

# The Dynamics of the Continuous Emulsion Polymerization of Methylmethacrylate

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## Synopsis

Experimental data on the dynamics of the continuous emulsion polymerization of methylmethacrylate are presented. Techniques for on-line reaction monitoring and digital data acquisition as reported previously are used to generate dynamic data on the monomer conversion and free emulsifier concentration. Data are reported confirming the existence of multiple steady states and limit cycles in the CSTR (continuous stirred tank reactor) emulsion polymerization of methylmethacrylate. Data are also reported suggesting the presence of steady states in the absence of micelles in the reactor. The possible causes of these phenomena, and the conditions under which they occur are discussed.

## INTRODUCTION

Since its first commercialization in the early 1930s, emulsion polymerization has grown to become one of the major processes for the production of synthetic polymeric materials. The loss of supply of natural rubber latex during World War II triggered a large research program by the Rubber Reserve Company, an agency of the U.S. government, aimed at producing styrene-butadiene rubber (SBR) by emulsion polymerization. Both batch and continuous reactors were studied and a rudimentary mechanism was formulated.<sup>1</sup> Following the war, the development of water-based paint widened the use of emulsion polymerization into acrylic resins as well as synthetic elastomers. Today a large variety of polymers are produced by emulsion polymerization including synthetic elastomers, bulk plastics, and plastic and elastomeric latices for coatings. While the industry is still dominated by batch reactors, continuous processes are becoming more widespread due to their economic and processing advantages.

In spite of the long history and widespread use of emulsion polymerization, the reaction mechanism and its relation to the dynamics of typical reactor configurations is not well understood. Emulsion polymerization has some unique features which make understanding and optimizing the process particularly worthwhile. The reaction history of a polymer is written into its molecular weight distribution. Sustained oscillations (limit cycles) in conversion, particle number, and free emulsifier concentration have been reported (e.g., Refs. 2-4) under isothermal conditions in continuous emulsion polymerization systems. This limit cycle behavior leaves its mark on the product in

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the form of disturbances in the particle size and molecular weight distributions which cannot be blended away. In addition, multiple steady states have been observed<sup>5</sup> compounding the problems of reactor control and product quality. The purposes of the present paper are to review the existing data, and to introduce some new dynamic data showing the unusual dynamics of the continuous stirred tank (CSTR) emulsion polymerization of methylmethacrylate (MMA).

## PROCESS

The process of emulsion polymerization is, in essence, an attempt by man to imitate the production of natural rubber (polyisoprene) latex by the rubber tree (*Hevea brasiliensis*). Natural rubber latex is an aqueous dispersion of polyisoprene particles stabilized by proteinaceous surfactants. By analogy, an emulsion-polymerized polymer latex is an aqueous dispersion of polymer particles (SBR, etc.) stabilized by a fatty acid soap or synthetic surfactant.

The polymer latex is formed by emulsifying monomer (usually relatively insoluble in water) into an aqueous surfactant solution. By applying shear to the mixture, an emulsion is formed in which the monomer is dispersed into droplets of typically 10  $\mu\text{m}$  diameter. The droplets are stabilized by a monolayer of surfactant at the monomer-water interface. Additional surfactant above the critical micelle concentration (CMC) is contained in micelles, or aggregates of typically 50–100 Å diameter surfactant molecules oriented so that their hydrophobic ends are toward the center of the micelle while the hydrophilic ends extend out into the aqueous phase. Polymerization is initiated by adding a free radical initiator (usually water-soluble) and, as the polymerization proceeds, polymer particles stabilized by a surfactant layer are formed. Figure 1 shows the main elements of emulsion polymerization: the continuous aqueous phase, monomer droplets, micelles, and polymer particles.

The emulsion polymerization process has significant advantages over other polymerization processes. The viscosity of the emulsion remains low even at high monomer conversion. Heat removal, a major consideration since most polymerizations are highly exothermic, is facilitated by the low viscosity and high heat capacity of the aqueous phase. For applications requiring a finished product in the form of a latex (i.e., latex paint), the polymerized emulsion may be used directly. Due to the nature of free radical polymerization kinetics, it is actually possible to attain a higher rate of polymerization in an emulsion system than in bulk polymerization.

## REVIEW OF PUBLISHED DATA

The amount of data from continuous emulsion polymerization reactors which is available in the open literature is surprisingly small. The type and origins of the various data are summarized in Table I. These data will be discussed by specific monomer.

### Styrene

The earliest published dynamic data on the continuous emulsion polymerization of styrene are those of Gershberg and Longfield.<sup>2</sup> They followed

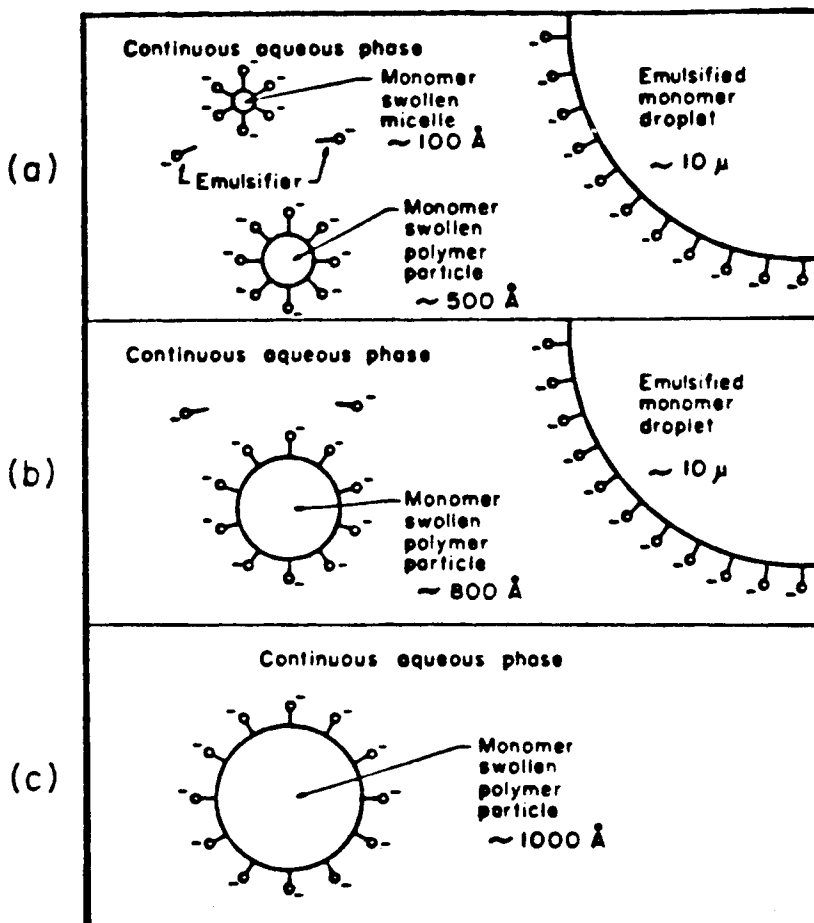


Fig. 1. The physical picture of emulsion polymerization showing Intervals I (a), II (b), and III (c). (Reprinted from Ref. 29.)

monomer conversion gravitometrically, and particle number by electron microscopy in a system of three CSTRs using a mixed emulsifier and potassium persulfate as the initiator. Dynamic data from at least one run indicate the presence of conversion oscillations on a start-up. In other runs the conversion settled to a steady state after an initial overshoot.

Gerrens and Kuchner<sup>7</sup> also employed a series of three CSTRs with potassium persulfate as the initiator. Their data show no abnormal behavior (multiple steady states or limit cycles). However, Gerrens, Kuchner, and Ley<sup>8</sup> present conclusive evidence of multiple steady states in the styrene system. For a series of three CSTRs operated at the same conditions, they report variations in steady-state conversion attributable to variations in start-up conditions. In a subsequent paper, Ley and Gerrens<sup>5</sup> show convincing evidence of limit cycles in both conversion (measured gravitometrically) and surface tension (measured with a stalagmometer).

DeGraff<sup>9-11</sup> used a single CSTR to study the effect of operating conditions on the steady-state conversion, particle size distribution, and molecular weight.

TABLE I  
 Continuous Emulsion Polymerization Data

Systems	Reference	Steady-state data	Dynamic data	Multiple steady states	Oscillations
Styrene	(10) DeGraff & Poehlein (1971)	✓			
	(27) Ueda et al. (1971)	✓			
	(23) Nomura et al. (1971)		✓		✓
	(8) Gerrens et al. (1971)			✓	✓
	(5) Ley & Gerrens (1974)			✓	
	(2) Gershberg & Longfield (1961)				✓
	(12) Brooks et al. (1978)				✓
Vinyl acetate	(6) Greene et al. (1976)				✓
	(14) Kiparissides et al. (1980)				✓
	(17) Nomura et al. (1980)				✓
Methylmethacrylate	(6) Greene et al. (1976)				✓
Vinyl chloride	(28) Berrens (1974)		✓		
	(19) Jacobi (1952)				✓
SBR	(18) Owen et al. (1947)				✓
Ethylene	(20) Senrui et al. (1974)		✓		
Methylacrylate	(7) Gerrens & Kuchner (1970)	✓			

Source: Ref. 30.

No dynamic data are given. Nomura et al.<sup>3</sup> used a series of two CSTRs to study the transient and steady-state behavior of a styrene system emulsified with sodium lauryl sulfate (SLS) and initiated with potassium persulfate. The dynamic data indicate transient overshoot of conversion, but no multiplicity or oscillatory behavior.

Brooks et al.<sup>12</sup> observed conversion oscillations using SLS as the emulsifier and ammonium persulfate as the initiator.

### Vinyl Acetate

As a component of latex coatings, vinyl acetate (VA) is widely polymerized in an emulsion; little data, however, is available in the open literature on its continuous polymerization. Poehlein and co-workers<sup>6</sup> studied the dynamics of the emulsion polymerization of vinyl acetate in a single CSTR using ammonium persulfate as the initiator and SLS as the emulsifier. They report dynamic data on monomer conversion showing overshoot and oscillations. From the data it is not possible to determine if the oscillations are damped or true limit cycles.

Kiparissides and co-workers<sup>13-16</sup> also studied the dynamics of continuous emulsion polymerization of vinyl acetate in a single CSTR, using potassium persulfate as the initiator and SLS as the emulsifier. Their steady-state data agree qualitatively with that of Greene. Their dynamic data show conversion cycling under some operating conditions. Normal reactor start-up consisted of filling the reactor with distilled water prior to introducing any feed streams.

Operation of the reactor in the batch mode for one residence time prior to beginning feed flow resulted in increased conversion overshoot. Start-up from an emulsion-filled reactor also resulted in aggravated overshoot.

Nomura and co-workers<sup>17</sup> using a similar recipe and reactor system, found clear evidence of stable limit cycles in monomer conversion. Their data show corresponding oscillations in the number of polymer particles as measured by electron microscopy.

### Methylmethacrylate

The only available dynamic data on methylmethacrylate (MMA) emulsion polymerization in a CSTR is that of Poehlein and co-workers.<sup>6</sup> Transient data are reported for two start-up procedures. Start-up from an empty reactor resulted in oscillation; start-up from a water-filled reactor resulted in smooth approach to a steady state. One set of data is reported showing conversion oscillations. The oscillations appear to be stable, although, since only two periods were observed, it is not possible to rule out a damped oscillation resulting in eventual approach to steady state. Particle size analysis of latex from this run shows the bimodal distribution characteristic of oscillatory behavior. One set of data is reported in which the conversion comes to steady state, then, due presumably to some disturbance, jumps to what appears to be a second steady state. The data are insufficient to say conclusively that this is the result of multiple steady-state phenomena.

### Other Monomers

Some data are available on other monomer systems. Although it was not recognized at the time, fluctuations in end-use properties of styrene-butadiene rubber (SBR) reported by Owen, Steele, and Parker<sup>18</sup> can be attributed to conversion oscillations in a CSTR train. Jacobi<sup>19</sup> noted oscillations in latex surface tension during the continuous emulsion polymerization of vinyl chloride (VC). Senrui, Kodama, and Takehisa<sup>20</sup> report damped oscillations in conversion for radiation-induced emulsion polymerization of ethylene in a CSTR.

## EXPERIMENTAL APPROACH

Data will be presented showing the types of dynamics observable in the CSTR emulsion polymerization of MMA. The data were taken with a bench-scale polymerization system and on-line sensors as described below.

### Reactor

A flow sheet for the reactor, sensors, and supporting equipment used for the continuous emulsion polymerization of methylmethacrylate are shown in Figure 2. The reactor consists of a 0.5 L glass resin kettle operated as a CSTR. Reactor temperature is maintained at setpoint by flowing cold water a stainless steel cooling coil located inside the reactor. The temperature of the coolant is adjusted by a time-proportioning controller in response to changes in reactor temperature. Agitation is provided by a two-bladed Teflon agitator driven by a variable speed motor. Some baffling is provided by the cooling

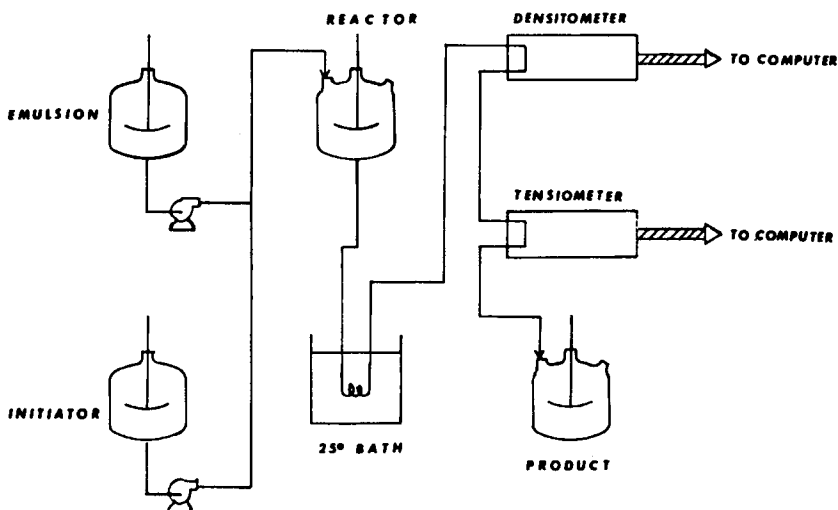


Fig. 2. Flowsheet for bench scale emulsion polymerization system.

coil. The vapor space above the emulsion is constantly purged by a slow flow of prepurified nitrogen. Reproducible kinetics are observed only when care is taken to exclude air from the reaction mixture to avoid destruction of initiator free radicals by oxygen. The nitrogen purge serves to exclude atmospheric oxygen. Emulsion is introduced into the reactor by a Milton Roy Duplex Minipump. Initiator is metered by an internally speed-controlled Masterflex tubing pump. Care must be taken to introduce the initiator directly into the vortex of the reactor to ensure immediate mixing and prevent emulsion instability (phasing) caused by locally high ionic strength.

Emulsion outflow from the reactor is via an overflow which maintains the liquid level in the reactor. Upon removal from the reactor the emulsion is pumped through a heat exchanger to reduce the temperature from the reaction temperature (40°C) to the analysis temperature (25°C). The emulsion then flows through a digital densitometer for determination of the density and monomer conversion, through a surface tensiometer for the determination of surface tension and free emulsifier concentration, and finally, into a product hold tank. A stopcock for collecting samples of the product is mounted just downstream of the surface tensiometer.

The methylmethacrylate (MMA) was supplied by Rohm and Haas containing 10 ppm hydroquinone (HDQ) as an inhibitor. The HDQ was removed just prior to polymerization by passing the MMA through a bed of Rohm and Haas Amberlyst A-27 ion exchange resin as detailed in the Amberlyst A-27 Technical Bulletin.<sup>21</sup> The surfactant used was BDH Chemicals Specially Pure Sodium Lauryl Sulfate, available in the United States from Gallard-Schlesinger Chemical Manufacturing Corporation, Carle Place, New York. The sodium bicarbonate used as a buffer and sodium chloride used to adjust the ionic strength of the aqueous phase were Fisher A.C.S. Certified. The ammonium persulfate used as the initiator was Fisher A.C.S. Certified. Baker purified hydroquinone was used to stop the polymerization. Unless otherwise noted, all reagents were used as received, with no further purification.

The emulsion was prepared in advance by agitation, under nitrogen, with two three-blade, propeller-type agitators, and stored, under nitrogen, in a 20 L agitated glass carboy. The initiator solution was prepared in advance and stored, under nitrogen, in a 5 L flask. A cold finger was used to reduce the temperature of the initiator solution about 20°C to prevent premature initiator decomposition. Emulsion and initiator were transferred to the reactor via polypropylene and silicone rubber tubing, using the pumps previously described. Provisions were made for purging all lines and vessels with nitrogen prior to start-up to prevent free radical destruction by atmospheric oxygen. Startup was from an empty reactor. This has been shown by Greene<sup>2</sup> to result in the most pronounced instabilities.

### Sensors

The data reported herein were collected on-line using instrumentation described previously.<sup>22,23</sup> Emulsion density (and hence, monomer conversion), was monitored via the Mettler/Par DMA 40 digital densitometer.<sup>22</sup> This produced a precision of better than one percent in monomer conversion and good agreement with independent dried solids measurement of conversion.<sup>24</sup> Emulsion surface tension (and hence, free surfactant concentration), was monitored by making use of the bubble surface tensiometer developed in this laboratory.<sup>23</sup> The precision of the surface tension measurement has been determined to be approximately  $\pm$  one dyne/cm. Transient data were recorded at one minute intervals via minicomputer. It was observed that baseline surface tension at the critical micelle concentration (CMC) as indicated by the constant surface tension from the tensiometer, varied slightly from run to run. This could be due to small variations in the concentrations of recipe components affecting surface activity, such as dissolved monomer or initiator.

## RESULTS

A number of interesting phenomena were found in the CSTR emulsion polymerization of methylmethacrylate. Each phenomenon will be discussed individually and possible explanations proposed based on the data.

In order to explore the unusual dynamics of emulsion polymerization, a factorial design of experiments was performed in the general area of parameter space shown by Greene<sup>6</sup> to exhibit conversion oscillations. Three parameters were varied over two levels each:

1. Surfactant concentration, [S]
2. Initiator concentration, [I]
3. Reactor residence time,  $\theta$

Polymerizations were run at each of the resulting sets of conditions and at the center point of the design. Parameter values for each experiment are shown in Table II.

Figure 3 is a plot of the design in three-parameter space indicating the type of transient conversion behavior observed at each point. It will be noticed that all instances of stable or damped oscillation occur in the left half of the cube.

TABLE II  
 Factorial Design Summary

Experiment number	Run	$\theta$	[S]	[I]
1	23	0	0	0
2	31	+	+	+
3	30	-	+	+
4	29	+	-	+
5	26	-	-	+
6	27	+	+	-
7	25	-	+	-
8	28	+	-	-
9	24	-	-	-

Residence time: + 50 min; 0 40 min; - 30 min. Surfactant concentration: + 0.03 mol/L water; 0 0.02 mol/L water; - 0.01 mol/L water. Initiator concentration: + 0.03 mol/L water; 0 0.02 mol/L water; - 0.01 mol/L water.

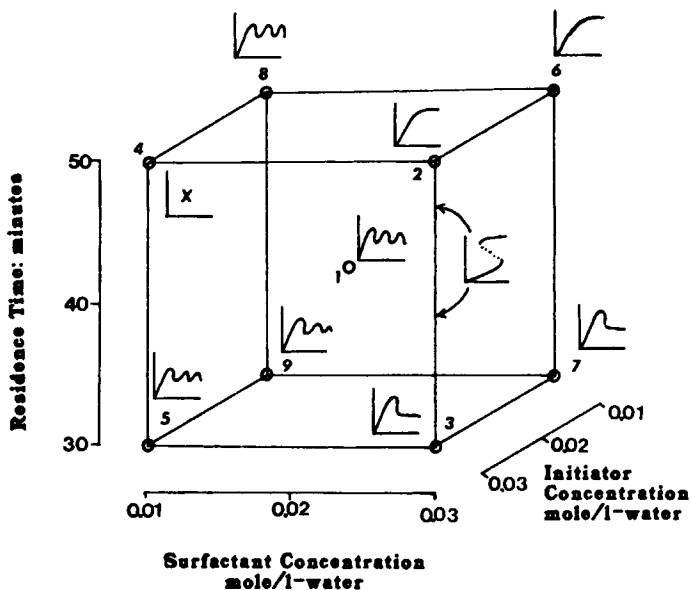


Fig. 3. Factorial design of polymerization experiments.

This is the region of low surfactant concentration, which is consistent with current understanding since oscillations can be induced by fluctuations in the free surfactant concentration, a condition that would be aggravated by low total surfactant concentration in the reactor.

The other half of the cube (high surfactant concentration) shows either smooth approach to steady state, or a single overshoot followed by smooth approach to steady state. Runs at low (30 minutes) residence time exhibit overshoot, while those at high residence time (50 minutes) do not. It may well be that the initial burst of particles which might cause overshoot occurs more slowly at 50 minutes residence time due to the slower rate of reactor filling.



(The reactor is operated semibatch for the first residence time.) Thus the total number of particles generated during the first residence time is lower at  $\theta = 50$  since subsequent particle formation is inhibited by the fact that the first particles have already begun to grow and adsorb surfactant, thus reducing the number of micelles available to form new particles. This view is supported by the fact that the surface tension rises above its baseline CMC value during initial overshoot.

Steady-state multiplicity is indicated in Figure 3 along the line joining Experiments 2 and 3. Multiplicity was discovered along this line by holding surfactant and initiator concentrations constant and varying the residence time.

Selected data, both on and off the cube will be presented. Complete data are available.<sup>24</sup>

### STEADY-STATE MULTIPLICITY

This study has resulted in strong evidence of steady-state multiplicity in the CSTR polymerization of MMA. Figure 4 is a plot of steady-state monomer conversion as a function of reactor residence time for  $[S] = [I] = 0.03$  mole/L water. A region of multiplicity is indicated by the fact that the upper and lower branches of the curve overlap between residence times of 30 and 50 minutes. Experimentally observed steady states are indicated by o's and x's. Multiple points at a given residence time indicate repeated experiments. Confirmed residence times (o's) maintained a constant conversion for at least three residence times. Apparent steady states (x's) remained constant for at least one residence time before being intentionally or unintentionally perturbed by some input to the system. The dotted line is an estimate of the shape of the unstable middle branch which is, of course, experimentally unobservable. The dashed lines indicate experimental instances of ignition and

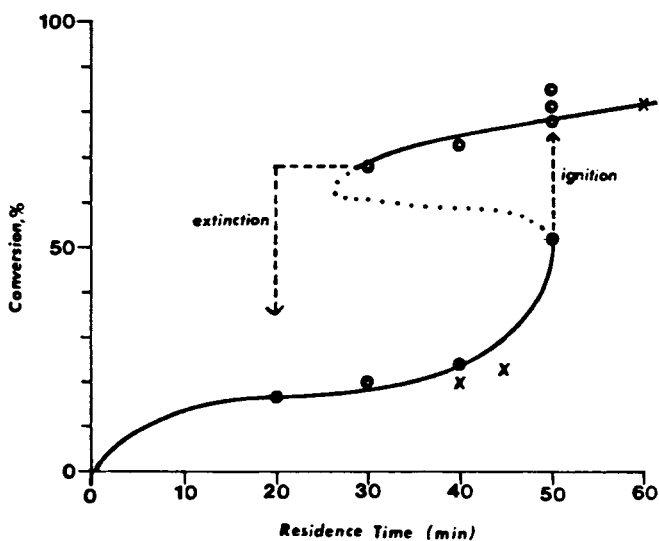


Fig. 4. Conversion multiplicity in a CSTR.  $[S] = 0.03$  mol/L water;  $[I] = 0.03$  mol/L water. (o) Confirmed steady state; (x) Apparent steady state.

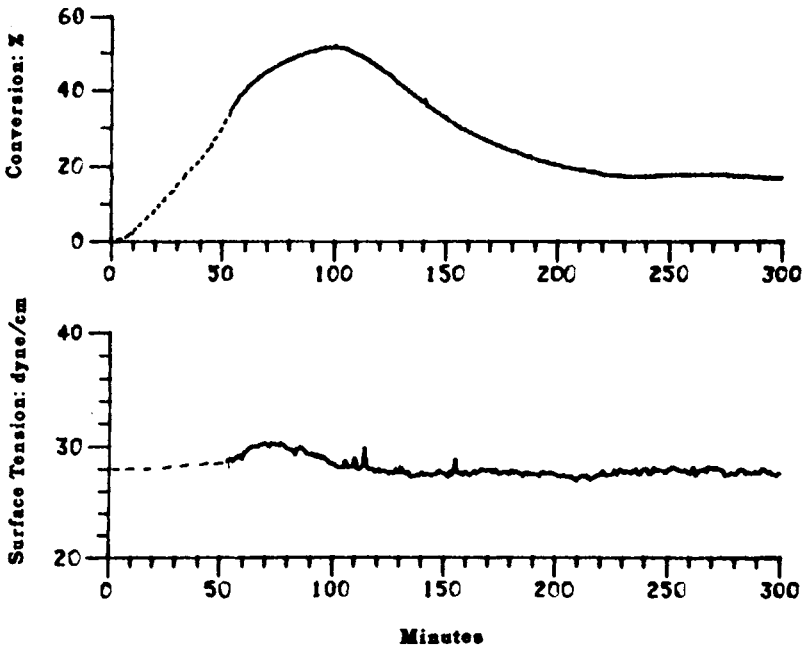


Fig. 5. Continuous polymerization. Residence time = 20 min;  $[S] = 0.03$  mol/L water;  $[I] = 0.03$  mol/L water.

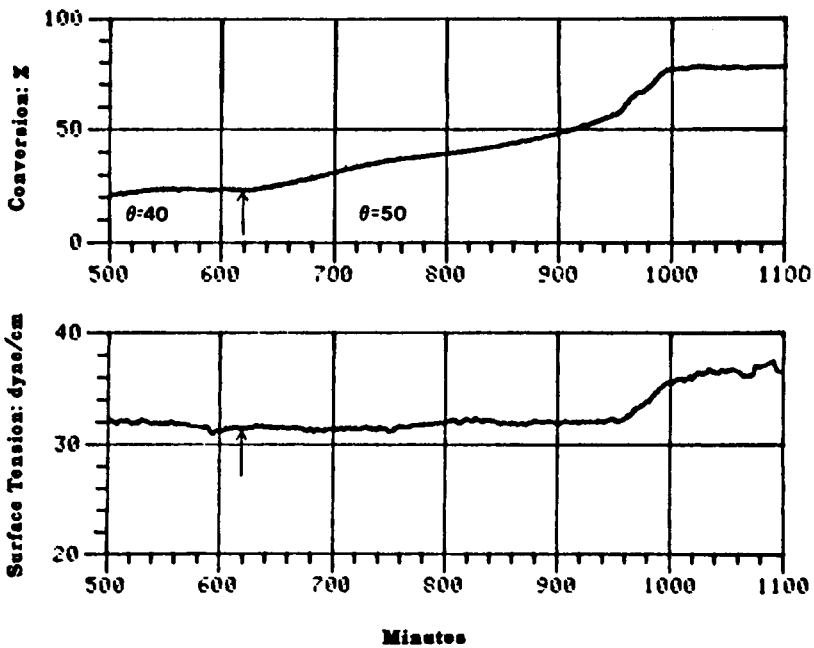


Fig. 6. Continuous polymerization showing ignition. Residence time = 40, 50 min.  $[S] = 0.03$  mol/L water;  $[I] = 0.03$  mol/L water.

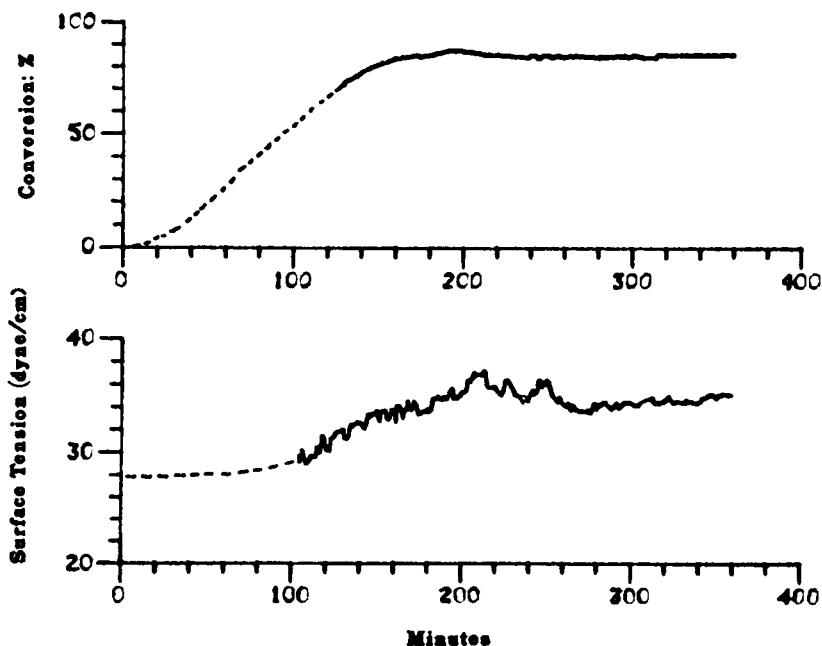


Fig. 7. Continuous polymerization. Residence time = 50 min.  $[S] = 0.03$  mol/L water;  $[I] = 0.03$  mol/L water.

extinction. At 50 minutes residence time the system has been observed to move from the lower steady state of 54% conversion to the upper steady state at approximately 80% with no discernible change in operating conditions (ignition). Extinction has been observed when the residence time is changed from 30 minutes to 20 minutes on the upper branch resulting in a drop in conversion from the upper to the lower steady-state values.

Figures 5, 6, and 7 show the transient data associated with Figure 4. Figure 5 shows the start-up and approach to steady state at a residence time of 20 min. After an initial overshoot, the conversion settles to a steady-state value of approximately 18%. The surface tension trace indicates a slight rise from the CMC value during the conversion overshoot, followed by a return to what appears to be the CMC value of 28 dyne/cm for this run. In this and all of the following transient data, dotted lines indicate the absence of data in this region, either because no emulsion is available on start-up prior to overflow, or due to plugging of the sensors. Transient data for a residence time of 30 min exhibit similar behavior.<sup>24</sup>

Figure 6 shows ignition caused by increasing the residence time from 40 to 50 min. From steady-state conversion of approximately 22% at a residence time of 40 min, the system climbs to a conversion of 78% when the residence time is increased to 50 minutes. Note the high rate of polymerization between 900 and 1000 min as the gel effect becomes pronounced. A corresponding rise in surface tension is also noted which can be due to the disappearance of micelles or the loss of monomer droplets which reduces the MMA concentration in the aqueous phase. Both phenomena affect the measured surface tension.<sup>23</sup> The surfactant effect arises because as the particles rapidly increase

in volume due to polymerization, more surfactant is required to stabilize the increased surface area. The adsorption of additional surfactant on the particle surface results in dissolution of micelles in order to keep the aqueous phase saturated with surfactant. The point at which the micelles disappear (CMC) may be detected by an increase in surface tension as the aqueous phase becomes unsaturated due to surfactant adsorption on the particles. Whichever cause dominates, the surface tension reaches a new steady state as particle growth and hence monomer conversion stabilize at the upper steady state. Both the surfactant and the monomer are then partitioned between the polymer particles and the aqueous phase, neither of which is saturated.

Figure 7 shows the start-up and rise to steady state at a residence time of 50 min. Note that, unlike at 20 and 30 min residence time, there is no overshoot at 50 min. The steady-state conversion of 84% agrees well with the values shown in Figure 6 for the same residence time. The surface tension rises with the conversion and settles to a steady-state value of 36 dyne/cm.

### OTHER TRANSIENTS APPROACHING STEADY STATE

Figure 8 shows the results of high surfactant and low initiator concentrations at a residence time of 50 min. It may be seen that steady state is rapidly achieved at approximately 76% conversion. A change in residence time to 30 min at 440 min into the reaction results in rapid reduction in conversion and surface tension. The surface tension trace indicates an increase in surface tension throughout the region of 50 min residence time.

Inspection of the surface tension traces in Figures 6, 7, and 8 indicates that at some point during the start-up transients, the reactor passes from a

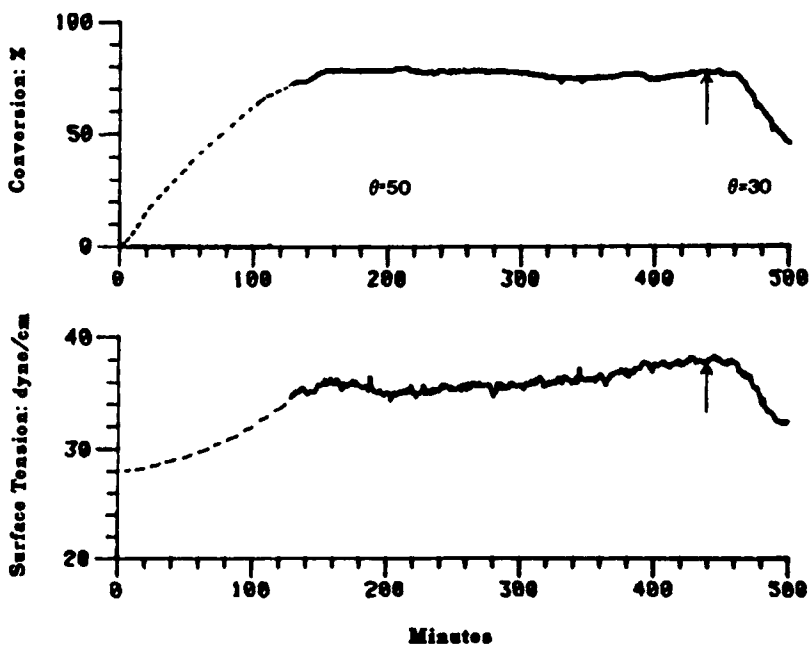


Fig. 8. Continuous polymerization. Residence time = 50 min.  $[S] = 0.03$  mol/L water;  $[I] = 0.01$  mol/L water.

condition of almost constant low value of surface tension into a condition in which there is a rise in the surface tension from its baseline value. The surface tension then comes to steady state at about the same time as the conversion. Note that monomer concentration in the aqueous phase decreases with increasing conversion so that the observed increase surface tension may not be due to changes in surfactant concentration. Unfortunately, we do not have significant data to determine whether or not the reactor is indeed operating below the CMC at these high conversion steady states. However, if this indeed were the case, there seems to be two possible explanations for a steady state in the absence of micelles. The first is homogeneous nucleation or precipitation of short-chain polymer molecules from the aqueous phase following polymerization of the monomer saturating the aqueous phase (1.4% at saturation). This mechanism has been studied by Fitch and Tsai<sup>25</sup> and others. A second explanation could be that radical entry into the micelles *in the feed* is to be significantly faster than micellar dissociation into the aqueous phase level so that polymer particles can be formed from micelles while the reactor surfactant concentration is below saturation (CMC). Further detailed experimentation would be required to clarify these mechanisms.

### OSCILLATORY BEHAVIOR

In this section, data will be presented for five polymerizations in which either stable or damped oscillations were observed. Four of these polymerizations constitute the low surfactant half (including the center point) of the factorial design in Figure 3. As noted previously, the reduced level of surfactant causes the system to oscillate. The fifth example of oscillatory behavior is not part of the factorial design, but occurs in the same region in parameter space. This experiment will be discussed first since it provides the best example for discussing the mechanism of oscillation.

Figure 9 shows evidence of a sustained oscillation (limit cycle). Surfactant and initiator concentrations were 0.02 and 0.01 mol/L water, respectively. Residence time was 47 min. Due to the long period of oscillation and feed supply constraints, it was only possible to observe two complete cycles. Judging from the heights of the conversion peaks however, this appears to be either a stable limit cycle or a very slowly decaying oscillation. Comparison of the monomer conversion and surface tension data graphically illustrates the mechanism of oscillation. It will be noted that the surface tension oscillates with the same period as the conversion (6–7 residence times). This is in agreement with the classical micellar initiation mechanism. Beginning at a time of about 300 min, the conversion rises rapidly as new particles form and old particles grow. As the particle surface area increases, additional surfactant is adsorbed on the particles. Meanwhile micelles dissociate to keep the aqueous phase saturated. Once all of the micelles have dissociated, it is no longer possible to maintain the aqueous phase at saturation and the surface tension begins to rise. This is observed at about 320 min. At the point at which micelles are no longer present, micellar initiation stops and the rate of polymerization slows. Eventually, since particles are washing out while no new particles are being formed, the conversion begins to fall. Since the total particle surface area is decreasing at this point, and since surfactant is

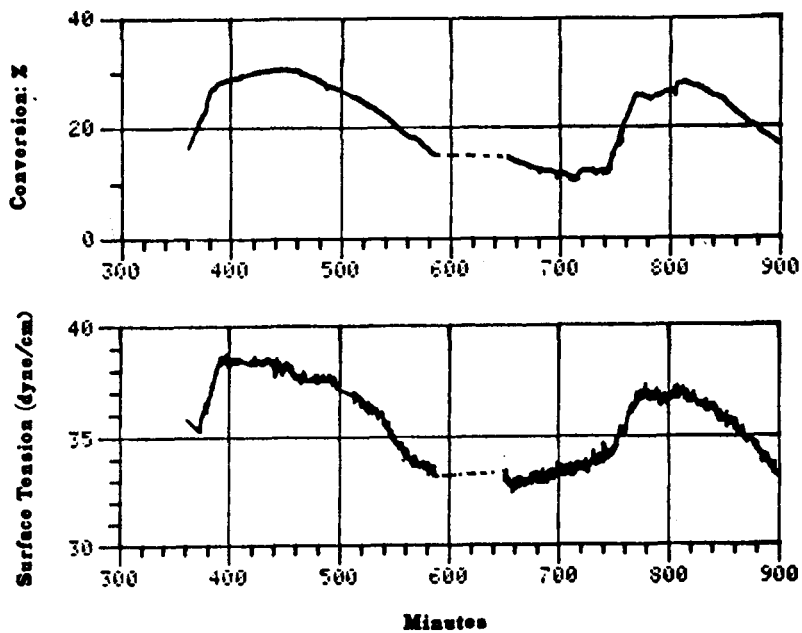


Fig. 9. Continuous polymerization showing limit cycle. Residence time = 47 min.  $[S] = 0.02$  mol/L water;  $[I] = 0.01$  mol/L water.

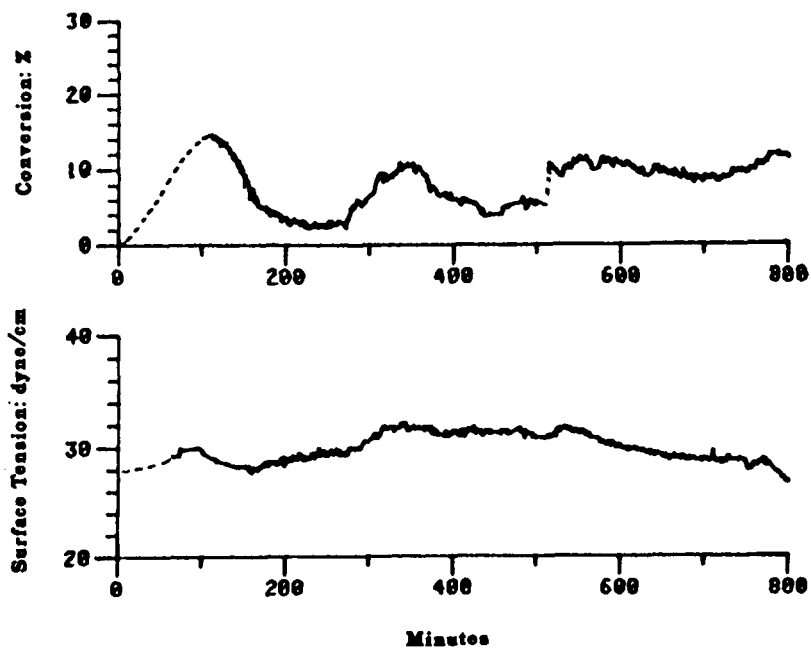


Fig. 10. Continuous polymerization. Residence time = 30 min.  $[S] = 0.01$  mol/L water;  $[I] = 0.01$  mol/L water.

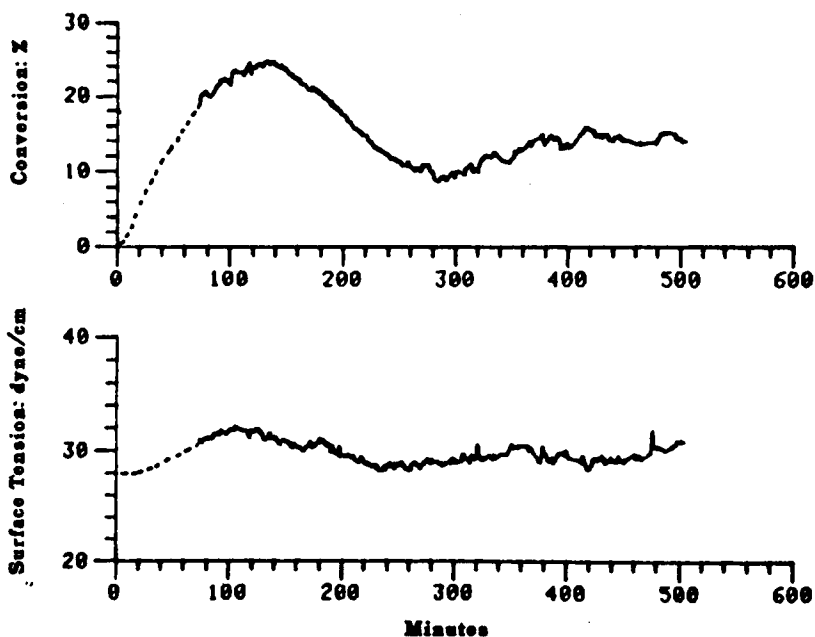


Fig. 11. Continuous polymerization. Residence time = 40 min.  $[S] = 0.02$  mol/L water;  $[I] = 0.02$  mol/L water.

continually being introduced with the feed, the surface tension falls as the aqueous phase reapproaches saturation. As the aqueous phase becomes saturated, micellar initiation begins again. Saturation of the aqueous phase may be observed by noting the point at which the surface tension reaches its CMC value. As new micelles are formed they adsorb free radicals, become polymer particles, and begin to grow and adsorb surfactant. The cycle then repeats. Recent results<sup>26</sup> show that while the instability arises above the CMC (and is promoted by large values of initiator concentration and residence time, and low surfactant concentration), it is the on/off nature of the micellar nucleation mechanism which governs the nature of oscillations in monomer conversion.

The surface tension oscillation leads the conversion oscillation by approximately one residence time. This is consistent with the above explanation since changes in surfactant concentration are quite rapid while changes in the number of particles and rate of reaction require a finite growth time to appear as changes in the monomer conversion.

Figures 10 through 13 show damped oscillations on start-up for various levels of surfactant and initiator concentration. Figure 10 shows the rather large oscillations in conversion resulting from low surfactant and initiator concentrations at a residence time of 30 min. Some slight fluctuations in surface tension are also observed, but due to the low overall conversion, the changes in surface tension are slight since it is not necessary to deplete the aqueous phase to any great extent in order to stabilize the particle surface area at peak conversion. The period of oscillation is about seven residence times which is approximately the same as in Figure 9.

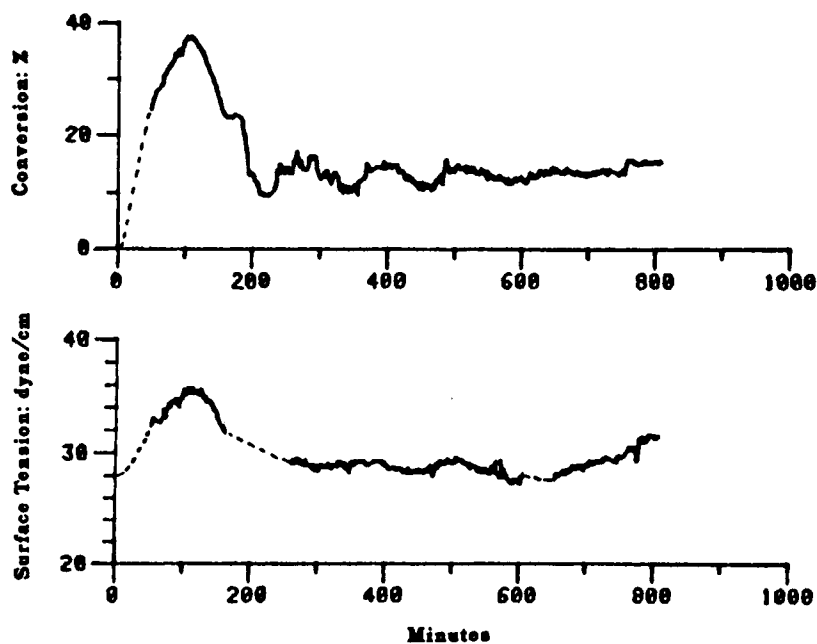


Fig. 12. Continuous polymerization. Residence time = 30 min.  $[S] = 0.01$  mol/L water;  $[I] = 0.03$  mol/L water.

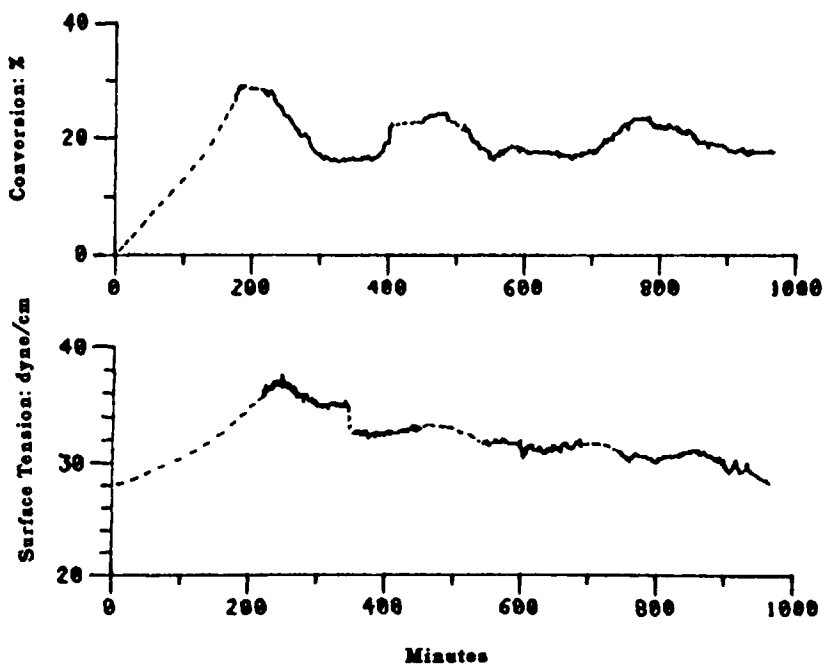


Fig. 13. Continuous polymerization. Residence time = 50 min.  $[S] = 0.01$  mol/L water;  $[I] = 0.01$  mol/L water.



Figure 11 shows the stabilizing effect of additional surfactant. Although both the initiator and surfactant concentrations were doubled over those of Figure 10, the stabilizing effect of the additional surfactant seems to have a greater influence than the destabilizing effect of the increased initiator concentration. (Increased initiator concentration will result in rapid particle generation and depletion of the micelles during the transient period.) In this case the overshoot is greater due to the increased initiator concentration, but the transients die out more rapidly. The steady-state conversion appears to be higher than in Figure 10 due to the combined effects of increased initiator and surfactant concentrations. Once again the surface tension shows slight oscillations which may indicate small deviations in surfactant concentrations around the CMC, or may be interpreted as noise in the measurement.

Figure 12 shows the destabilizing effect of increased initiator concentration. In this run the initiator concentration was high (0.03 mol/L water) and the surfactant concentration was low (0.01 mol/L water). The effect of a high initiator concentration is a large overshoot on the first oscillation. The effect of low surfactant concentration is a long transient period consisting of low amplitude oscillations in conversion. The corresponding surface tension data indicate a long initial period during the first conversion overshoot when micelles are not present, followed by less extreme oscillations as the system approaches steady state. The period of oscillation appears to be about four residence times.

Figure 13 shows the transient results for surfactant and initiator concentrations of 0.01 mol/L water. The conversion shows oscillations which may be stable or damped. More than three cycles would be necessary to decide conclusively. The period of oscillation is about 7 residence times. The conversion oscillates between 18% and 25%. This may be compared with Figure 10 which was run at the same surfactant and initiator concentrations, but at a residence time of 30 min. The conversion in Figure 10 oscillates between 3% and 12% due to the lower residence time. The surface tension trace in Figure 13 shows a large overshoot corresponding to the first conversion oscillation. The surface tension then shows a downward drift superimposed on possible damped oscillations, though the data are obscured by two instances of instrument fouling (dashed lines). The fouling is more pronounced in this case because the high residence time and low surfactant concentration led to a chronic shortage of the surfactant necessary to stabilize the particles.

No data are reported for Experiment 4 (Table II). This is because the low surfactant concentration, high residence time (50 min), and destabilizing effect of high initiator concentration (0.03 mol/L water) combined to cause total coagulation of the emulsion in the reactor.

## CONCLUSIONS

This paper presents the first comprehensive dynamic data for the continuous emulsion polymerization of methylmethacrylate over a wide range of operating conditions. Results from this work and studies with other monomers indicate that there are a number of interesting phenomena in continuous emulsion polymerization systems which are not fully understood. Among these are steady-state multiplicity, limit cycles, and other oscillatory tran-

sients. Evidence of all of these has been found in the current study. While these phenomena are not all well understood, their existence has been documented, and the conditions under which they occur have been explored.

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