latex particles with highly reactive and bound SH groups. Subsequent polymerization would then presum chain transfer of the "critical length" oligomers when they entered t. The third method involved placing a highly water insoluble inhibito latex followed by polymerization and isolation of the radicals that with the inhibitor. This latter technique was used for the vinyl ace The inhibitor 2,5-di-tert butyl hydroquinone was transported to poly particles by adding an acetone solution to the latex. The acetone removed by a nitrogen purge. The VAc polymerization was carried o

the presence of monomer droplets and the terminated VAc oligomers isolated by methanol extraction.

Wang's first experiments involved both seeded and unseeded S-AA emulsion copolymerizations. Reaction samples were injected into cold hydroquinone solutions. The dried polymer samples were then dissolved in dioxane and the solution dispersed in water (1 part solution/15 parts water) to precipitate the polymer. The water phase was separated and evaporated to obtain a dry sample of the water soluble components. FTIR was used to measure composition, ^{13}C -NMR was used to measure copolymer sequence distributions and mass spectroscopy was used to measure molecular weights. Figs. 10 and 11 show the composition and the relative mass of the oligomeric materials from seeded and unseeded experiments. SA-10 represents an unseeded reaction with 10wt%AA in the monomer mixture. SAS-40 is a seeded run with 40%AA. The trends are as expected-higher AA content and oligomer amounts are produced with increased AA in the recipe and near the end of the polymerization when the styrene is depleted.

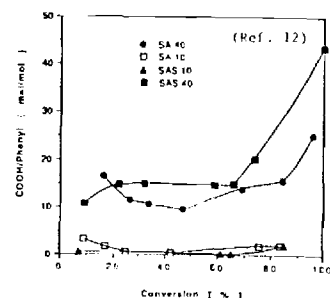


Figure 10 Oligomer composition in four polymerization reactions at different conversion levels.

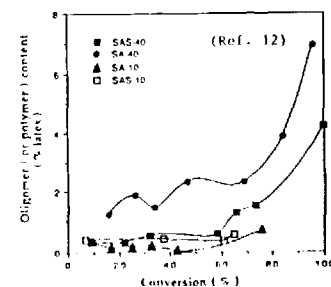


Figure 11 Content of water soluble oligomer or polymer in latex at different conversions

The mass spectra of the SAA oligomers were quite cluttered as would be due to the distribution of molecular species that could be formed by reaction with the inhibitor, by other chain transfer reactions and by aqueous termination. Nevertheless upper-bound peaks with reasonable concentrations could be identified and the associated oligomer molecular weights estimated. Table I gives some data for samples taken at low to medium conversions for experiments SA-10, SA-40, SAS-10 and SAS-40. Entry critical sizes (Z) vary from 6 to 16 monomer units with 1 to 3 being styrene and the remainder AA. Similar results were obtained for the S-AA system seeds containing SH chain transfer groups were used.

Copolymerizations with seeds containing SH groups were also carried out with styrene-methacrylic acid and styrene-methyl methacrylate. Tables II and III summarize the results of these experiments. The critical entry lengths decreased and the fraction of styrene units in the oligomers increased as the solubility of the comonomer decreased. The mass spectra of the vinyl oligomers isolated from VAc emulsion polymerization in the presence of a DVB seed contained a minor peak corresponding to oligomers with 12

units. This was attributed to PVAc formed by aqueous-phase termination. A stronger peak at a lower molecular weight was attributed to "critical length" oligomers containing 5-6 VAc units. Maxwell et al (Ref. 10) predict this value to be 7-8.

Table I Critical Free Radical Size for Entry and Their Composition (Ref. 12)

Sample Code	Conversion (%)	M_n^*	Composition			
			AA/S (mol/mol)	N_{AA}	N_S	Z
SA-10	9.19	599	3.25	6 (5.8) ^b	2 (1.8) ^b	8
	16.99	511	1.69	4 (3.8)	2 (2.3)	6
SA-40	16.33	1046	14.89	13 (13.2)	1 (0.9)	14
	26.32	1000	9.91	12 (12.1)	1 (1.2)	13
SAS-10	7.09	787	1.99	6 (6.3)	3 (3.2)	9
	21.16	767	1.93	6 (6.1)	3 (3.2)	9
SAS-40	9.11	1113	10.64	14 (13.6)	1 (1.3)	15
	22.09	1175	14.67	15 (14.8)	1 (1.0)	16

* $M_n = M^*/Z \times 90$, where M^*/Z is the end weight divided by its charge number in MS and 90 is added group weight of the sulfate and oxoalkylhydroxymethyl in oligomer.

^b The numbers bracketed are those calculated before conversion to an integer.

Table II Oligomer Composition and Size in SMAA Copolymerization System (Ref. 13)

	SMAA-5	SMAA-10	SMAA-20	SMAA-30
Molecular Weight	477	479	491	562
Methacrylic Acid/Styrene (mol/mol)	0.923	1.385	6.506	18.220
Methacrylic Acid Units				
Measured	2.40	2.97	4.81	6.12
Rounded	2	3	5	6
Styrene Units				
Measured	2.60	2.14	0.74	0.34
Rounded	3	2	1	0
Oligomer Units	5	5	6	6

Table III Oligomer Composition and Size in SMMA Copolymerization System (Ref. 13)

	SMMA-20	SMMA-40	SMMA-60
Molecular Weight	274	290	374
MMA/Styrene (mol/mol)	3.774	4.385	5.712
MMA Unit			
Measured	2.08	2.34	3.16
Rounded	2	2	3
Styrene Unit			
Measured	0.63	0.53	0.55
Rounded	1	1	1
Oligomer Unit	3	3	4

ACKNOWLEDGEMENTS

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POLYMERIZATION OF ACRYLONITRILE IN CONTINUOUS
STIRRED-TANK REACTORS

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ABSTRACT

The mechanism of precipitation polymerization of acrylonitrile (AN) in an aqueous continuous phase is similar, in some ways, to that of emulsion polymerization. A kinetic model based on emulsion polymerization concepts suggests that the main site of polymerization is the polymer particles as is the case with most emulsion polymerization reactions. Results from a tube-CSTR reaction system show that the nucleation and growth mechanisms for polymer particles are similar to emulsion polymerization. The tube-CSTR reactor system has been employed to demonstrate that a steady-state conversion can be achieved and the results suggest that particle nucleation in the CSTR can be prevented by this reactor system. Polymerization of AN in a tube-CSTR process can be used to manufacture a product with stable characteristics.

INTRODUCTION

Heterogeneous polymerizations with a continuous water phase and monomers and polymers that are not completely miscible (such as acrylonitrile, vinyl chloride and tetrafluoroethylene) are of considerable industrial importance, but there is no generally accepted theoretical framework from which to discuss such systems. On the other hand, there has emerged an extensive amount of theoretical and experimental techniques whereby mechanistic information can be gained on emulsion polymerization systems in which the monomer and polymer are mutually soluble. In addition, continuous reactor systems for emulsion polymerization, which are important for large-scale commercial production, have been studied extensively.

The objective of this study was to apply these techniques to a nonswelling heterogeneous polymerization system, the polymerization of acrylonitrile, and to clarify the mechanisms. In particular, this paper explores polymerization phenomena in the continuous polymerization of acrylonitrile dispersed in a water phase and provides information for the design and development of commercial reactors.

A major problem in the mechanistic investigation of any multiple-phase polymerization system is the number and complexity of the reactions that must be taken into account. In the polymerization of AN, the mechanism is more complex because of the unique properties of monomer and polymer: AN is highly water-soluble (1.5 mol dm^{-3} at 50°C) but PAN does not dissolve in AN monomer or water. As soon as polymerization starts the polymer separates as a granular solid.

Peebles (1964) proposed that three separate loci of polymerization exist during the heterogeneous polymerization of acrylonitrile. These are: the solution phase and the surface and the interior phases of the polymer particles. Dainton et al. (1959a, b, c & d) and Ito (1983, 84 & 85) proposed that most of the polymerization occurs in the aqueous phase.

Peebles (1964), however, suggested that polymer chains become insoluble after adding only five or ten monomer units. Lewis and King (1969) and Tazawa et al. (1972), on the other hand, report that the surface of polymer particles is the major locus for propagation. Bamford, Jenkins et al. (1953 a & b, 1954, 55 & 57) detected free radicals in polyacrylonitrile, and proposed an occlusion theory in which polymerization occurs in the interior phase. Clearly polymer particles play an important role in the polymerization as shown by the results of Parts and Elbling (1975 & 1976) and Moore and Parts (1960). Thomas et al. (1957) have concluded that AN polymerization systems are similar to emulsion polymerization through microscopic observation of the growth and aggregation of polymer particles. McCarthy, et al. (1986 a & b) have treated the polymerization loci of acrylonitrile in the same manner as polymer particles in emulsion polymerization. They propose that the locus of polymerization is the particle surface. Their results suggest that the average number of free radicals per particle is extremely high and radical capture efficiency of the particles is near 100%.

PAN is sometimes produced in a continuous stirred-tank reactor with little or no emulsifier. Conversion oscillations are often observed as has been reported for emulsion polymerization with more conventional monomers. The oscillations of monomer conversion, particle number and average molecular weight for polymers in emulsion polymerization are well known. Greene et al. (1976) clearly demonstrated that the conversion oscillation problem in a CSTR could be eliminated by installing a continuous tubular reactor upstream of the CSTR. When the conversion in the tubular reactor was maintained at an adequate level, small particles were formed as a seed latex before the reacting stream entered the CSTR. Under this condition, the continuous reactor could be operated at a stable steady-state. Nomura and Harada (1981) have also suggested that a tube-CSTR series may be

an optimal reactor design for the continuous production of polymer latex. Hence, experimental data from kinetic studies in a tube-CSTR system would be of value for both the understanding of reaction kinetics and the development of commercial processes.

KINETIC MODEL

The rate of free radical polymerization in a homogeneous medium is given by Equation 1.

$$R_p = k_p[M][R\cdot] \quad (1)$$

where $[M]$ is monomer concentration, k_p is the propagation rate coefficient and $[R\cdot]$ is the molar free radical concentration. When the polymerization occurs predominantly in the colloidal polymer particles, the rate of emulsion polymerization per unit volume of aqueous phase can be expressed as:

$$R_p = k_p[M]_p(\bar{n}N/N_A) \quad (2)$$

Here \bar{n} is the average number of free radicals per particle, $[M]_p$ is the monomer concentration in the polymer particles, N is the particle number per volume of water, and N_A is Avogadro's number. The swelling of PAN by AN monomer is very limited and diffusion of free radicals may restrict the reaction to locations at or near the particle surfaces. Hence there is some question as to the value of $[M]_p$ at the reaction site. The average number of free radicals per particle is given by

$$\bar{n} = \sum_i i N_i / \sum_i N_i \quad (3)$$

where N_i is the number of particles that contain i free radicals. The time evolution of these last quantities for a batch reaction is given by the generalized Smith-Ewart (1948) equation as treated by Gilbert & Napper (1983), Ugelstad & Hansen (1976) and Whang et al. (1982):

$$\begin{aligned} dN_i/dt = & \rho[N_{i-1} - N_i] + k[(i+1)N_{i+1} - iN_i] \\ & + c[(i+2)(i+1)N_{i+2} - i(i-1)N_i] \end{aligned} \quad (4)$$

Here ρ is the (first-order) rate coefficient for the transfer of free radicals to the polymerizing locus (ρ is the entry rate in an emulsion polymerization system), k is the rate coefficient for first-order loss of a polymerizing free radical from this locus, and c is the (pseudo-first-order) rate coefficient for second-order loss of free radical activity from this locus; c will be proportional to k_t , the second-order termination rate coefficient. The coefficients $(i+1)$ etc. in Equation 4 arise from simple combinatorics.

Gilbert and Napper (1983) have proposed that a rigorous mathematical treatment of the various possible aqueous events shows that one can take account of all these possibilities by writing

$$\rho = \rho_A + \alpha k \bar{n} \quad (5)$$

ρ_A is the contribution to radical absorption of free radicals arising directly from initiator (and background thermal sources) and α is a "fate parameter" whose value lies between ± 1 . If reentry is dominant $\alpha = +1$; if the dominant fate of desorbed free radicals is heterotermination $\alpha = -1$, and if all desorbed free radicals undergo self termination in the aqueous phase or a first-order loss occurs within the particles $\alpha = 0$. In

the particular case that $c = 0$ (no second-order loss), Equation 4 can be multiplied by i and summed over all i to yield

$$d\bar{n}/dt = \rho_A - (1-\alpha)k\bar{n} \quad (6)$$

Equation 6 has the steady-state solution

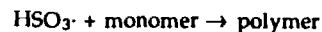
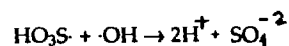
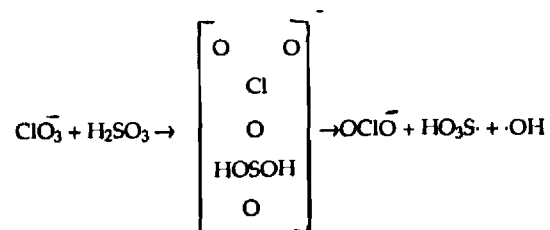
$$\bar{n}_{ss} = \rho_A / (1-\alpha)k \quad (7)$$

If α is exactly +1, equation 6 is undefined, and in such a case, second-order loss must become important. When this is true \bar{n}_{ss} is no longer proportional to ρ_A . Please note that one cannot assume, a priori, that the free radical capture efficiency is 100%, which would imply that

$$\rho_A = R_i (N_A/N) \quad (8)$$

where R_i is the rate of initiation reaction. The use of Eq. 8 would, therefore, yield an upper limit for ρ_A .

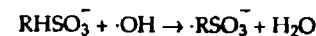
Gleason et al. (1951) studied acrylonitrile polymerization in aqueous suspension initiated by the $\text{NaClO}_3 - \text{Na}_2\text{SO}_3$ redox system. They have suggested the following radical generation mechanism.



They measured the rate of disappearance of sulfite, and have proposed that the reaction rate is formulated as

$$-d[\text{ClO}_3^-]/dt = 3.3 \times 10^7 e^{-11000/RT} [\text{ClO}_3^-] [\text{H}_2\text{SO}_3]$$

Mitra et al. (1966), on the other hand, have shown that the hydroxyl radical cannot exist in the presence of RHSO_3^- ion because the hydroxyl radical reacts with it as follows:



Hence the reaction route proposed in this study is shown in Figure 1, and the rate of initiation of the redox system is given as:

$$R_i = 6f_i k_d [\text{I}_\text{O}] [\text{I}_\text{R}] \quad (9)$$

where $[\text{I}_\text{O}]$ and $[\text{I}_\text{R}]$ are the concentration of oxidative and reductive initiators respectively, k_d is the decomposition rate coefficient of the initiators and f_i is the initiation efficiency. The mathematical form of the initiator radical balance for a CSTR is given by:

$$V_{\text{H}_2\text{O}} d[\text{I}_\text{O}]/dt = F_{\text{H}_2\text{O}}([\text{I}_\text{O}]_f - [\text{I}_\text{O}]) - R_i V_{\text{H}_2\text{O}} = 0 \quad (10)$$

$$V_{\text{H}_2\text{O}} d[\text{I}_\text{R}]/dt = F_{\text{H}_2\text{O}}([\text{I}_\text{R}]_f - [\text{I}_\text{R}]) - R_i V_{\text{H}_2\text{O}} = 0 \quad (11)$$

where $V_{\text{H}_2\text{O}}$ is the volume of water phase in the reactor, $F_{\text{H}_2\text{O}}$ is the volumetric flow rate of water phase, and $[\text{I}_\text{O}]_f$ and $[\text{I}_\text{R}]_f$ are the

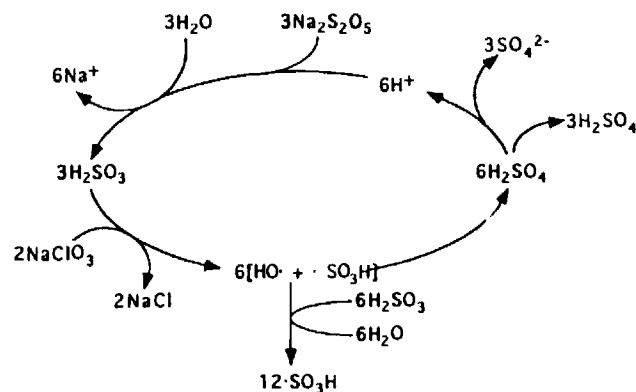


Figure 1: Radical Generation Mechanism of Chlorate-Sulfite System

concentrations of the feed oxidative and reductive initiators. At steady-state the derivatives are equal to 0.

Two reaction sites are active in the reaction system: the aqueous phase and the polymer particles. Hence the total rate of polymerization is given as follows:

$$R_p = R_{pw} + R_{pp} \quad (12)$$

where R_{pp} is the rate of polymerization in polymer particles as given by Equation 2. R_{pw} and R_i are given by Equations 13 and 14.

$$R_{pw} = k_p[M]_w[R\cdot]_w \quad (13)$$

$$\begin{aligned} R_i &= \rho_A - \sum k_n N_n + 2k_i[R\cdot]_w^2 \\ &\approx \rho_A - k_n N + 2k_i[R\cdot]_w^2 \end{aligned} \quad (14)$$

where $[M]_w$ and $[R\cdot]_w$ are the monomer and radical concentrations in the aqueous phase. Both R_{pw} and R_{pp} are rates per unit volume of water phase. When no monomer droplets are present, the relationship between the overall monomer concentration and the concentrations in the aqueous phase and polymer particles is as follows:

$$[M] = [M]_w(1 - \phi_p) + [M]_p\phi_p \quad (15)$$

$$q = [M]_p/[M]_w \quad (16)$$

where q is a partition coefficient of monomer between the aqueous phase and polymer particles and ϕ_p and ϕ_w are the volume fractions of the polymer particles and aqueous phase expressed as the volume per unit volume of mixture.

EXPERIMENTAL

Acrylonitrile, sodium metabisulfite, sodium chlorate, and sulfuric acid of reagent grade were used as supplied by the Aldrich Company without further purification. PVA (polyvinyl alcohol) was supplied by Air Products & Chemical Company. The water was deionized.

A schematic diagram of the experimental apparatus of tube-CSTR is shown in Figure 2. It was comprised of a tubular prereactor, which was constructed of 1/8-inch diameter Teflon tubing of variable length, and a CSTR. The tubular prereactor was operated in a plug-flow mode (thus this reactor is also referred to as a Plug Flow Reactor (PFR)) by injecting purified nitrogen plugs into the flowing mixture. Experiments were carried out with and without the PFR. The reagents in these experiments were added independently to the CSTR without premixing. Recipes are given in Table 1.

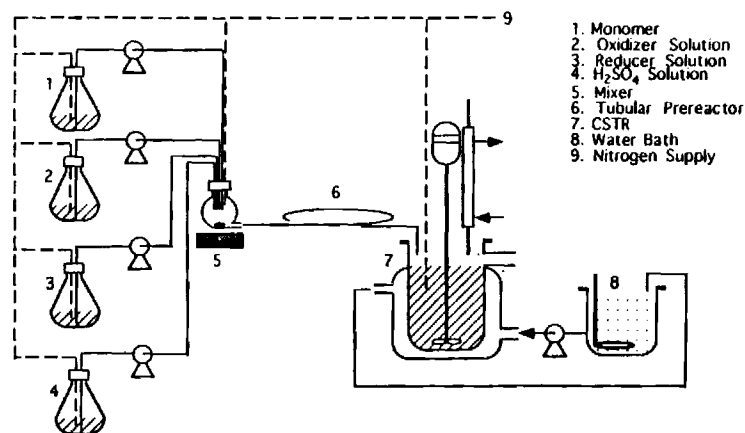


Figure 2: Schematic Diagram of the Experimental Apparatus

The system was operated by first filling the CSTR with deionized water adjusted to pH 2.0 with sulfuric acid. Then the flows of the ingredients in the polymerization recipe were started. Polymer yields were determined by a gravimetric method. The rate of polymerization in the CSTR at steady state can be computed from the conversion values with the following equation:

$$R_p = [M]_f(X_2 - X_1)/\Theta \quad (17)$$

where $[M]_f$ is the feed monomer concentration in moles per volume of water, X_1 is the fractional conversion of monomer in the effluent from the PFR, X_2 from the CSTR, and Θ is the mean residence time of the CSTR. Particle size distributions were measured by a Malvern Autosizer and a SALD-2000 TLM (Shimazu).

TABLE 1
Recipes for AN Polymerization in Aqueous Solution

Feed solution	run 1	both runs	run 2
AN monomer flow rate (ml/min)	0.23		0.27
Oxidizer solution concentration (mol/L) flow rate (ml/min)		3.7x10 ⁻³	1.2
Reducer solution concentration (mol/L) flow rate (ml/min)	1.0	4.0x10 ⁻³	1.5
H ₂ SO ₄ solution concentration (mol/L) flow rate (ml/min)	1.5	4.4x10 ⁻³	1.2
Reaction Temperature			
PFR			Room Temperature
CSTR			55°C
Mean Residence Time			
PFR			160 seconds
CSTR			54 minutes
Reactor Volume in CSTR			225 ml

A scanning electron microscope (JEOL) and an optical microscope were used for some measurements. The polymer mixture which was collected for a sample was diluted with deionized water that contained PVA for the stabilization of the particles and sodium hydroxide for the inhibition of the initiation reaction. The number of particles per unit volume of aqueous phase can be calculated by:

$$N = (MW)_M[M]_fX/\rho_p(\pi/6)D^3 \quad (18)$$

where $(MW)_M$ is the molecular weight of monomer, ρ_p is the density of polymer particles, and D is the mean diameter of the dried polymer particles. The molecular weight distribution was measured by GPC

(Waters 510, Shodex Column). The monomer concentration in the clear aqueous phase from collected samples was measured by GC (Varian 3700).

RESULTS AND DISCUSSION

Figure 3 shows conversion as a function of space time in the PFR. A light blue latex was obtained from the PFR. The space time was varied by changing the tube length and this part of the polymerization was done at room temperature (25°C). Temperatures of the PFR and the CSTR are usually the same. However, when the polymerization in the PFR was carried out at 55°C, the temperature of the CSTR, the PFR conversion was 15% and precipitation occurred within 25 seconds. A target of 5 to 10% conversion was chosen for the PFR. A space time of more than 100 seconds was needed at room temperature to achieve this conversion.

Conversion-time results for AN polymerization in the tube-CSTR system are shown in Figure 4. The conversion is plotted against dimensionless time, which is the reaction time divided by the CSTR mean residence time. These data clearly demonstrate that a tube-CSTR reactor system can be employed to prevent conversion oscillations. The conversion of the product from the tube-CSTR reaches a steady-state value after about 4 mean residence times. The monomer conversion in the tubular reactor effluent was about 6%.

Figure 5 shows the experimental data for polymerization in an unseeded CSTR. Conversion oscillations obviously take place with a cycle of about 6 to 8 mean residence times. These cycles are similar to those that have been observed with emulsion polymerization

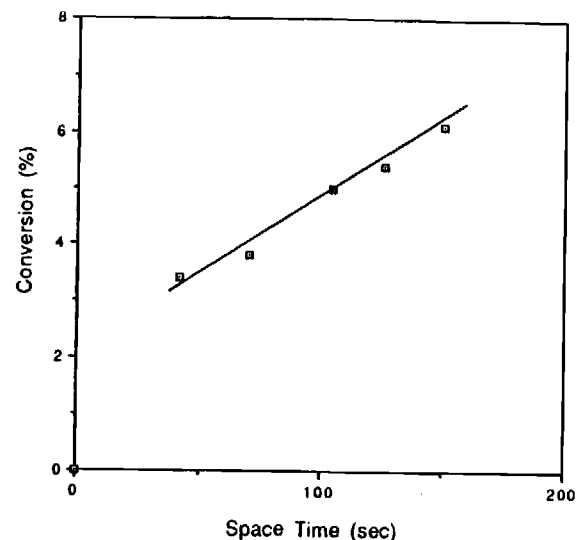


Figure 3: Conversion vs. Space Time in Tubular Reactor

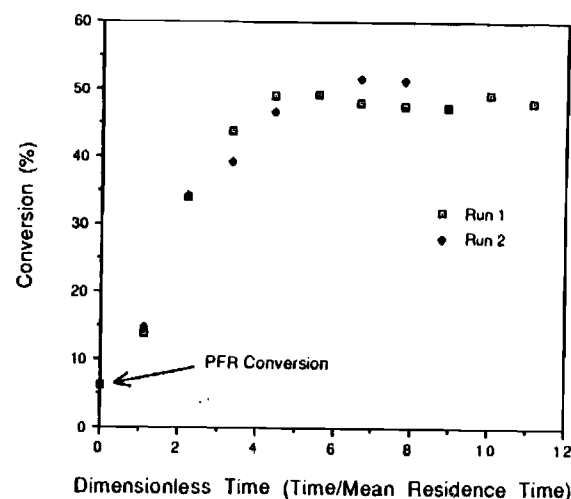


Figure 4: Conversion Curve in Tube-CSTR

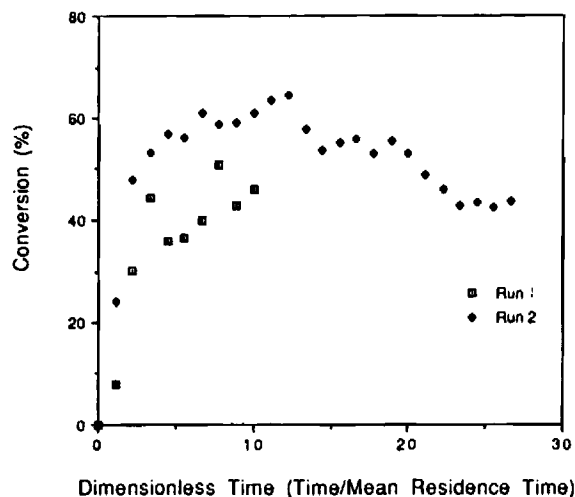


Figure 5: Conversion Curve in Nontube-CSTR

reactions. The conversion instability in continuous reactors is often caused by on-off particle nucleation coupled with particle growth mechanisms. As a result of the above observations, the similarity of precipitation polymerization of AN to emulsion polymerization is confirmed and the nucleation mechanism for AN precipitation polymerization leads to results similar to emulsion polymerization.

Molecular weights of different polymer samples are summarized in Table 2. These samples were taken at the end of the runs shown. The polydispersity of the polymer from tube-CSTR is less than that from the unseeded CSTR. This result suggests that variations in molecular weight may be correlated to the oscillations, and the breadth of the distribution of molecular weights (MWD) can be decreased by preventing these oscillations. The MWD of the product AN is fairly

TABLE 2
Molecular Weight of Polyacrylonitrile

	Mn ($\times 10^4$)	Mw ($\times 10^5$)	Mz ($\times 10^5$)	Mw/Mn
Seed Polymer	5.60	1.46	3.84	2.60
Polymer in tube-CSTR	5.56	4.19	41.8	7.54
Polymer in nontube-CSTR	5.18	4.82	44.3	9.31

broad in comparison with some other emulsion polymers, whose Mw/Mn ratios are often in the range 2.5 to 3.0. The Mw/Mn ratios of the seed or PFR polymer is similar to that of emulsion polymers.

The MWDs (molecular weight distribution) of tube-CSTR polymer and seed polymer are shown in Figure 6. The fraction of high molecular weight polymer in the final product is greater than that in the seed polymer. McCarthy et al. (1986) have proposed that the locus of polymerization is an isolated macroradical on the surface of a glassy latex particle. If this is true, it is possible that higher molecular weight polymers are produced at this site. These results suggest that polymer may be formed by two reaction mechanisms, one which is similar to conventional emulsion polymerization mechanisms, i.e., the nucleation part in the PFR and a second on the particle surfaces in the CSTR.

Particle size data are summarized in Table 3. The average diameter of the polymer in the PFR effluent is $0.14 \mu\text{m}$, which is in the region of emulsion particles. The diameter of the final product particles is about

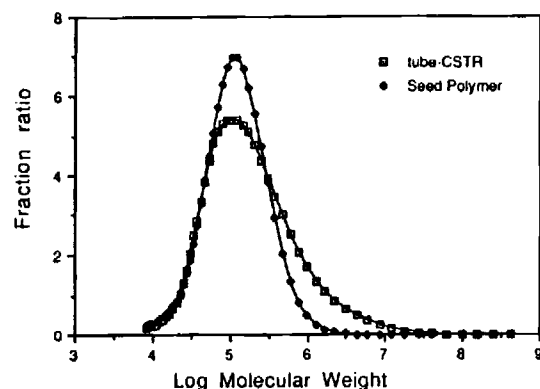


Figure 6: MWD Curve of Seed Polymer and Final Polymer

TABLE 3
Particle Size and Particle Number in Aqueous Solution

	Mean Diameter (μm)	Particle Number ($\#/\text{dm}^3$)
in tube-CSTR	136.0	1.8×10^{10}
End of Run	130.0	1.8×10^{10}
At max Conversion in nontube-CSTR	86.0	9.0×10^{10}
At min Conversion in nontube-CSTR	99.3	4.0×10^{10}
Seed Particles	0.14	2.5×10^{18}
On surface of Coagulated Polymer Particles	0.25	2.9×10^{18}

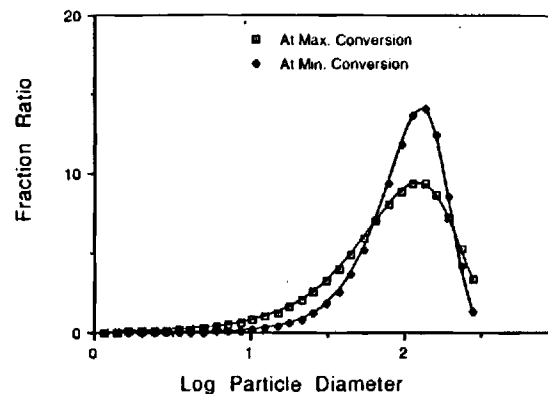


Figure 7: PSD at Max. and Min. Conversion in Nontube-CSTR

130 μm . The average diameter of the final particles is in the same range for both cases: tube-CSTR and nontube-CSTR. The instability of the PSD (Particle Size Distribution) in the nontube-CSTR is shown in Figure 7, with the PSDs at the points of maximum and minimum conversion for the nontube-CSTR in Figure 5. The fraction of smaller particles and the number of polymer particles at maximum conversion is higher than at minimum conversion. This result agrees with the results of Thomas et al. (1957) and Parts and Elbing (1975) which show that the polymerization rate is proportional to the number of polymer particles.

SEM pictures of the surface of the large particles show numerous particles, in the size range of 0.1 to 0.3 μm . The inside of the coagulated or composite polymer particles appears to be porous. We propose the number of particles does not change significantly from the number of seed polymer particles produced in the PFR although coagulation occurs as shown in Table 3. Our proposal is based on the assumption

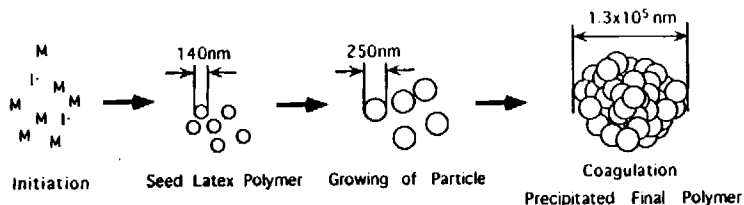


Figure 8: Particle Growth Mechanism

that the nucleation of polymer particles does not occur or is very limited in the CSTR. The PFR or seed polymer particles grow as in emulsion polymerization and then larger porous particles are produced by coagulation. This proposed mechanism of polymer particle formation, growth and coagulation is shown in Figure 8.

KINETICS DISCUSSION

Comparison of kinetic model predictions with experimental results is difficult for AN polymerizations because of uncertain values for parameters such as k_p , k_t , α , k and $[M]_p$. Nevertheless some calculations can be made and perhaps used to speculate on the dominant polymerization site. The mass balance relationship, Eq. 17, can be used to compute the experimental rate of polymerization. The result for the tube-CSTR run with Recipe 2 is $R_p = 1.36 \times 10^{-4}$ mol/dm³-s. This rate is the sum of the rates in the aqueous and particle phases as given by Eq. 12.

$$R_p = R_{pp} + R_{pw} \quad (12)$$

One must be able to estimate values of R_{pp} and R_{pw} in order to compare theory with the experimental R_p value. We begin with R_{pp} by

combining Eqs. 2, 7 and 8 to yield:

$$R_{pp} = k_p [M]_p R_i / k(1-\alpha) \quad (19)$$

The initiation rate is about 2×10^{-6} mol/dm³-sec and McCarthy et al. (1986a, b) estimate $k(1-\alpha)$ to be 7×10^{-3} sec⁻¹. A linear relationship for, $[M]_p (= q [M]_w)$ is assumed and for the tube-CSTR run with Recipe 2 $[M]_w$ is 0.47 moles/dm³. Hence the particle polymerization term from Eq. 2 is given by:

$$R_{pp} = (1.3 \times 10^{-4}) k_p q \quad (20)$$

McCarthy et al. (1986a, b) suggest a value of 600 for $k_p q$. If this value is used Eq. 20 predicts the particle polymerization rate to be 7.8×10^{-2} mol/dm³-sec which is several orders of magnitude higher than the measured R_p in our experiment. A $k_p q$ value of 4 ($k_p = 200$ and $q \approx 0.02$) yields an R_{pp} value of 5×10^{-4} in reasonable agreement with experiment. We must point out, however, that our experimental conditions -- i.e., no added emulsifier and a smaller number of larger composite particles -- are very different from those of McCarthy et al. (1986a, b). Clearly the above computed figures are quite uncertain but higher than the measured rate.

The polymerization rate in the aqueous phase can be rewritten as shown in Eq. 13.

$$R_{pw} = k_{pw} [M]_w [R]_w \quad (13)$$

The maximum value of $[R]_w$ is $(R_i / 2k_{tw})^{1/2}$. If this substitution is made and the numerical values of R_i and $[M]_w$ are inserted one obtains:

$$R_{pw,max} = [-0.7 \times 10^{-6}] k_{pw}/k_{tw}^{1/2}$$

Dainton et al. (1959 a, b, c & d) suggest k_{pw} and k_{tw} values of 100 and 3×10^3 dm³/mol-sec respectively, which yield a $R_{pw,max}$ estimate of 1.2×10^{-6} mol/dm³-sec which is two orders of magnitude less than the total experimental rate. Hence one must conclude that the particle phase is the major locus of polymerization.

CONCLUSIONS

The mechanism of polymerization of AN in aqueous solution appears to be similar to that of emulsion polymerization and can be at least partially understood by using the theories that have resulted from numerous studies of emulsion polymerization. The kinetic model suggests that the main site of polymerization is the polymer particles as is the case with emulsion polymerization. A similarity of nucleation mechanisms is suggested and oscillations of conversion occur in polymerization of AN in an unseeded CSTR. The tube-CSTR system can be employed to eliminate such oscillations. A light blue seed particle latex was obtained from the PFR and these particles grew and were observed on the surface of precipitated polymer particles in the CSTR effluent. However, the unique property, that PAN does not dissolve in its monomer, leads to a suggested mechanism that the locus of polymerization is isolated macroradicals on or near the surface of a glassy latex particle. This mechanism is supported by the migration of MWD to higher molecular weights in the CSTR.

Polymerization of AN in the tube-CSTR system provides a method for obtaining stable production quality. The tube-CSTR prevents oscillations, decreases the polydispersity of the polymer and yields a narrower PSD product. Hence, this reactor system improves not only the stability of product properties, but also provides a stable operation.

GLOSSARY OF SYMBOLS

c	pseudo-first-order rate coefficient for second order loss of free radical activity by termination (sec ⁻¹)
D	mean diameter of dried polymer particles (dm)
F _{H2O}	flow rate of water phase (dm ³ sec ⁻¹)
f _i	initiation efficiency (-)
[I _o]	concentration of oxidative initiator (mol dm ⁻³)
[I _o] _f	concentration of feed oxidative initiator (mol dm ⁻³)
[I _r]	concentration of reductive initiator (mol dm ⁻³)
[I _r] _f	concentration of feed reductive initiator (mol dm ⁻³)
k	rate coefficient for first-order loss of free radical activity (sec ⁻¹)
k _d	decomposition rate coefficient of initiator (dm mol ⁻¹ sec ⁻¹)
k _p	propagation rate coefficient (dm mol ⁻¹ sec ⁻¹)
k _t	termination rate coefficient (dm mol ⁻¹ sec ⁻¹)
[M]	monomer concentration (mol dm ⁻³)
[M] _f	concentration of feed monomer (mol dm ⁻³)
[M] _p	monomer concentration in polymer particles (mol dm ⁻³)
[M] _w	monomer concentration in aqueous phase (mol dm ⁻³)
(MW) _M	molecular weight of monomer (g mol ⁻¹)
n	average number of free radicals per polymer particle (radical #/particle)
N	particle number per volume of water (particle # dm ⁻³)
N _A	Avogadro's number (# mol ⁻¹)
N _i	number of polymer particles that contain i free radicals (particle # dm ⁻³)
q	partition coefficient of monomer between aqueous phase and polymer particles (-)
[R]	polymer radical concentration (mol dm ⁻³)
[R] _w	polymer radical concentration in aqueous phase (mol dm ⁻³)

R_i	rate of initiation ($\text{mol dm}^{-3} \text{sec}^{-1}$)
R_p	rate of polymerization ($\text{mol dm}^{-3} \text{sec}^{-1}$)
R_{pp}	rate of polymerization in polymer particles ($\text{mol dm}^{-3} \text{sec}^{-1}$)
R_{pw}	rate of polymerization in aqueous phase ($\text{mol dm}^{-3} \text{sec}^{-1}$)
V_{H_2O}	volume of water phase in reactor (dm^3)
X	fractional conversion to polymer (-)
α	"fate parameter" given relative importance of reentry, heterotermination, etc., if free radicals desorb (-)
ϕ_p	volume fraction of polymer particles (-)
θ	mean residence time of CSTR (sec)
ρ	over all entry rate coefficient into polymer particle (sec^{-1})
ρ_A	contribution to radical attachment of free radicals arising directly from initiator (sec^{-1})
ρ_p	density of polymer (g dm^{-3})

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E-19-X71

#2

Annual Progress Report

National Science Foundation Grant No. CTS-9417306

Georgia Tech Project Number: E19-X71

Project Title: Copolymerization in Dispersed Systems

Project Director: F. Joseph Schork (transferred from Gary W. Poehlein)

**To: Dr. Maria Burka, Program Director
Division of Chemical and Transport Systems
National Science Foundation
4201 Wilson Blvd.
Arlington, VA 22230**

Period Covered: December 1995 to December 1996

Introduction

Work on this grant has continued in the area of copolymerization in dispersed phase. Studies on dispersion polymerization have been concluded with the doctoral dissertation of Dr. S. F. Ahmed. Work in the use of phase transfer catalysts in emulsion polymerization was completed with the MS thesis of Mr. Robert Racz. Work has continued in the area of copolymerization in miniemulsions.

Research Summaries

Summaries of research areas pursued during 1996 are included below:

Dispersion Polymerization of Styrene

Dispersion polymerization in polar organic media is a heterogenous polymerization process that combines solution polymerization in the continuous phase with microbulk polymerization in the disperse particle phase. The relative prevalence of the two polymerization modes are dependent on a number of reaction variables. A mechanistic picture of dispersion polymerization during the particle growth phase has been developed and mathematical models of the rate of polymerization and particle growth during seeded batch and continuous polymerization have been written.

Predictions of monomer conversion, polymerization rate and evolution of particle size distribution during seeded batch and continuous dispersion polymerization obtained from simulation have been compared to experimental results.

An understanding of the kinetic mechanisms governing the relative prevalence of solution and microbulk polymerization has been gained. Estimates of parameters in the radical transport rate coefficient models compares favorably with values reported in literature.

Relative Shear Stability of Mini- and Macroemulsion Latexes

The shear stability of mini- and macroemulsion latexes has been compared and quantitatively evaluated with respect to their particle size distributions. The effect of a few externally added large particles on the shear stability of these two types of latexes was also investigated. All the latexes selected were in the colloidal size range (less than one micron). The original particle sizes for the macroemulsion latexes ranged from 141 - 241 nm, and those for the miniemulsion latexes ranged from 96 - 209 nm.

The miniemulsion latexes were found to be more shear stable than their macroemulsion latex counterparts over the particle size range investigated. This trend was repeated even in the presence of a few large particles. Additionally, seeding experiments suggest that mini- and macroemulsion latexes incur different levels of shear aggregation due to inherent differences in their particle size distributions. The shear rate used along with the particle size and number were quantitatively shown to significantly influence the aggregation process. Finally, a quantitative method for evaluating relative shear stability in emulsion polymerization has been demonstrated, which, though not very rigorous, could serve as a starting point for further quantitative isolation and investigation of the various parameters that affect the shear aggregation process.

Miniemulsion Copolymerization in the Presence of Alkyd Resin

Emulsion and miniemulsion copolymerizations were carried out with acrylic monomers (MMA, BA and AA) in the presence of an alkyd resin. PMMA was used as a hydrophobe or cosurfactant in the miniemulsion reactions. The results demonstrate that miniemulsion polymerization is the preferred process; probably because of mass transport limitations of the alkyd in the conventional emulsion polymerization reactions. The monomer emulsions prepared for the miniemulsion reactions were much more stable and the polymerizations were free of coagulum. Reaction rates, particle size characteristics, grafting efficiencies and some film properties were measured.

Miniemulsion Polymerization In Continuous Reactors

Miniemulsion polymerization offers some advantages over conventional emulsion polymerization. First, miniemulsions have been shown to be more robust to inhibitor, initiator and agitation levels. Secondly, miniemulsion systems may provide a means of producing latexes that are impossible to produce (due to monomer water insolubility) using conventional emulsion techniques. Miniemulsion polymerization with polymeric hydrophobes provides some advantages over the use of more conventional hydrophobes such as hexadecane. They are innocuous in the product,

and do not add volatile organic compounds to the formulation.

Work has focused on using continuous reactors to examine the underlying kinetic features of miniemulsion reactions, especially with polymeric hydrophobes. In addition, computer models have been developed to isolate and analyze certain aspects of these systems such as monomer transport, competitive growth rates and molecular weight distributions.

Use of Phase Transfer Catalysts in Emulsion Polymerization

The effects of a phase transfer catalyst on the emulsion polymerization of styrene have been examined. The parameters investigated include the rate of polymerization, and the time to reach a given conversion. Both seeded and unseeded systems were tested. Phase transfer catalysts were added at the beginning of the reaction to improve monomer uptake by the seed particles. Phase transfer catalysts were added late in the reaction to facilitate conversion of residual monomer. When

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Published

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Accepted

Wang, S., G. W. Poehlein, and F. J. Schork, "Miniemulsion Polymerization of Styrene with Chain Transfer Agent As Cosurfactant" J. Polymer Science , 35 595-603 (1997).

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Ahmed, S. Farid and Gary W. Poehlein, "Kinetics of Dispersion Polymerization of Styrene in Ethanol; I. Model Development" I&EC Fundamentals (in press).

Ahmed, S. Farid and Gary W. Poehlein, "Kinetics of Dispersion Polymerization of Styrene in Ethanol; II. Model Validation", I&EC Fundamentals (in press).

Poehlein, g. W., "Reaction Engineering for Emulsion Polymerizaiton," in Polymeric Dispersions: Proinciples and Theory, J. Asua (editor), Kluwer Academica Pub., Dordrecht, the Netherlands (in press).

Presentations

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Rodrigues, J, and F. J. Schork, "Relative Shear Stabilities of Mini- and Macroemulsion Latexes", AIChE Annual Meeting, Chicago, November, 1996.

Gooch, J. W., G. W. Poehlein, F. J. Schork and S. T. Wang, "Low VOC Alkyd Coating Resins by Miniemulsion Copolymerization, Green Chemistry and Engineering Conference on June 23-25, 1997.

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G. w. Poehlein, "Continuous Emulsion Polymerization Reactors." NATO Advanced Study Institute, Spain (1996).

Research Plans

Personnel

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Dr. Gary W. Poehlein*
Dr. Shouting Wang, Research Scientist
Mr. Mehmet Sinangil, Research Engineer
Mr. Syed Ahmed, PhD Candidate
Mr. Charles Samer, PhD Candidate
Mr. Henry Hipps, MS Candidate
Mr. Robert Racz, MS Candidate
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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: 12/94	To: 11/97	
4. Institution and Address	GA Tech Res Corp - GIT Administration Building Atlanta GA 30332		
5. Award Number	9417306		
6. Project Title	Copolymerization in Dispersed Systems		

**You are encouraged to submit your Final Project Report electronically
through the NSF FastLane home page (www.fastlane.nsf.gov).**

**This Packet Contains
NSF Form 98A
And 1 Return Envelope**

**NSF Grant Number CTS-9417306
G. W. Poehlein, F. Joseph Schork, P.I.'s**

Final Report

Part II: Summary

Work on this grant has focused on copolymerization in dispersed media. Specifically dispersion polymerization, and emulsion and miniemulsion polymerization systems have been investigated.

Dispersion polymerization in polar organic media is a heterogeneous polymerization process that combines solution polymerization in the continuous phase with microbulk polymerization in the dispersed particle phase. A mechanistic picture of dispersion polymerization during the particle growth phase has been developed and mathematical models of the rate of polymerization and particle growth during seeded batch and continuous polymerization have been written. Predictions of monomer conversion, polymerization rate and evolution of particle size distribution obtained from simulation have been compared to experimental results.

Emulsion and miniemulsion copolymerizations were carried out with acrylic monomers in the presence of an alkyd resin. The results demonstrate that miniemulsion polymerization is the preferred process; probably because of mass transport limitations of the alkyd in the conventional emulsion polymerization reactions. This process leads to a graft copolymer of acrylic and alkyd which should have significant applications in air-cured, water-based coatings.

In addition, studies on continuous miniemulsion polymerization, and the shear stabilities of emulsion and miniemulsion products have been carried out.

**NSF Grant Number CTS-9417306
G. W. Poehlein, F. Joseph Schork, P.I.'s**

Final Report

Part III: Technical Information

Introduction

Work on this grant has continued in the area of copolymerization in dispersed phase. Studies on dispersion polymerization have been concluded with the doctoral dissertation of Dr. S. F. Ahmed. Work in the use of phase transfer catalysts in emulsion polymerization was completed with the MS thesis of Mr. Robert Racz. Work has continued in the area of copolymerization in miniemulsions.

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Miniemulsion Polymerization in Continuous Reactors

A typical emulsion polymerization recipe includes monomer, water, surfactant and initiator. Particle formation occurs when an oligomeric radical, growing in the aqueous-phase, is captured by a monomer-swollen micelle (micellar nucleation) or, for the case of more water-soluble monomers, the growing radical reaches a critical chain length and precipitates (homogeneous nucleation). However, if the monomer droplet size is made small enough (i.e. < 500 nm), radical capture by monomer droplets (droplet nucleation) becomes the principal site for particle formation.

The most important feature of droplet nucleation is the addition of a monomer-soluble, water-insoluble, stability agent. A variety of these hydrophobic stability agents have been used successfully to effect predominant droplet nucleation. In this work, hexadecane (HD) and polymethylmethacrylate (PMMA) have both been used in a single continuous stirred tank reactor (CSTR). Systems using HD are referred to as miniemulsions since they resist diffusional degradation for several months. However, systems using polymeric hydrophobes are stable for only a few hours, hence the name stabilized droplet polymerization (SDP). PMMA is preferred since it is innocuous in the final latex, although slower polymerization rates are incurred due to a slight increase in the initial monomer droplet size.

It has been shown, using continuous emulsion polymerization experiments, that the rate of a miniemulsion polymerization is a function of the initiator concentration, residence time and initial droplet concentration. In most cases the rate of polymerization using miniemulsions is much greater than that for a conventional emulsion (also called macroemulsion) recipe at the same operating conditions. Initial experiments with SDP systems suggest behavior similar to that of miniemulsions,

however the rate of polymerization have been shown to lie between mini and macroemulsions. Both miniemulsion and SDP reactions have been shown to follow conventional emulsion polymerization kinetics, such that the final latex properties for all of these systems are approximately the same.

Use of Phase Transfer Catalysts in Emulsion Polymerization

The effects of a phase transfer catalyst (PTC) on the emulsion polymerization of styrene have been examined. The parameters investigated include the rate of polymerization, and the time to reach a given conversion. Both seeded and unseeded systems were tested. PTC's were added at the beginning of the reaction in an attempt to increase the number of radicals per particle. PTC's were added late in the reaction to facilitate conversion of residual monomer. When PTC was added at the beginning of the reaction, the rate of polymerization and the particle number increased, while the time to 50% conversion decreased. Seeded experiments determined that the increase in rate is due to the increase in particle number, and not to an increase in the number of radicals per particle. Thus, the PTC did not have the desired effect. The addition of PTC near the end of the reaction did not significantly increase the conversion of residual monomer.

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Presentations

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"Continuous Processes", Chapter 8 in Emulsion Polymerization, M. S. El-Aasser and P. A. Lovell, editors, Wiley & Sons, New York, 1997.

"Process Modeling and Control", Chapter 10 in Emulsion Polymerization, M. S. El-Aasser and P. A. Lovell, editors, Wiley & Sons, New York, 1997.

F. J., G. W. Poehlein, S. Wang, J. Reimers, J. Rodrigues and C. Samer", International symposium on Advanced Technology of Fine Particles, Yokohama, Japan, October 12-16, 1997.

Personnel

Dr. F. Joseph Schork
Dr. Gary W. Poehlein*
Dr. Shouting Wang, Research Scientist
Mr. Mehmet Sinangil, Research Engineer
Dr. Syed Ahmed, PhD Candidate (degree awarded)
Mr. Charles Samer, PhD Candidate
Mr. Henry Hipps, MS Candidate
Mr. Robert Racz, MS Candidate (degree awarded)
Mr. Jeffrey Rodrigues, MS Candidate (degree awarded)

* Currently on temporary assignment at NSF

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	2				3					
B. Total, Permanent Residents										
U.S. Citizens or Permanent Residents ² :										
American Indian or Alaskan Native										
Asian										
Black, Not of Hispanic Origin										
Hispanic										
Pacific Islander										
White, Not of Hispanic Origin										
C. Total, Other Non-U.S. Citizens										
Specify Country										
1. Peoples Republic China			1							
2. Turkey			1							
3. India					2					
D. Total, All participants (A + B + C)	2		2		5					
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 for all U.S. Citizens and Non-citizens with Permanent Residency. (If more than one category applies, use the one category that most closely reflects the person's recognition in the community.)

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

AMERICAN INDIAN OR ALASKAN NATIVE: A person having origins in any of the original peoples of North America and who 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.