# Tubular Reactors for Emulsion Polymerization: I. Experimental Investigation

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*Experimental results using a pulsed tubular reactor are presented. The use of a pulsation source eliminates the reactor fouling and plugging issue that has occurred in previous investigations. Startup data and steady-state profiles are presented. Comparisons in monomer conversion and particle-size distribution for batch, CSTR and tubular reactor are made. The influence of pulsation on the particle-size distribution is discussed. It is shown that high-conversion latex with a narrow particle-size distribution can be produced continuously in the pulsed tubular reactor.*

## Introduction

Emulsion polymerization is a widely used process for the production of polymer. The product latex, a submicron suspension of colloidally stable polymer particles in (usually) aqueous medium, has many desirable properties. The low viscosity of the latex reduces pumping and agitation equipment requirements and improves heat transfer to the reactor walls. The heterogeneous nature of the process enables the simultaneous achievement of high molecular weight polymer and high reaction rates in many cases. Latices can also have desirable properties in coating applications so that performance and environmental concerns suggest an increased use of aqueous-based products for architectural and structural coatings.

Economics favor a continuous process over a batch system when product volumes are large enough or when product grades differ slightly. A continuous process also offers improved quality by eliminating batch to batch variations. A continuous stirred-tank reactor (CSTR) and a tubular reactor are two potential candidates for such a process.

Emulsion polymerization in a CSTR offers several challenges. Multiple steady states occur due to the termination gel effect (Schork, 1981; Rawlings and Ray, 1987). In addition, the steady states can be unstable. Experimental and theoretical studies have confirmed the presence of sustained oscillations in reactor composition and polymer properties for a wide range of operating conditions. Oscillatory behavior should be avoided as varying product quality is not acceptable.

Sometimes it is possible to achieve a stable steady state in a CSTR. However, unlike a batch reactor which produces a latex with a relatively narrow particle-size distribution (PSD), the exponential residence time distribution of a CSTR produces a broad particle-size distribution. The PSD has a direct influence on the film forming properties of the latex. There is also an indirect effect of the PSD on the molecular weight distribution since the radical concentration in the particles depends on the particle size. Thus, the end-use properties of a latex prepared in a CSTR may differ greatly from one produced in a batch reactor. This complicates scaling up new formulations from a laboratory batch reactor to continuous production.

A tubular reactor appears as a natural alternative to the CSTR as a continuous process. The large surface area of the tube is particularly advantageous for the strongly exothermic polymerizations. The narrow residence time distribution in laminar or turbulent flow suggests that a tubular reactor will produce latex with a narrow particle-size distribution. Stable operation is also expected from a tube with its greatly reduced backmixing. Unfortunately, these advantages can be overwhelmed if there are fouling and plugging of the reactor.

To explore the feasibility of tubular reactors for emulsion polymerization, a detailed study was carried out. First, we review previous emulsion polymerization studies involving a tubular reactor, which shows that reactor plugging can be a problem. We then describe an experimental program with a tubular reactor. To avoid plugging in the tubular reactor, a pulsation source is added to the system. Residence time distribution (RTD) experiments show that there is very little backmixing in the experimental tubular reactor. Methyl methacrylate polymerization results are presented for batch, CSTR and tubular reactors under similar operating conditions. Comparisons in monomer conversion and particle size are made to

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assess the viability of the tube as a continuous replacement of the batch reactor. Tubular polymerizations at different Reynolds numbers and pulsation rates are performed to determine the influence of pulsation on the reactor performance. Finally, we discuss some possible processes that exploit both the heat-transfer capabilities and the spatially distributed nature of the tubular reactor.

## Literature Review

Emulsion polymerization has been studied extensively in batch reactors and to a lesser extent in CSTRs; however, very little work has been done with tubular reactors. This is surprising in light of the potential advantages of such processes. We present a review of reported work in tubular emulsion polymerization. We categorize the studies by reactor type: loop, seed, high conversion, and other spatially distributed reactors.

### *Loop reactors*

Rollin et al. (1977) studied the influence of the Reynolds number on the rate of polymerization of styrene in a closed-loop reactor. Using a fixed recipe (styrene/water: 1/4 by volume; potassium persulfate, sodium lauryl sulfate, and a temperature of 60°C), they varied the Reynolds number from 415 to 13,600 in a 7.7-mm-ID stainless-steel tube reactor, 18.9 m long and shaped in a loop with two straight sections. The loop reactor was operated in batch mode. Plugging occurred in two of the ten runs reported.

Rollin and coworkers consistently found a limiting conversion well below the final conversion ($\approx 97\%$) obtained in a batch reactor with the same operating conditions. Their results showed a maximum in the rate of polymerization and in the value of the limiting conversion when the flow was in the transition from laminar to turbulent regime. The lower limiting conversion ($\approx 28\%$ at $N_{Re} = 415$) and lower rate in the laminar regime were thought to be due to diffusional limitations of the monomer. Inefficiencies (limiting conversion of 12% at $N_{Re} = 13{,}600$) in turbulent flow were thought to be due to a low micelle concentration. Because turbulent flow produced smaller monomer drops which absorbed more surfactant, this leads to fewer micelles and hence fewer polymer particles.

Lynch and Kiparissides (1981) simulated the turbulent flow regime experiments of Rollin et al. (1977). Their monodisperse model included axial dispersion of initiator (which they found to contribute negligibly to the initiator concentration profile), micellar nucleation, and particle loss by coalescence. By varying the coalescence rate constant with the Reynolds number, they obtained excellent agreement between the model and the experimental conversion data of Rollin et al.

Bataille and Dalpe (1989) studied the polymerization of vinyl acetate in a batch loop reactor at 60°C. The reactor consisted of glass tubes of 1.9 cm ID and a total length of 8 m. Studying Reynolds numbers in the range 4,300–8,600, they found an optimum recirculation rate and limiting conversions occurred for all cases.

U. S. Patent #3,551,396 (Lanthier, 1970) describes a continous loop recycle reactor in which the recycle loop flow rate is much greater than the reactor feed flow rate. The patent establishes the feasibility of a reactor fabricated of aluminum tubing with 1 cm OD and a loop length of 3–4 m in the polymerization of vinyl acetate. As an example, a recipe with a residence time of 7 min at 40°C with a redox initiator yields a product latex 0.3 μm in diameter with 97% monomer conversion and approximately 52% solids.

Lee et al. (1990) investigated the polymerization of styrene in a continuous loop recycle reactor. The reactor consisted of glass tubes of 4.6 cm ID and 1.56 m in length.

### *Seed reactors*

Ueda et al. (1971) used a stainless-steel helical coil, 4 mm ID × 19 m, to produce seed particles for a CSTR. A number of workers have used low residence time tubes as seed reactors for larger downstream reactors. The reaction system studied was styrene/water (1/4 by volume) at 60°C, with potassium persulfate initiator and sodium oleate surfactant.

Greene et al. (1976) used a 3.18 mm OD fluoropolymer tube as a seed reactor for a CSTR. By introducing intermittent nitrogen plugs to control the residence time, the reactor operated as a plug-flow reactor. These workers limited the conversion to less than 10% and found that the tubular reactor operated identically to a batch reactor under these conditions.

### *High-conversion reactors*

Several early patents discuss a tubular reactor process in which turbulent flow is induced by adding baffles to the reactor. Most of these attempts failed due to coagulation problems. Two of these patents highlight a problem prevalent in the use of a tubular reactor. U. S. Patent #2,161,481 (Mark, 1939) suggests using turbulent flow in the polymerization of methyl methacrylate. U. S. Patent #2,394,396 (Calcott, 1946) claims that the earlier patent produces coagulum when polymerizing "soft" latexes such as isoprene and suggests that laminar flow eliminates this problem.

One of the earliest detailed reports using tubes was by Feldon et al. (1955) for GR-S rubber polymerization. Feldon and coworkers investigated a laminar-flow reactor consisting of 20-gauge stainless-steel tubing, 116 m × 1.58 cm OD in successive 2.69 m straight sections connected by small "U" sections. The reactor was submerged in a tank to maintain isothermal operation at 50°C. They studied a 2/1: aqueous/organic copolymerization of styrene (25%) and butadiene (75%). Feldon et al. operated in the laminar-flow regime with a Reynolds number of less than 1,000 and concluded that the product latex was similar to that produced in batch. After producing approximately 700 kg of polymer (45 days of operation), they report that there had been no buildup of polymer in the reactor.

Ghosh and Forsyth (1976) studied a tubular reactor for polystyrene using 1.27-cm-OD 316-stainless-steel tube, 73.2 m long, in a helical coil configuration. They investigated the laminar-flow regime with Reynolds numbers in the range 100–1,000. Reactor plugging occurred, especially at high temperatures (>70°C) and low soap concentrations (<0.014 M). It was reported that the tube thermocouples contributed to the reactor plugging, while intense agitation of the emulsion feed reduced plugging. In addition to their experimental work, Ghosh and Forsyth formulated a model assuming laminar flow with radial dispersion and a monodisperse particle-size distribution.

Vatanatham (1979) studied emulsion copolymerization in a

6.35-mm-OD 316-stainless-steel tube, 57 m long, in the laminar-flow regime ($N_{Re}=300$–$1{,}000$). Homopolymerization experiments with styrene and copolymerization experiments of styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS) were performed. Some plugging occurred at low soap concentrations and high initiator concentrations; however, the author reported some operating conditions for which coagulum did not form. Particle-size data for the tubular reactor (electron microscopy) suggested that the particle-size distribution of the product latex was only slightly broader than in a batch system. Using a model similar to the one developed by Ghosh and Forsyth (1976), Vatanatham and Forsyth (1979) determined scaleup factors for evaluating laboratory data.

Lee and Forsyth (1981) studied the seeded polymerization of vinyl acetate in the tubular reactor built by Vatanatham. The reactor recipe used both anionic and nonionic surfactants. The use of a seed latex in the presence of secondary nucleation produced bimodal particle-size distributions. Phase separation occurred in all runs. They also reported stable oscillations in conversion when the exit conversion was >30%.

Rollin and coworkers (1979) continued their batch loop work (Rollin, 1977) in a continuous 2.23-cm-ID and 155.7-m-long fluorinated polymer tube. The reactor was shaped into four helical coils of 42.3 cm diameter. Each coil was submerged in a separate bath to maintain isothermal operation. There was a sampling point at the exit of each coil. The recipe was similar to their previous work: styrene/water 1/4; potassium persulfate; sodium lauryl sulfate; and temperature 60°C. They varied the Reynolds number from 1,330 to 10,600 and reported steady-state conversion vs. residence time for 15 experiments. They found limiting conversions for $N_{Re}=1{,}300$.

The results obtained in the continuous-loop reactor were similar to the batch-loop experimental results. They found a maximum rate of polymerization at the transition from laminar to turbulent flow ($N_{Re}=5{,}000$ for this helical coil geometry). Insufficient reactor length prevented the investigation of limiting conversions at $N_{Re}>1{,}400$. Plugging did not occur in any of the runs presented. The highest exit conversion produced was 75%. Three experiments had temperature deviations of more than 5°C from isothermal behavior.

Another study by Bataille et al. (1985) involved the copolymerization of styrene and $\alpha$-methylstyrene in the 155.7-m reactor. The copolymerization results were similar to the homopolymerization results mentioned above with a maximum reaction rate at the transition from laminar to turbulent flow.

Two German patent applications by Sutterlin et al. suggest the use of a tubular reactor for emulsion polymerization. The first patent (Sutterlin, 1982) focuses on the material type for the reactor. Whereas both a stainless-steel reactor and a poly(vinylchloride) reactor plugged, a polyolefin and fluoropolymer reactor were operated without producing any coagulum. In the several examples described for acrylic monomer polymerization, the latex product was 30% solids with a narrow particle-size distribution.

The second patent application (Sutterlin, 1983) specifies the use of a tubular reactor as a finishing reactor for reacting residual monomer. Exploiting the greater heat-transfer area, the patent reports a lower residual monomer content of a tubular finishing reactor as compared to a CSTR reactor with the same residence time.

Shoaf and Poehlein (1988) studied the copolymerization of ethyl acrylate and methacrylic acid in batch, CSTR and tubular reactors. Tubes of different inside diameters [1/8 in.-3/16 in. (3.2 mm-4.8 mm)] were used. One set of experiments involved injecting intermittent nitrogen plugs into a 1/8-in. (3.2-mm)-ID tube to achieve plug flow and reduce backmixing. For these experiments, 85% conversion was achieved. The nitrogen flow was difficult to control because of the heating and expansion of the gas. Another set of experiments were performed by Shoaf and Poehlein in the small tube without nitrogen injection. At 70°C and a residence time of 20.9 min, the reactor effluent had a 100% conversion. They also obtained complete conversion at 55°C and lower flow rates. The average particle size of 140 nm was similar to that produced in a batch reactor. However, they reported phase separation and plugging for some of the experiments at the low flow rates. To eliminate the plugging, they increased the flow rate and added a larger diameter tube to the end of the smaller tube. The feed Reynolds number was 28. The authors report that the conversion of the latex entering the larger diameter tube was high enough to eliminate plugging altogether. Nearly complete conversion was achieved with results similar to a batch reactor. They report exit conversion for various tube lengths. From these studies, they discuss scaleup to a commercial system.

## *Other reactor types*

Hoedemakers and Thoenes (1990) used pulsed packed columns (5 cm ID × 5 m packed with glass Raschig rings $d_r=1$ cm and a 5.5 cm ID × 5 m packed with stainless steel Sulzer SMV8-DN50 internals) for continuous styrene emulsion polymerization. The amount of axial dispersion could be varied by adjusting the stroke rate and length of the positive displacement pump used for pulsation. They reported steady-state conversion and particle number vs. residence time for several operating conditions. Under certain conditions of low backmixing, plug-flow behavior was achieved. At low pulsation rates, monomer phase separation occurred. Hoedemakers (1990) developed a steady-state axial dispersion model and a series of CSTRs model using Smith-Ewart case II kinetics.

Meuldijk et al. (1992) have recently reported results for vinyl acetate polymerization in a pulsed packed column. Similar to the styrene polymerizations of Hoedemakers, they demonstrate that high-conversion latex can be continuously produced.

## *Discussion*

*Turbulent Flow Regime.* As mentioned above, the earliest patents for a tubular reactor suggest that turbulent flow is necessary to maintain a well-mixed emulsion. Internal mixers were used to induce turbulence. As Feldon and coworkers (1955) mentioned, internal baffles can lead to reactor plugging and should be avoided.

Unlike bulk or solution polymerization where the viscosity can rise several orders of magnitude during a reaction, emulsion polymerization has a comparatively small viscosity rise; it is usually less than 2 orders of magnitude. Equipment is readily available to produce turbulent flows without baffles for low-viscosity fluids. Thus, the turbulent flow regime is a viable option when designing a tubular reactor for emulsion polymerization.

One design variable associated with the turbulent regime is the reactor size. With a 2.23 cm × 155.7 m reactor, Rollin and

**Table 1. Parameters Used to Calculate the Number of Micelles**

| Sodium Dodecyl Sulfate |
|---|
| $S_{cmc} = 6.4 \times 10^{-6}$ mol/cm$^3$ (Gerrens, 1975, p. II-485) |
| $r_m = 2.5 \times 10^{-7}$ cm (Min, 1978) |
| $a_{em} = 57 \times 10^{-16}$ cm$^2$ (Ahmed, 1971) |
| $a_{ed} = 57 \times 10^{-16}$ cm$^2$ (Ahmed, 1971) |

coworkers (1979) could only study limiting conversions for $N_{Re} < 1{,}400$. Moreover, a typical reaction consumed 200 L of emulsion.

In the batch loop experiments of Rollin et al. (1977), limiting conversions were thought to be due to a lower micelle number. The high shear of the turbulent flow reduced the monomer droplet size, thereby increasing the droplet surface area. Since more surfactant was needed to cover the drops, fewer micelles were produced.

Material balances on monomer and surfactant determine the number of drops and micelles formed. Monomer is present in the aqueous monomer droplet and micellar phases:

$$(1 - V_w) = V_w M_{w\,\mathrm{sat}} + N_d \frac{4}{3} \pi r_d^3 + N_m \frac{4}{3} \pi r_m^3. \tag{1}$$

Surfactant is also present in the aqueous droplet and micellar phases:

$$V_w S_o = V_w S_{cmc} + N_d A_{ed} 4\pi r_d^2 + N_m A_{em} 4\pi r_m^2. \tag{2}$$

Table 1 lists the surfactant parameters used to determine the number of micelles for the experimental conditions of Rollin et al. From Figure 1, it can be deduced that the number of micelles is negligibly affected for droplet diameters greater than 10 $\mu$m. Obviously, as the surfactant level approaches the CMC, the effect of monomer droplet surface area will be more pronounced. Under the sole influence of mechanical shear (agitation), a lower bound on the droplet diameter is 10 $\mu$m (Barnette, 1983; El Aasser, 1986). Thus, it is thought that turbulence should not influence the micelle number.

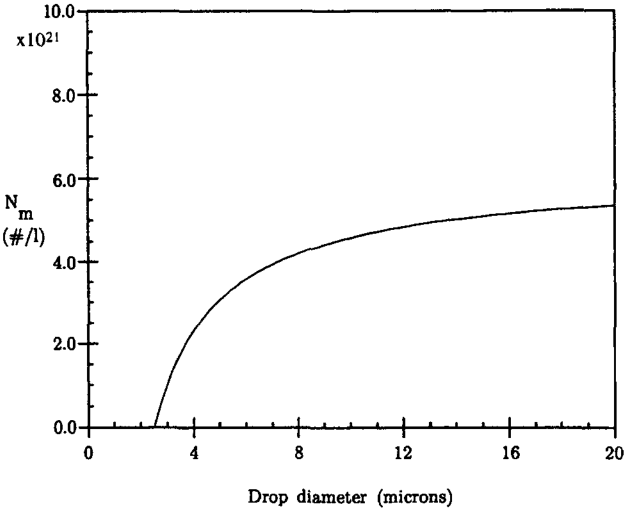

**Figure 1. Micelle number as a function of monomer droplet diameter.**

Conditions: styrene; $V_{wo} = 0.81$; $S_o = 0.01$.

Another issue related to the turbulent operating regime is shear-induced coagulation. Lynch and Kiparissides (1981) successfully modeled the turbulent closed-loop experiments of Rollin et al. (1977) when a coalescence term was included. Shear-induced coagulation occurs when the additional kinetic energy imparted to a particle due to shear overcomes the electrostatic barrier. Zeichner and Schowalter (1977) studied shear coagulation using a detailed two-particle model. The relative influence of shear could be expressed in a Peclet number:

$$P_{es} = \frac{6\pi r_{ps}^3 \gamma_s}{A}$$

where $\gamma_s$ is the shear rate, and $A$ is the Hamaker constant and is a measure of the attractive forces. They concluded that for $P_{es} < 100$, Brownian stability was sufficient. For a 100 nm dia. particle, a shear rate of $10^6$ s$^{-1}$ is needed before shear becomes influential. Under most conditions, this shear rate is not attained. The strong dependence on size suggests that for larger particles, shear-induced coagulation could be important.

Lowry et al. (1984) studied the influence of shear in a concentrated latex (30% solids) in a stirred tank. Kolmogorov's theory of isotropic turbulence was used to determine the dependence of the rate of coalescence on the shear rate and on the particle concentration. They demonstrated that impeller shear can coagulate a weakly stabilized latex. To obtain some coagulation, however, the ionic concentration had to be increased (by adding salt) to destabilize the latex.

*Laminar Flow Regime.* Most of the reported work using a tubular reactor has been in the laminar-flow regime. Emulsion polymerization is a heterogeneous reaction which relies on transport between the various phases. For tank reactors, the low viscosity of the emulsion permits simple stirring to satisfy the heat- and mass-transfer requirements. Characteristic of the laminar-flow regime in a tube is the lack of radial mixing. It is necessary to consider how this affects the heat and mass transfer in the reacting emulsion.

In laminar flow, buoyancy effects and monomer-phase separation must be considered. The lack of radial mixing could cause monomer drops to coalesce and separate from the polymerizing emulsion. Such phase separation could result in diffusion-limited reactions. To estimate the magnitude of this problem we will use the following analysis. The Stoke's settling velocity of a spherical particle of radius $r_{ps}$, and density $\rho_{ps}$ in a fluid of density $\rho_f$ is:

$$v_s = \frac{2 r_{ps}^2 (\rho_{ps} - \rho_f) g}{9 \eta_f}. \tag{3}$$

As a test case, let us consider styrene ($\rho_m = 0.906$ g/cm$^3$, $\rho_p = 1.11$ g/cm$^3$) in an aqueous medium at 60°C ($\rho_f = 1.0$ g/cm$^3$, $\eta_f = 0.0065$ poise), for which the settling (or rising) velocity is:

- $2.0 \times 10^{-10}$ cm/s for a micelle of radius 0.0025 $\mu$m
- $3.7 \times 10^{-7}$ cm/s for a polymer particle of radius 0.05 $\mu$m
- $7.9 \times 10^{-4}$ cm/s for a droplet of radius 5 $\mu$m.

For typical reaction times of 1 h, buoyancy effects are clearly negligible for polymer particles and micelles. For monomer droplets, however, the situation is not so well defined. Under typical polymerizations, the droplets are present for 10-20 min of the reaction and droplet depletion occurs during this time period. Thus, phase separation for 10 $\mu$m dia. drops is not expected to occur under these conditions. However, in situations where the reaction rate is slow (low initiator, high inhibitor, or high chain transfer concentrations), the monomer droplets are present for a longer time and phase separation could occur. Phase separation could also be caused by poor emulsification in which the average droplet diameter is larger than 10 $\mu$m. For example, 20 $\mu$m dia. droplets will have a terminal velocity four times larger than a 10 $\mu$m droplet and phase separation can easily occur.

A phase-separated emulsion may limit monomer transport to the particles resulting in lower reaction rates because of the reduced mass-transfer area and larger diffusion path of the monomer into the aqueous phase. Another result of phase separation is the possibility of coagulum formation. Vanderhoff (1980) states that any stagnant flow regimes (such as near sample points or thermocouples) can lead to coagulation by the following mechanism: phase separation in the stagnant regime occurs; radicals enter the monomer pool and polymerize; and the bulk polymer solution then fouls the reactor. Ghosh and Forsyth (1976) reported reduced fouling when thermocouple wells were removed. For a tubular reactor, phase separation and subsequent coagulum formation must be avoided.

Although there is a large increase in the surface area of a tube for heat transfer, heat-transfer problems can still occur. In stirred-tank reactors, simple agitation is needed to maintain a uniform temperature of the emulsion. Maintaining the emulsion at the *desired* temperature is difficult due to the limited surface area for heat transfer. In the tube, heat removal is not as much of a problem. However, the lack of radial mixing in a laminar-flow tubular reactor permits the formation of radial temperature gradients. Significant temperature gradients may arise in large tubes with fast reactions.

## Experiments

This section describes an experimental program that evaluates three reactor types for polymer latex production. Batch, CSTR and pulsed tubular reactors are compared under similar operating conditions for two case studies of methyl methacrylate homopolymerization. The reactors and their operating procedure are described, and comparisons in monomer conversion and product particle size distribution are drawn.

### *Batch experiments*

Experiments were performed in a 1-L glass vessel with an external jacket for heating/cooling. To improve mixing, removable baffles made of type 316 stainless steel were added. The temperature control system used had both a heating and cooling source. A constant temperature bath, with its temperature set slightly higher than the desired reactor temperature, supplied the heating capacity. The reactor temperature was maintained at its setpoint value ($\pm 0.5^\circ$C) by injecting cold water into the heating/cooling line as needed. Direct injection of water produced a rapid response and facilitated the control.

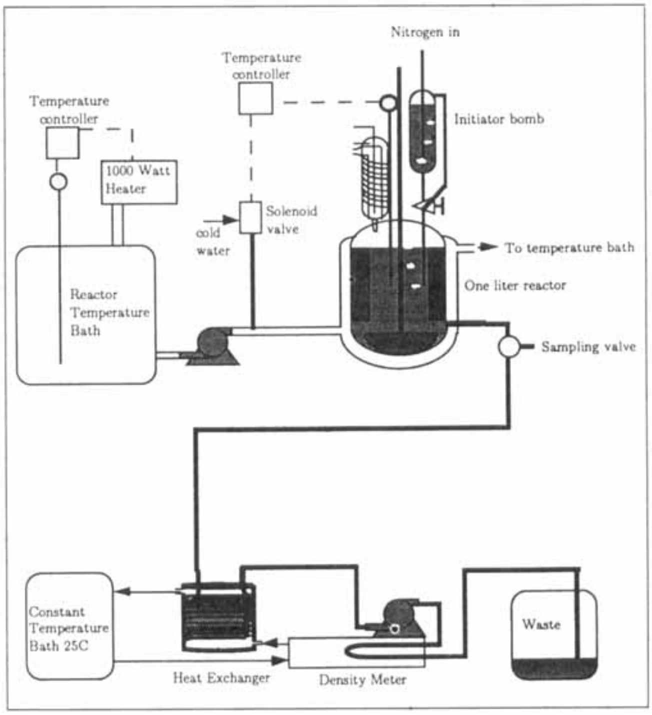

**Figure 2. Batch emulsion polymerization apparatus.**

The apparatus is shown in Figure 2. A detailed description of the system and a standard operating procedure is given by Paquet (1993).

Methyl methacrylate, supplied by Rohm and Haas, contained 10-15 ppm hydroquinone inhibitor. The inhibitor was removed by vacuum distillation at 27 in. Hg ($\approx 40^\circ$C). The surfactant, sodium dodecyl sulfate, was obtained from British Drug House and used without further purification. The initiator, potassium persulfate, was supplied by Aldrich Chemical and used without further purification. The water used in all of the experiments was purified by a Millipore milli-$\Omega$ filtration system.

To prepare for a reaction, the initiator was dissolved in 50 mL of water and placed in the initiator bomb. The remaining chemicals (monomer, water, surfactant) were added to the reactor. Both the initiator solution and the preemulsion (monomer, water, and surfactant under very low agitation rates) were sparged overnight ($\approx$1,100 min) with ultrahigh-purity (UHP) nitrogen supplied by Matheson and Liquid Carbonic. The following day, the reactor was heated to the desired temperature. While heating, an emulsion was formed by stirring at approximately 300 rpm. All experiments were performed with this stirring rate. The reaction was started by injecting the initiator. Samples were taken at regular intervals for monomer conversion determination (by dry solids) and for particle-size measurements.

An additional sample was continuously withdrawn for on-line determination of conversion by density measurement. The sample was cooled to 25°C by a heat exchanger and passed through the density meter. A constant temperature bath was used to keep the density meter at 25°C. Monomer conversion is determined from density by assuming volume additivity of the monomer and polymer (Schork, 1981):

**Table 2. Conditions for Batch Emulsion Polymerizations of Methyl Methacrylate**

| | |
|---|---|
| Monomer Volume Fraction | 0.2 |
| Temperature (°C) | 60 |
| Surfactant (mol/L – aq) | 0.01 |
| Initiator (mol/L – aq) | 0.001 |

$$x=\frac{1/\rho_{x=0}-1/\rho}{1/\rho_{x=0}-1/\rho_{x=1}} \tag{4}$$

where $\rho_{x=0}$, $\rho_{x=1}$ are the densities at zero and 100% conversion, respectively. These two densities are related by:

$$\frac{1}{\rho_{x=1}}=\frac{1}{\rho_{x=0}}+w_m\frac{1}{\rho_m}\left(\frac{\rho_m}{\rho_p}-1\right). \tag{5}$$

An emulsion is a nonideal system, and predicting the initial density ($\rho_{x=0}$) is difficult. To avoid this difficulty, the density meter is "calibrated"; the initial density is determined using the dry solids conversion for one sample.

Samples taken for particle-size measurement were diluted immediately to 1-2% solids. A drop of Triton X-100 nonionic surfactant was added to the 5-10 mL sample to prevent agglomeration during storage. Particle-size distributions were determined by photon correlation spectroscopy (PCS) and scanning electron microscopy (SEM).

Malvern components were used for particle-size measurement PCS; the apparatus is described by Tomski (1991). To prepare for an experiment, the sample was diluted and filtered with a 0.4-$\mu$m filter. The dilution was adjusted by a trial-and-error procedure to obtain rates of 75-150 counts per second as detected by the photomultiplier tube. All of the experiments were performed with a 12 s duration and were repeated ten times. The scattering angle was 90 degrees for all of the experiments. The method of cumulants was used to determine the intensity average diameter. Mie scattering factors were not included. Delgado and Matijevic (1991) concluded that the factors did not significantly alter the mean diameter for narrow distributions.

Particle-size distributions for some of the experiments were determined by SEM. The reactor sample was diluted by a factor of $\approx 100$ (the diluted solution had a faint blue color). One drop of the solution was placed on an aluminum stub. To improve spreading of the latex, a drop of acetone and/or isobutanol was added to the stub. The sample was dried overnight and sputter-coated with gold. A JEOL-35C scanning electron microscope was used. Photographs were taken at accelerating voltages of 15 kV and at a magnification of 30,000. The Polaroid film (type 55) was scanned with an Apple Scanner. The resulting figure was saved in a TIFF format with a 50% reduction resulting in $a \approx 6$-nm/pixel resolution. Particles were counted *individually* with the NIH Image software. Macros were written to facilitate the particle counting. At least 800 particles were counted for each distribution.

Complete reaction in 1 hour served as a guide for selecting the experimental conditions. To reduce plugging concerns, a monomer volume fraction of 20% was used. Simulations of possible batch reactions were performed using the POLYRED (Ray, 1989) simulation package to screen experimental conditions. The selected conditions for experiments are given in Table 2.

Figure 3 shows the conversion histories for four runs with the conditions in Table 2. The results indicate that the reproducibility is acceptable.

### *Continuous stirred-tank experiments*

The next candidate system is the CSTR. The reactor in Figure 4 was a 1/2-L glass jacketed reactor. The temperature control system was the same one used in the batch experiments. Reagent preparation was as described above for the batch experiments. Two streams, one a pure monomer and the other an aqueous solution of initiator and surfactant, were combined by a tee coupling just prior to entering the reactor. Peristaltic pumps were used for both feed streams. Care was taken to

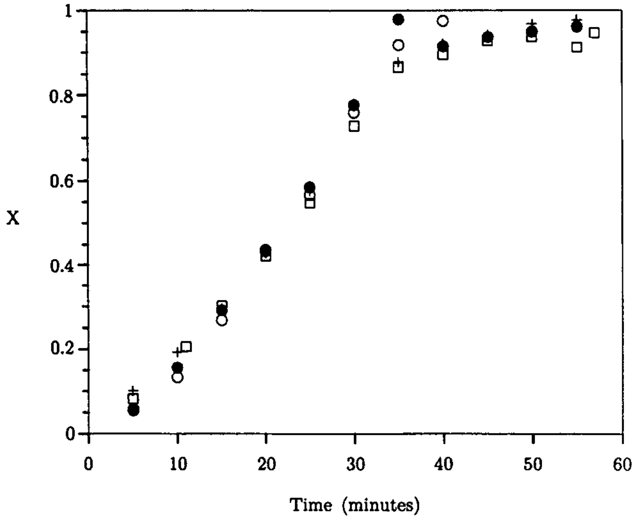

**Figure 3. Monomer conversion vs. time.**

Four replicate batch emulsion polymerization experiments with methyl methacrylate. See Table 2 for the experimental conditions.

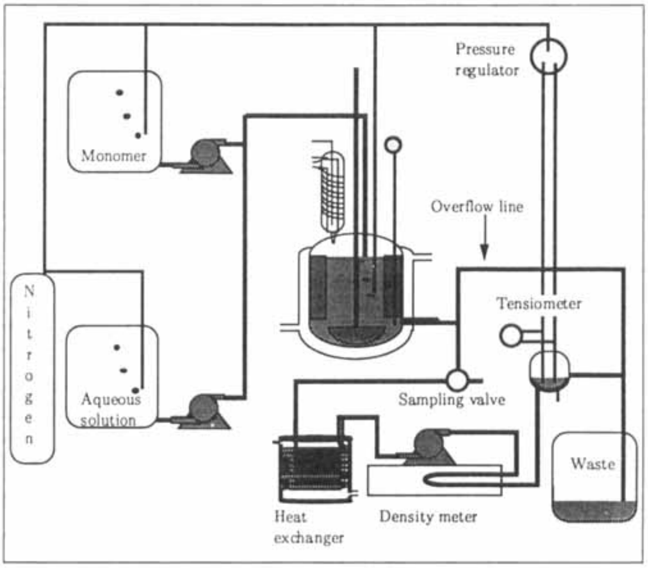

**Figure 4. Continuous stirred-tank reactor system.**

**Table 3. Case 1 Conditions for the Continuous Emulsion Polymerizations with Methyl Methacrylate**

| Variable | Feed | Initial |
|---|---|---|
| Monomer Volume Fraction | 0.2 | 0 |
| Temperature (°C) | 60 | 60 |
| Surfactant (mol/L – aq) | 0.01 | 0.0 |
| Initiator (mol/L – aq) | 0.001 | 0.0 |

monitor the flows to compensate for any tubing degradation. The effluent was split into two streams. The first stream was used for on-line density and surface tension measurements at 25°C (Schork, 1981); the other stream was an overflow line used to control the volume in the reactor. The reactor volume, and hence residence time, could be altered by adjusting the height of the overflow line. As in the batch experiments, samples were taken at regular intervals for conversion determination (by dry solids) and particle-size measurements.

The reactor was initially filled with water. The reactor and both feed tanks were sparged overnight (≈1,100 min) with nitrogen. The following day, the reactor bath was heated to the desired temperature. While the reactor was heating up, the feed pumps were started and adjusted to the target flow rates. The feed streams were diverted to a waste container, while the flows were being adjusted. Once the desired feed rates were achieved and the reactor temperature was at its setpoint, the feeds were diverted to the reactor.

Two experiments were performed with the feed conditions equal to the initial conditions of the batch experiment. Table 3 lists the initial and feed conditions. The residence times for the two experiments were 30 and 60 minutes, as shown in Figure 5. Whereas the 30-min residence time experiment was oscillatory, the 60-min run ignited to a high-conversion steady state. Average particle size was measured using light scattering for some of the samples of the 60-min run, as shown in Figure 6.

### *Tubular reactor experiments*

The final reactor candidate was the open-loop tubular reactor. The apparatus was built by Hamer (1981) for solution polymerization experiments. The reactor was 0.533 cm ID × 8,794 cm coiled in 50-cm loops. Several modifications were made for use in emulsion polymerization. The modified reactor is shown in Figure 7.

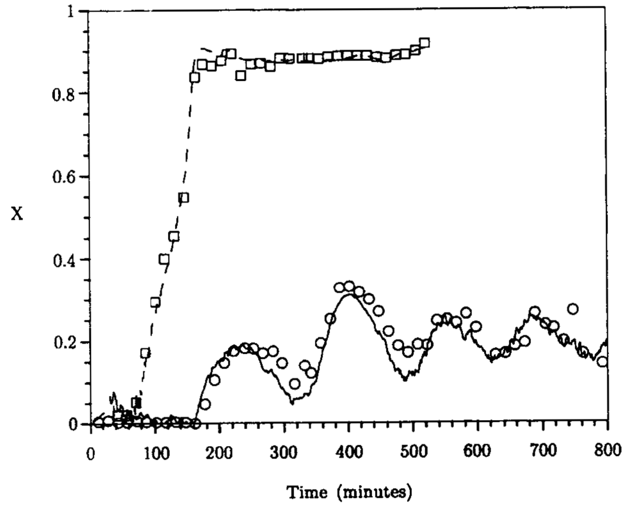

**Figure 5. Monomer conversion vs. time.**

Continuous stirred-tank emulsion polymerization experiments with methyl methacrylate. See Table 3. Data symbols: □—dry solids; dashed line—density meter, 60 min; ○—dry solids; solid line—density meter, 30 min.

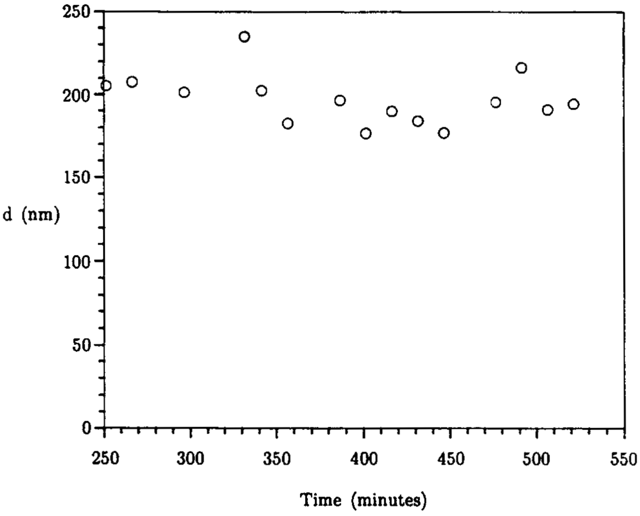

**Figure 6. Average particle diameter vs. time for a mean reactor residence time of 60 min.**

Continuous stirred-tank emulsion polymerization experiments with methyl methacrylate.

Sample valves were located at 0, 6.3, 16.3, 32.0, 59.6 and 100% of the tube's length. The exit stream was split into two streams. One stream passed through a heat exchanger (shell side at 25°C) and a density meter. A peristaltic pump placed after the meter pumped the latex into the waste container. The time delay from the reactor exit to the meter was about 1 min. The second stream (the overflow stream) accounted for the difference in flow rates of the reactor feed and density-meter feed. This stream went directly into a waste container.

Two feed tanks and pumps were used: one for an aqueous initiator solution and the other for an emulsion feed. The

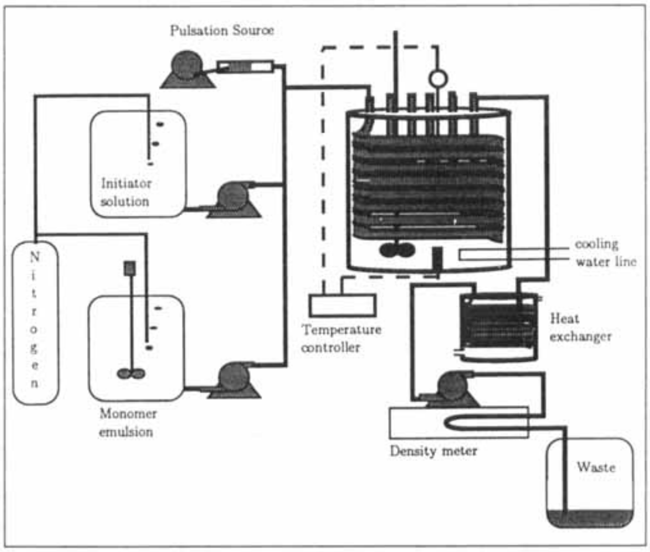

**Figure 7. Continuous tubular reactor system.**

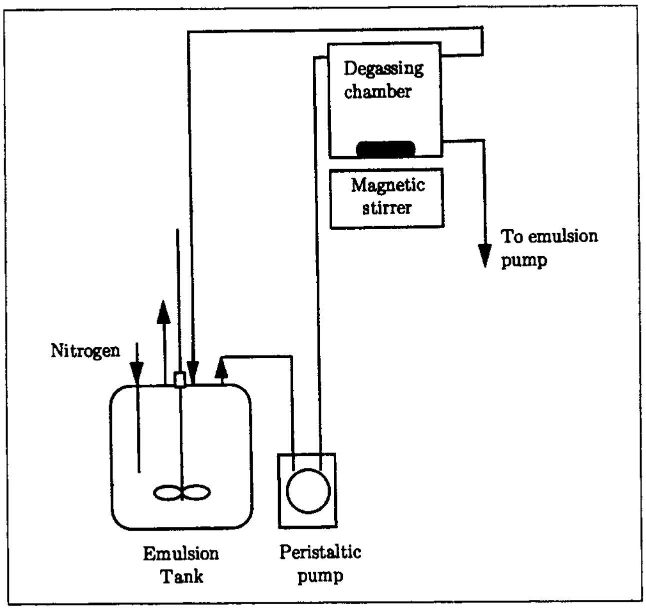

**Figure 8. Continuous tubular reactor emulsion feed system.**

emulsion feed pump was a Milton Roy industrial Minipump model MM2-C-58-SM. Each cylinder of the duplex pump had a 1/4-in. (6.4-mm)-dia. plunger. The pump operated at 58 rpm, and the stroke length could be varied with a maximum of 1 in. (25.4 mm). To avoid pump priming problems (since the emulsion tank could not be pressurized), an elevated degassing chamber was added. The chamber volume was 39 mL. The elevation was sufficient to maintain a constant pressure head on the pump. A peristaltic pump was used to recirculate the emulsion between the feed tank and the degassing chamber. To further emulsify the feed, a magnetic stirrer bar was placed in the chamber. A detailed depiction of the emulsion feed system is shown in Figure 8.

Heat loss from the reactor drum walls and lid were insufficient to remove the heat generated by polymerization, and thus a cooling water line was added to the reactor bath to remove the heat produced. A temperature controller maintained the bath temperature by powering a 2,000-W heating element using proportional control. The large volume of the reactor bath aided in the temperature control. Deviations were less than ±0.5°C from the 60°C setpoint.

Finally, a pulsation source was added to the feed stream. Hoedemakers and Thoenes (1990) avoided plugging by superimposing a pulsatile flow on the nominal axial flow. Pulsation prevents plugging in two ways. First, the pulsation enhances mixing and reduces the possibility of monomer phase separation which can cause fouling (Vanderhoff, 1980).

Secondly, pulsation increases radial mixing and displaces the slow moving fluid at the wall. In addition to reducing reactor fouling, the increased radial mixing from pulsed flow eliminates any radial temperature gradients. In this study, a piston pump was used to generate the pulse. The pump was a Milton Roy pump model RGMC-C-96 Constametric with a 1/4-in. (6.4-mm)-dia. stainless-steel plunger. The pump had a fixed stroke length of 1/2 in. (12.7 mm). The stroke rate could be adjusted from 0–100 spm. To add the pulse, the check valves from the pump's inlet and outlet chambers were removed and the inlet chamber valved off. The feed stream to the reactor was diverted to the pump and back to the reactor inlet. The piping from the point at which the two feeds were mixed to the pulsation pump was ≈28 mL. The pump volume and connecting fittings had a combined volume of ≈5 mL. The tubing from the pump to the reactor inlet had a volume of ≈19 mL.

### *Residence time distribution studies*

As discussed in the introduction, the broad residence time distribution of a CSTR produces a broad particle-size distribution for stable reactors. This contrasts with the relatively narrow PSD (due to the narrow RTD) of a batch reaction. It is important to study the RTD of tubular reactors to ascertain its influence on the experimental tubular system. The RTD of this experimental system will be influenced by the helical nature of the reactor and the pulsation source.

Residence time distribution studies in the tubular reactor were performed using step inputs of a 1% wt. NaCl solution. A conductivity meter was placed at the exit of the reactor. The time delay from the reactor exit to the meter was approximately 15 s. Experiments were performed at three residence times (20, 30 and 60 min) and four different pulse rates (0, 50, 75 and 99 spm). The residence time was based on the reactor volume and did not consider the travel time between the feed mixing point and the reactor inlet. To account for the travel time, the response curves were shifted by this amount (1/2–2 min depending on the feed conditions). An analytic solution for the exit concentration exists for the dispersion equation:

$$\frac{\partial C}{\partial \tau}+\frac{\partial C}{\partial z}+\frac{1}{N_{Pe}}\frac{\partial^2 C}{\partial z^2}=0 \tag{6}$$

with approximate boundary conditions:

$$C=0 \quad \text{for} \quad z,\, t\leq 0 \tag{7}$$

$$C=1 \quad \text{for} \quad z\rightarrow -\infty,\, t>0 \tag{8}$$

$$C=0 \quad \text{for} \quad z\rightarrow \infty,\, t>0 \tag{9}$$

that is,

$$C=\frac{1}{2}\left[1-\text{erf}\left(\frac{\sqrt{N_{Pe}}}{2}\,\frac{1-t/\theta}{\sqrt{t/\theta}}\right)\right]. \tag{10}$$

Figure 9 shows a typical experimental result along with the analytic RTD for laminar flow in a straight tube.

An interesting result is the response curve in the absence of pulsation shown in Figure 10. The curve is much narrower than the theoretical values, and the Peclet number is much higher than those determined by Trivedi and Vasudeva (1975) for helical coils. One possible explanation is the influence of mixing in the bends at our tube sampling points. Saxena and Nigam (1984) further reduced the axial dispersion of a helical coil by adding periodic bends in the coil. The bent or sharply coiled coils eliminated any established secondary flows. Their results, however, did not produce Peclet numbers as high as those found in this work. The feed pumps used may also contribute to the narrowing of the RTD. The two-feed pumps are positive displacement duplex piston pumps. Although the

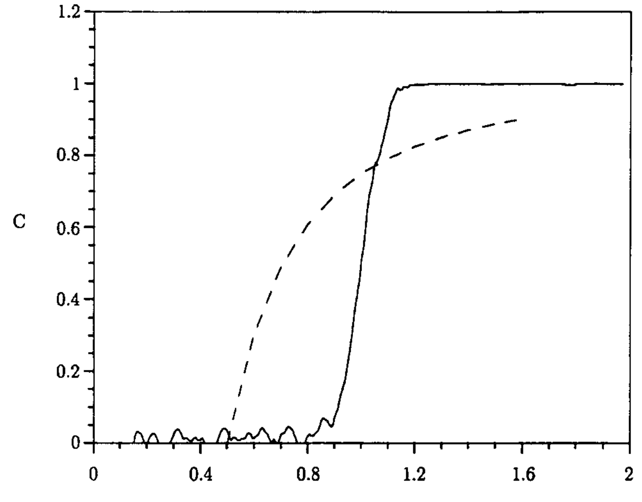

**Figure 9. Residence time distribution for a pulsed tubular reactor.**

Average residence time of 60 min and a pulsation rate of 99 spm. Solid line—experimental data; dashed line—theoretical laminar-flow RTD.

two pistons of each pump are 180 deg apart, some pulsation still exists. Evidence of this pulsation is the oscillatory behavior of the sight ball in the feed flowmeters. This low pulsation may reduce the dispersion.

The experimental RTDs were fit to Eq. 10 using MatLab. The objective function minimized was the norm:

$$E_{rtd} = \Sigma \, | C(t) - C_{\exp}(t) \, |^2. \qquad (11)$$

Peclet numbers which satisfy

$$\frac{E_{rtd,\min}}{0.95} \qquad (12)$$

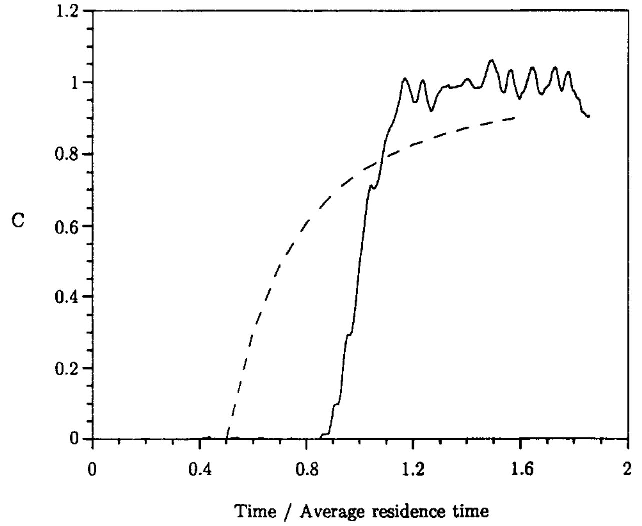

**Figure 10. Residence time distribution for an unpulsed tubular reactor.**

Average residence time of 30 min. Solid line—experimental data; dashed line—theoretical laminar-flow RTD.

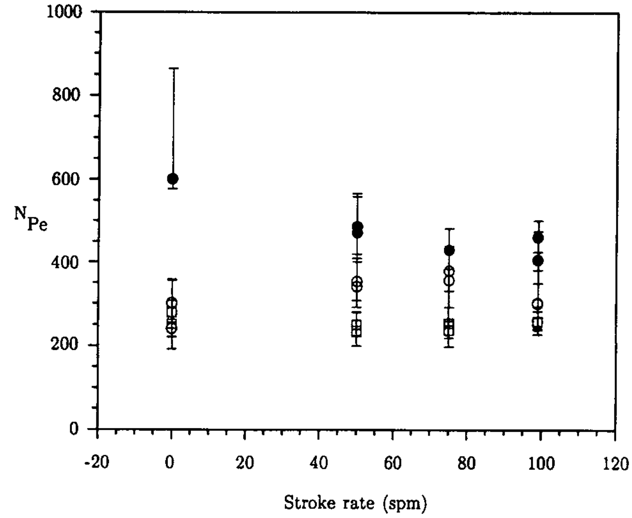

**Figure 11. Peclet number vs. pulsation rate.**

Average residence times (min): ●—60; ○—30; □—20.

were used to measure the sensitivity of the results. The results of the data fitting are shown in Figure 11. Unfortunately, the error norm was not very sensitive to the value of the Peclet number. As a consequence, the Peclet numbers in Figure 11 have wide bounds, and no clear trend with pulsation rate can be determined.

### *Polymerization experiments in the tubular reactor*

The first experiments were performed without any pulsation. The feed stream, produced by mixing the initiator and emulsion feeds, was directed into the reactor via a straight tube. Four runs were performed with feed conditions in Table 2 and a residence time of 1 h. Only one of the runs was successful; the other three plugged at some point between three and four residence times into the experiment. Another experiment with vinyl acetate (Paquet, 1993) was successful, but plugged during the cleanup of the system. The plugging problem that occurred so frequently in these runs prompted the use of pulsed reactor operation.

The next experiments were run with three different pulsation rates. Experiments were run for at least four residence times before taking samples. After samples were taken, the reactor was flushed with water for two to three residence times and then with ethyl acetate for one to two residence times. The reactor was allowed to cool overnight filled with ethyl acetate.

Figure 12 shows the conversion vs. residence time for the batch reactor, CSTR, and tubular reactors. No clear dependence on pulsation rate can be determined from the tubular data. The tubular reactor is rather close to the conversion history of the batch reactor, suggesting a low dispersion system (consistent with the RTD results). The oscillatory behavior at a residence time of 30 min for the CSTR demonstrates the advantages of the tubular system at low residence times. At a residence time of 1 h, however, conversion does not distinguish the reactors and additional information is needed. Figure 13 shows the average particle diameters for the three systems. The average diameters are similar for the batch and tubular runs, while the average for the CSTR is twice as large. The larger

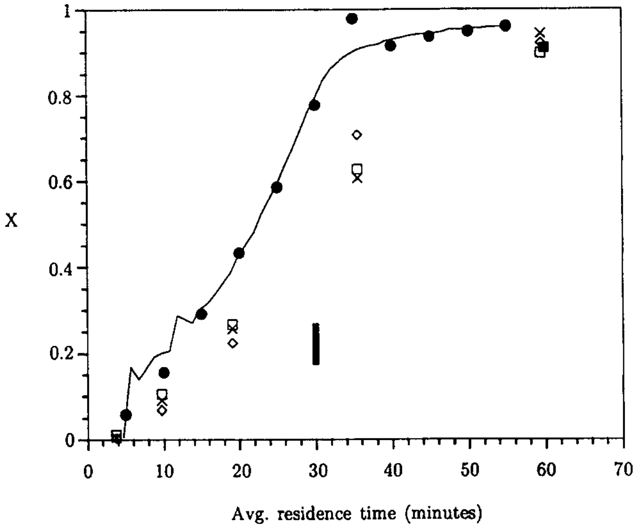

**Figure 12. Monomer conversion vs. residence time for batch, CSTR, and tubular reactors.**

Emulsion polymerization experiments of methyl methacrylate. See Tables 2, 3 for initial and feed conditions. Data symbols: ●—batch reactor; ×—no pulse; ◇—78 spm; □—91 spm; ■—CSTR; vertical bar—CSTR (height of bar represents the amplitude of oscillations).

particles produced by the CSTR differentiate the CSTR latex from the others.

### *A second case study*

The previous experiments suggested that the tubular reactor could approach the plug flow behavior, and that impurities in the feed may have reduced the performance slightly below that of the batch reactor. In addition, conversion alone could not distinguish the CSTR from the tube at high residence times.

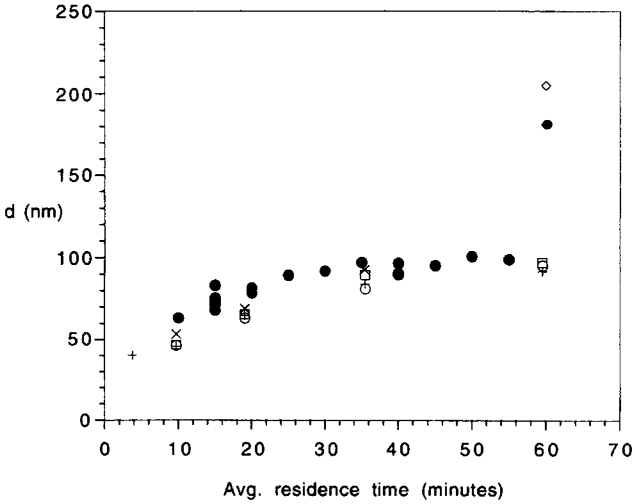

**Figure 13. Average particle diameter vs. residence time.**

Emulsion polymerization experiments of methyl methacrylate. Comparison of different reactor types. Data symbols: ●—batch; ◇—CSTR (QLS average from samples taken at 300-525 min into the reaction); ●—CSTR (SEM 417 particles counted for the sample taken at 300 min); ×—tube no pulse; ○—tube (50 spm); □—tube (78 spm); +—tube (91 spm).

**Table 4. Batch Reactor Conditions for the Second Experimental Case Study**

| | |
|---|---|
| Monomer Volume Fraction | 0.3 |
| Temperature (°C) | 60 |
| Surfactant (mol/L – aq) | 0.008 |
| Initiator (mol/L – aq) | 0.005 |

With these results, a second case study was performed in the three reactors. The following guidelines were used in choosing the conditions.

- The reaction should be fast with complete conversion in less than 1 h. This emphasizes the productivity of the tube. The larger heat-transfer area of the tube permits fast reactions at industrial scale.
- The particle size should be large enough for particle-size measurements by scanning electron microscopy. This will allow a direct comparison of the full distribution and investigate whether the pulsation influences the breadth of the distribution.
- The reaction should be less sensitive to impurities.
- Conversion alone should be capable of differentiating the CSTR and tubular reactors at residence times that produce complete conversion in a batch reactor. To balance the competing requirements for meeting each objective, a higher initiator concentration and a lower surfactant concentration were used.

Table 4 gives the conditions for the second case study in a batch reactor. The value for surfactant is quite low. This is important since Ghosh and Forsyth (1976) had plugging problems at low surfactant concentrations. Also, Rollin et al. (1977) showed that limiting conversions occurred at low surfactant concentrations. The increased monomer volume fraction serves as a test for higher monomer ratios found in industrial operation. Further, at 30% solids, the viscosity increase during polymerization may influence the reactor performance.

A batch experiment was performed with the conditions in

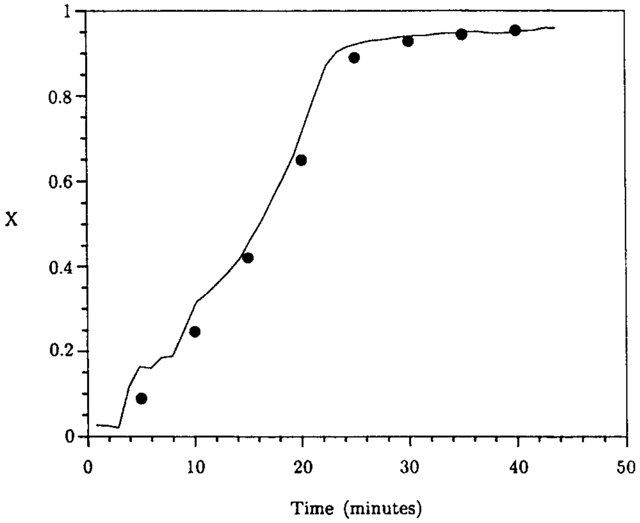

**Figure 14. Monomer conversion vs. residence time for a batch reactor.**

●—dry solids; solid line—density meter.

**Table 5. Case 2 Conditions for the Continuous Emulsion Polymerizations of Methyl Methacrylate**

| Variable | Feed | Initial |
|---|---|---|
| Monomer Volume Fraction | 0.3 | 0 |
| Temperature (°C) | 60 | 60 |
| Surfactant (mol/L – aq) | 0.008 | 0.0 |
| Initiator (mol/L – aq) | 0.005 | 0.0 |

Table 4. The conversion profile is shown in Figure 14. The limiting conversion is reached in less than 40 min.

A CSTR experiment was performed with a mean residence time of 30 min. For this run, sodium persulfate was used instead of potassium persulfate as initiator. This prevented any precipitation when mixed with the surfactant and water. The operating conditions are given in Table 5. The conversion history is shown in Figure 15. The conversion shows damped oscillations with an average conversion of 15%.

Experiments were performed in the tubular reactor with conditions similar to the CSTR. The pulse rate was fixed at 75 spm and the feed flow rate varied; the average residence time varied from 20 to 40 min. Two runs were performed with an average residence time of 30 min. The startup behavior and steady-state conversions of the two runs are shown in Figures 16–17. The results show good reproducibility.

From the startup figure, a rapid rise from zero conversion is observed. The exit conversion reveals that steady state is achieved in less than two residence times. The rapid rise of the exit conversion is consistent with the residence time distribution experimental results. Hoedemakers (1990) found similar results with a pulsed packed column under conditions of low dispersion.

The steady-state conversion profiles for all of the reactors are shown in Figure 18. Again, there is no dependence on feed rate at fixed residence time for the pulsed tubular experiments. The oscillatory behavior of the CSTR is depicted as a vertical bar with height equal to the amplitude of the oscillation. The results clearly show the superior performance of the tube over the CSTR. Although the tube has a slightly lower conversion than the batch reactor, the conversion is significantly higher than in the CSTR. Moreover, the exit conversion in the tube is stable, whereas the CSTR shows oscillatory behavior.

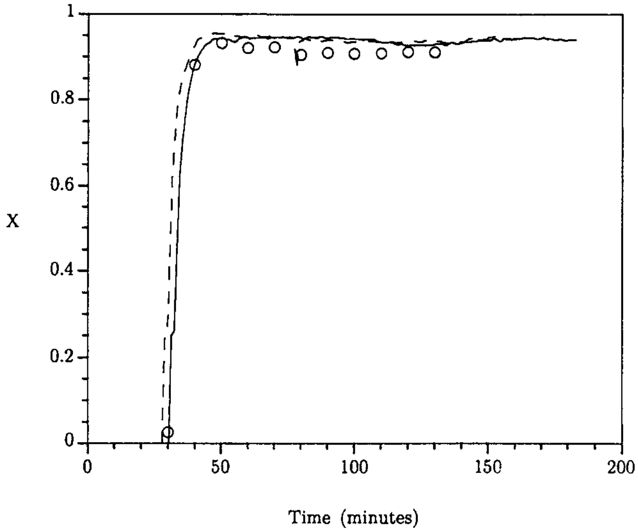

**Figure 16. Replicate runs of exit monomer conversion vs. time for a pulsed tubular reactor.**

See Table 5 for the initial and feed contains. 30-min residence time, pulse rate of 75 spm. o —dry solids; solid, dashed line—density meter.

Particle-size data by PCS are shown in Figure 19 for the batch and tube experiments. (Oscillations in the CSTR produce multimodal distribution that vary continuously, and thus no attempt was made at measuring the particle size.) The batch and tube show no significant differences.

A further comparison of the batch and tubular latexes is performed using SEM. The particle-size distributions for the batch reaction at 20 and 40 min are shown in Figure 20. The

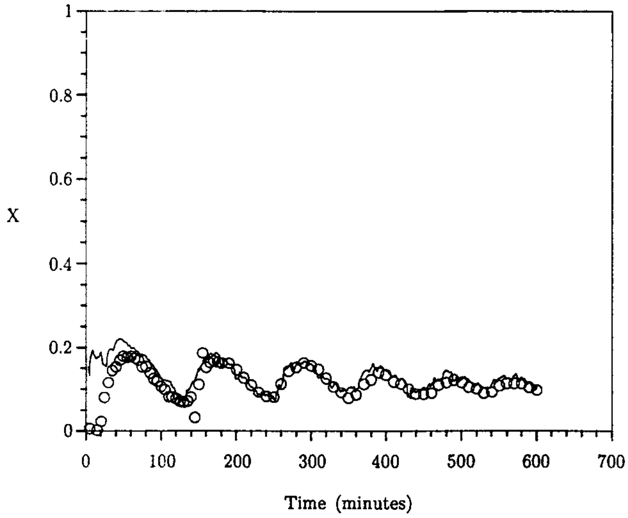

**Figure 15. Monomer conversion vs. time for a continuous stirred-tank reactor.**

See Table 5 for the initial and feed conditions. 30-min residence time. o —dry solids; solid line—density meter.

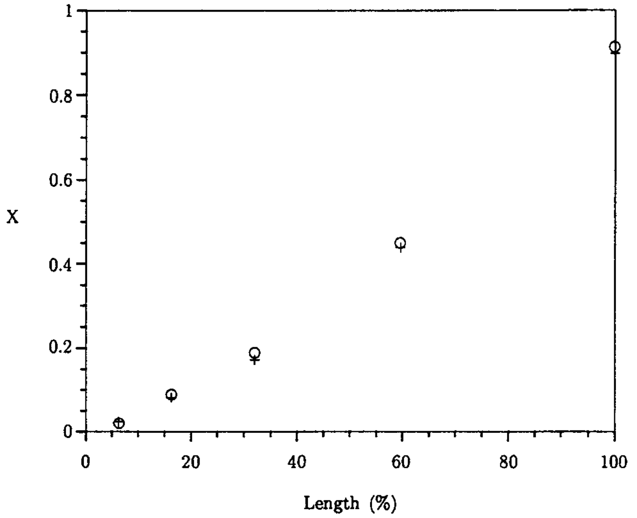

**Figure 17. Replicate runs of monomer conversion vs. length for a pulsed tubular reactor.**

See Table 5 for the initial and feed conditions. 30-min residence time, pulse rate of 75 spm.

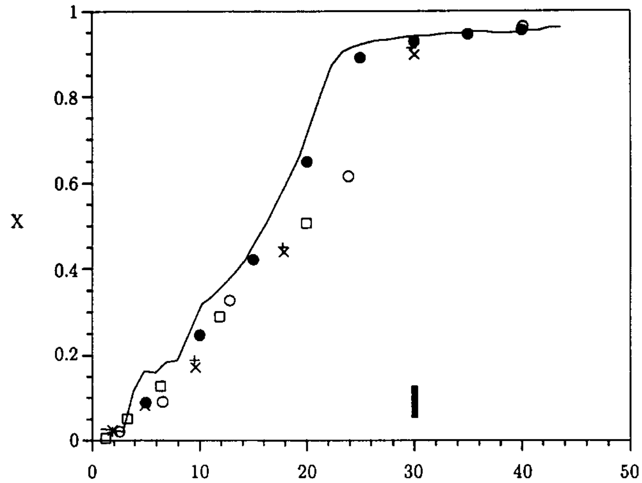

**Figure 18. Monomer conversion vs. residence time for batch, CSTR, and tubular reactors.**

Emulsion polymerization experiments of methyl methacrylate. See Tables 4-5 for the initial and feed conditions. ●, solid line—batch; □-tube (75 spm, 20-min residence time); ×, +—tube (75 spm, 30-min residence time); ○—tube (75 spm, 40-min residence time); vertical line—CSTR (height of bar represents the amplitude of oscillations).

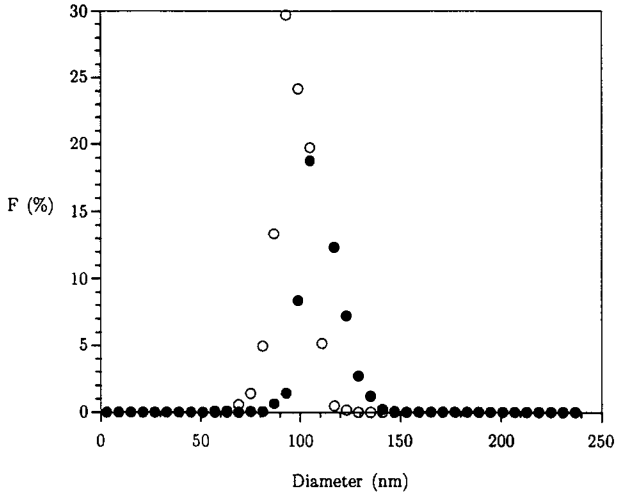

**Figure 20. Particle-size distributions by SEM for batch latex.**

○—batch sample taken at 20 min (1,063 particles counted). ●—batch sample taken at 40 min (1,257 particles counted).

shapes of the two distributions are quite similar, suggesting a translation of the PSD by growth. PSDs for the two tubular runs with a 30-min residence time are shown in Figure 21. The similarity of the PSDs are further evidence of the experimental reproducibility.

A direct comparison of the distributions obtained from batch and tubular experiments is given in Figures 22-24. (In Figure 23, the batch latex PSD at 40 min was used in the comparison with the tubular latex at 30 min.) In the comparisons, the distribution of the tubular latex is slightly broader and is shifted to higher mean size. The average diameter and standard deviation of the distributions are shown in Figure 25. It appears that the larger mean size of the tubular latex is independent of pulsation rate.

Figure 26 shows the tube latex to be somewhat broader than the corresponding batch latex. This increase in breadth, however, is small when compared with the PSD produced in a stable CSTR. DeGraff and Poehlein (1971) studied the influence of the RTD of a stable CSTR on the particle-size distribution. Assuming Smith-Ewart case II kinetics (the radical concentration in the particles is independent of particle size), they obtained an analytic solution for steady-state particle-size distribution:

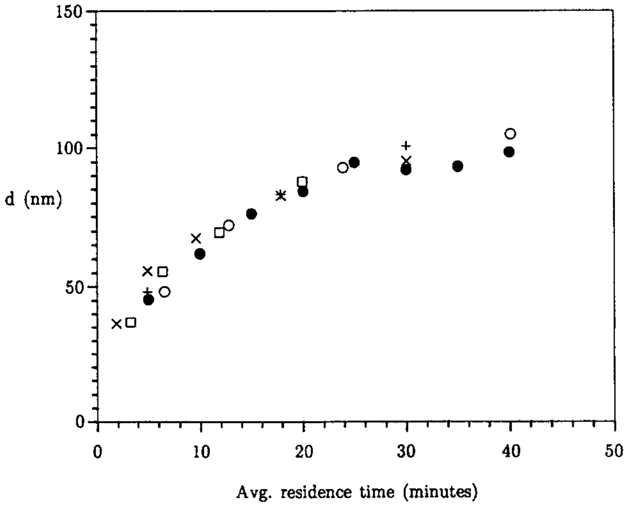

**Figure 19. Number average particle diameter of PCS vs. residence time for batch and pulsed tubular reactors.**

See Tables 4-5 for the initial and feed conditions. Data symbols: ●—batch; pulsed tubular reactor average residence time (min), □—20, ×, +—30, ○—40.

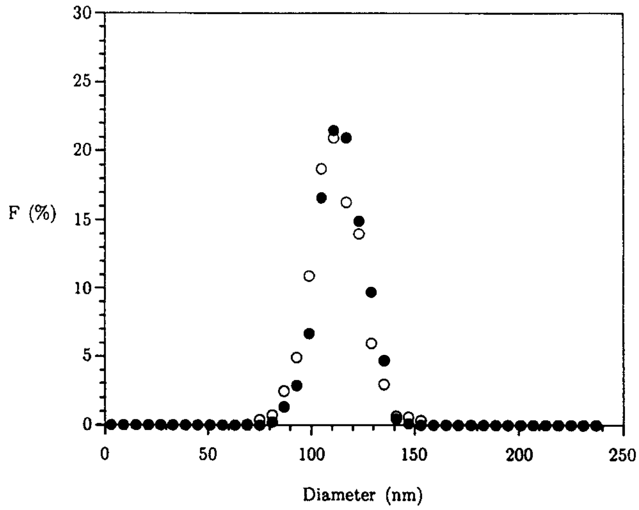

**Figure 21. Particle-size distributions by SEM for two replicate tubular reactor runs.**

Average residence time of 30 min and pulse rates of 75 spm. Samples taken at reactor exit. ○—1,209 particles counted. ●—898 particles counted.

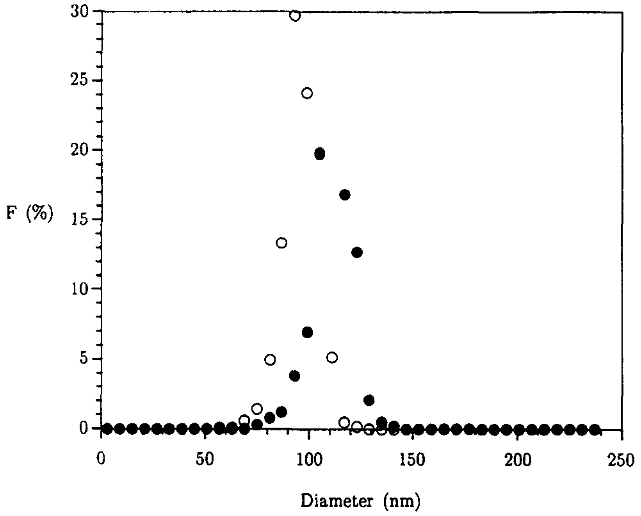

**Figure 22. Particle-size distributions by SEM for batch and tubular latex.**

● —batch sample taken at 20 min (1,063 particles counted). ○ —tubular run with average residence time of 20 min. Sample taken at reactor exit (1,027 particles counted).

$$F(r) = 3Kr^2 \exp(-Kr^3) \tag{13}$$

where $K$ is a constant accounting for the rate of polymerization and the mean residence time. $K$ can be obtained from knowledge of the mean particle size. The standard deviation can be expressed as:

$$\text{std. dev.} = \bar{d}\sqrt{\frac{\Gamma(5/3)}{\Gamma^2(4/3)} - 1} \tag{14}$$

where $\bar{d}$ is the mean diameter and $\Gamma(\cdot)$ is the Gamma function. Assuming a mean diameter of 100 nm, the standard deviation for a stable CSTR is 36.3 nm. This is much larger than the standard deviations for the batch and tubular reactors. The value of 36.3 is a lower bound on the actual value, since no particle-size dependence on the growth rate was assumed. Because the growth rate of methyl methacrylate shows a strong dependence on particle size (deviations from Smith-Ewart case II kinetics), a broader PSD would result from a stable CSTR. This result is in general agreement with experimental experience. Thus, the increased broadening of the PSD in a pulsed tube is insignificant when compared to the broad PSD of a CSTR.

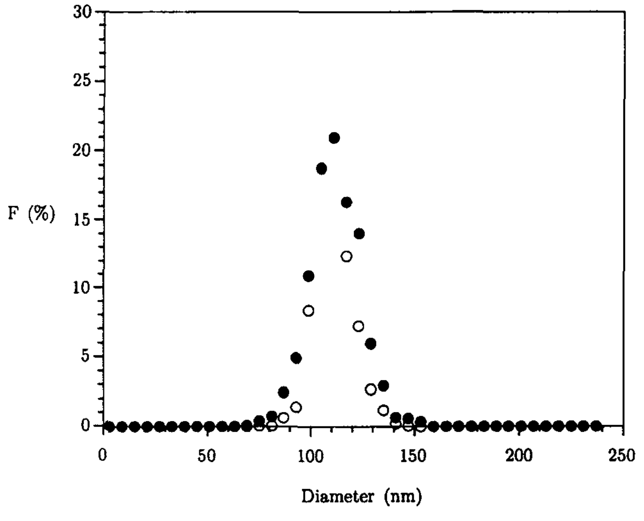

**Figure 23. Particle-size distributions by SEM for batch and tubular latex.**

● —batch sample taken at 40 min (1,257 particles counted). ○ —tubular run with average residence time of 30 min. Sample taken at reactor exit (1,209 particles counted).

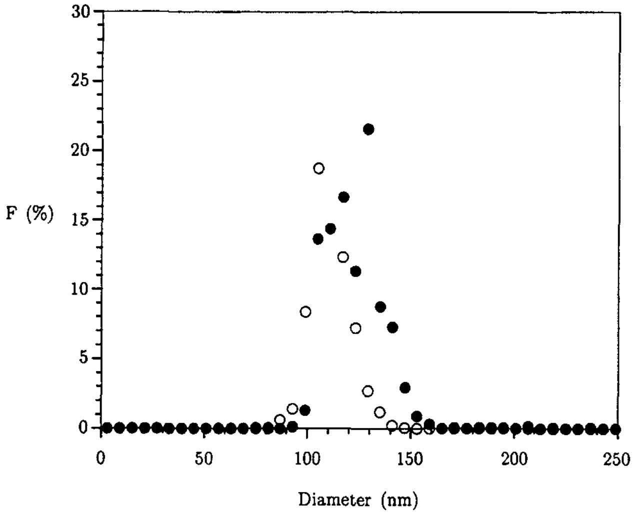

**Figure 24. Particle-size distributions by SEM for batch and tubular latex.**

● —batch sample taken at 40 min (1,257 particles counted). ○ —tubular run with average residence time of 40 min. Sample taken at reactor exit (1,223 particles counted).

## Conclusions

Homopolymerization experiments of methyl methacrylate were performed in batch, CSTR and open-loop tubular reactors. Open-loop experiments in a stainless-steel tubular reactor plugged frequently. To avoid reactor plugging, a pulsatile flow was added. Residence time distribution studies were performed in the tube at different rates of flow and pulsation. A lack of sensitivity in the RTD data permitted only a qualitative estimate of the Peclet number. The Peclet numbers obtained without pulsation were much higher than those predicted even when the helical tube geometry and sampling bends were taken into account. Pulsation did not dramatically alter the Peclet number.

Polymerization experiments with methyl methacrylate were performed in a pulsed tubular reactor. The exit conversion of the reactor showed a sudden and dramatic increase at one residence time. Steady state was achieved within two residences times. No oscillatory behavior was observed; the exit conversion remained constant for three residence times. Excellent reproducibility of the tubular experiment was demonstrated. No plugging of the reactor was observed. The steady-state conversion approached the equivalent batch conversion. No clear dependence of the pulsation rate on conversion was revealed.

The results for the tubular reactor were compared with

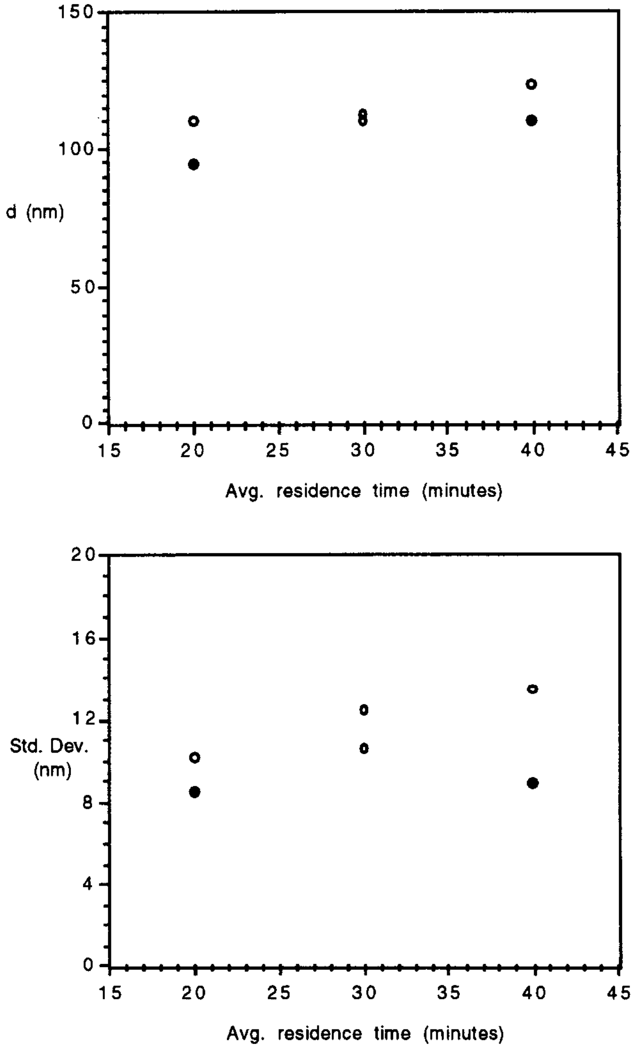

**Figure 25. Number average particle diameter and PSD standard deviation from SEM vs. residence time for batch and pulsed tubular reactors.**

● —batch; ○ —pulsed tubular.

polymerizations in batch, continuous stirred-tank reactors under similar conditions. At low residence times, monomer conversion in a CSTR was low and oscillatory. Conversions were much higher in the batch and tube. At higher residence times, the conversion was the same for all three reactors. Particle sizes, however, show that the average particle diameter obtained from the CSTR latex was twice as large as those obtained in the batch and tubular reactors.

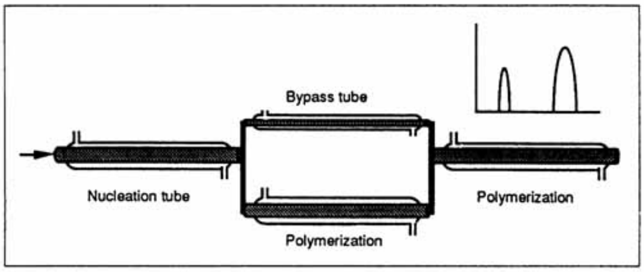

**Figure 26. Process for continuous production of a latex with a bimodal PSD.**

Conversions were somewhat higher in batch experiments than in the tubular experiments. While the average particle diameters determined by light scattering were similar for the batch and tube, distributions obtained by SEM show a slight broadening and a shift to higher mean size for the tubular latex. The increased broadening, however, is small when compared to the standard deviation expected for an equivalent stable CSTR. It is concluded that a pulsed tubular reactor offers superior performance over a CSTR and represents a continuous alternative to a batch reactor.

## Possible New Processes

One can imagine processes based on tubular reactors in series or in parallel. One exemplary use of tubes in series would be a high-temperature inhibitor removal section followed by a normal polymerization tube. Most monomers are processed with inhibitor to prevent unwanted polymerization during monomer production, shipping and storage. For some polymerizations, inhibitors are removed prior to reaction; otherwise, lengthy induction periods occur resulting in lost productivity. Monomer purification represents an additional processing step. With tubes, the purification step could be replaced by an inhibitor consumption step. By taking advantage of the high activation energies of persulfate initiators and the ability to change temperature in a tube quickly, an entrance zone at high temperature can be used to consume the inhibitor. The high temperature compresses this "induction zone" to a small length resulting in a much smaller loss in productivity. By having no uninhibited monomer outside of the reactor (as would be necessary in the purification step), process safety is improved.

A latex with a bimodal particle-size distribution could be continuously produced using tubular reactors in parallel, as shown in Figure 26. Each peak would have a narrow distribution. By varying the temperature and flow rates in the two parallel zones, the mean size and particle number of each peak could be controlled.

## Acknowledgment

The authors are indebted to the National Science Foundation and the industrial sponsors of the University of Wisconsin Polymerization Reaction Engineering Laboratory for support of this research.

## Notation

$a_{em}$ = area covered by a surfactant molecule on a micelle, cm$^2$
$a_{ep}$ = area covered by a surfactant molecule on a polymer particle, cm$^2$
$A$ = Hamaker constant
$C$ = dimensionless salt tracer concentration
$d$ = dry polymer particle diameter, nm
$\bar{d}$ = mean polymer particle diameter, nm
$d_r$ = Raschig ring diameter, cm
$F$ = particle-size distribution function
$g$ = gravitational constant
$M_{w\,sat}$ = aqueous-phase monomer concentration at saturation, mol/cm$^3$·water
$N_d$ = monomer droplet number, mol/cm$^3$·water
$N_m$ = micelle number, mol/cm$^3$·water
$N_{Pe}$ = Peclet number
$N_{Re}$ = Reynolds number
$P_{es}$ = shear Peclet number

$r$ = particle radius, cm
$r_d$ = radius of a monomer droplet, cm
$r_m$ = radius of a monomer swollen micelle, cm
$r_s$ = radius of a monomer swollen particle, cm
$S_{cmc}$ = critical micelle concentration, mol/cm$^3$·water
$S_o$ = initial surfactant concentration in the reactor, mol/cm$^3$·water
$t$ = time, s
$v_s$ = Stoke's terminal velocity, cm/s
$V_w$ = water volume fraction, cm$^3$·water/cm$^3$
$V_{wo}$ = initial water volume fraction, cm$^3$·water/cm$^3$
$w_m$ = weight fraction of monomer
$x$ = monomer conversion
$z$ = axial coordinate

### *Greek letters*

$\eta_f$ = fluid viscosity, poise
$\gamma_s$ = shear rate, s$^{-1}$
$\rho_{ps}$ = density of a monomer swollen particle, g/cm$^3$
$\rho_f$ = fluid density, g/cm$^3$
$\rho_m$ = monomer density, g/cm$^3$
$\rho_p$ = polymer density, g/cm$^3$
$\theta$ = mean residence time, s
$\tau$ = dimensionless time

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*Manuscript received Apr. 5, 1993, and revision received Oct. 6, 1993.*