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Miniemulsion copolymerization of vinyl acetate and butyl acrylate in a tubular reactor

Scott A. Adamec
Lehigh University

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**MINIEMULSION COPOLYMERIZATION OF VINYL ACETATE
AND BUTYL ACRYLATE IN A TUBULAR REACTOR**

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MS Thesis*

by

SCOTT A. ADAMEC

A RESEARCH REPORT

**IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE**

in

DEPARTMENT OF CHEMICAL ENGINEERING

LEHIGH UNIVERSITY

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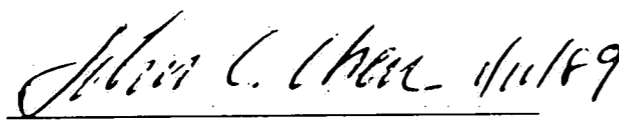
CERTIFICATE OF APPROVAL

This research report, submitted by Scott A. Adamec, is accepted and approved in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

Professor in Charge

 1/10/89
Mohamed S. El-Aasser

Department Chairman

 1/11/89
John Chen

Date: 1/10/89

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ABSTRACT

Miniemulsion copolymerizations of vinyl acetate (VAc) and n-butyl acrylate (BuA) were carried out using a tubular reactor in simulated batch conditions. Plug flow of the emulsion was induced by isolating relatively equal volumes of the miniemulsion with slugs of nitrogen to effectively produce a small batch reactor (the plug of emulsion). Variations in the mean particle residence time and initiator concentration levels were studied and their effects were found on the overall conversion and composition of the copolymer product.

Conversions increased from 40% to 60% as the reactor residence time was increased from 67 to 126 minutes for a constant initiator level of 4.4 mM. A maximum conversion of 70% was reached for an initiator level of 8.8 mM and a reactor residence time of 115 minutes. Oscillations in the conversion occurred once a maximum conversion had been reached after two residence times. Raising the initiator concentration above 8.8 mM had no effect on the conversion but seemed to dampen the oscillations.

Comparative runs with identical residence times and initiator levels were made using a conventional batch reactor and the tubular reactor operated in batch mode. Conversion-Time curves for these two systems varied, which should not have happened. For an initiator level of 4.4 mM and a residence time of 115 minutes, the continuous run attained 50% conversion while the batch reacted to 95% conversion. The teflon tubing that comprised the tubular reactor was found to retard the rate of polymerization.

Chapter 1 Introduction

There are three processes common to any chemical reaction by which emulsion polymerizations are carried out: (1) batch processes, (2) semicontinuous processes and (3) continuous processes. Even though batch and semicontinuous processes are preferred for emulsion copolymerizations because of their flexibility, continuous processes are more attractive in terms of productivity, low operation cost and uniform heat load.

Continuous stirred tank reactors (CSTRs) and tubular reactors are the two types of reactors used for continuous emulsion polymerizations. Two problems are associated with the use of CSTRs. One is the handling of partially converted monomer mixtures from one reactor to another while the second and more important is the oscillatory nature of the product specifications (conversion, number of particles and molecular weight) as a result of intermittent particle generation [1]. Two solutions are commonly used to solve the latter problem: (1) to design a battery of reactors in such a way that particle generation only takes place in the first CSTR and then the oscillatory behavior is dampened out by the rest of the tanks, or (2) to feed a partially converted monomer emulsion to the CSTR. This is done by using a tubular pre-reactor for particle generation [2]. The second approach is more efficient to the extent that some of the inherent problems, such as colloidal instability, can be resolved, giving this method excellent potential. It was shown by Gonzalez [3] that the second approach was successful in eliminating the conversion's oscillatory behavior in the polymerization of methyl methacrylate.

Apart from the better heat elimination and easier control, the main advantage of the tubular reactor over the CSTR is the higher conversion attained for similar residence times. The main disadvantage is the higher sensitivity of the reactor to the emulsion stability and particle coagulation. Due to the absence of agitation inside the tubular reactor, nonstable emulsions

may phase separate inside the reactor forming large amounts of coagulum which can obstruct the reactor leading to a process shut-down.

A special emulsification technique developed at the Emulsion Polymers Institute of Lehigh University allows the preparation of stable emulsions that, which upon polymerization, have been shown to produce less coagulum than conventional emulsions under the same experimental conditions [4]. This type of stable emulsion, known as a miniemulsion, seems promising for use in continuous polymerization processes and especially in tubular reactors because of the extremely good stability, which allows the miniemulsions to be transferred and pumped without loss of stability.

The comonomer system chosen to be used in this research is that of vinyl acetate (VAc) and butyl acrylate (BuA). This system, widely used in the coatings and adhesive industry, has been the subject of numerous studies in this Institute including polymerization kinetics and colloidal and bulk properties of the copolymers obtained in batch and semicontinuous processes using both conventional emulsions [5] and miniemulsions [6].

Chapter 2 Background

Miniemulsions are oil-in-water emulsions prepared using a mixed emulsifier system which is comprised of an ionic surfactant and a cosurfactant such as a fatty alcohol or a long chain alkane in concentrations of 1 to 3% by weight based on the oil phase [4]. They are characterized by high stability and small droplet size, which ranges from 100 to 400 nm in diameter. The name miniemulsions arises from this droplet size to distinguish them from the conventional emulsions, or macroemulsions, with droplets larger than 1000 nm in diameter and from microemulsions with droplets less than 100 nm in diameter. Some of the distinguishing characteristics between these three classifications of emulsions are their physical appearance, the emulsifier system, and the emulsification method used for their preparation. Macroemulsions are opaque and milky, tend to separate on standing, and are usually prepared with one ionic or non-ionic surfactant or a mixture of both. Microemulsions are clear or translucent and are usually prepared using a mixture of an ionic emulsifier and a short chain alcohol. The order of mixing of components is not critical, nor is the rate of shear applied during preparation. Miniemulsions are opaque and milky, do not separate on standing for long periods of time, and are prepared using an ionic surfactant and a long chain alcohol or alkane. The order of mixing of the components is critical and varies depending on the cosurfactant used — long chain alkane or an alcohol with at least 12 carbon atoms.

The stability of the miniemulsions is dependent upon the order of mixing of the components and the surfactant/cosurfactant ratio. In the case of a long chain alcohol as the cosurfactant, the most stable miniemulsions are formed when a pre-emulsification step is performed where the surfactant and the fatty alcohol are mixed in the aqueous phase at an elevated temperature before the oil phase is added [10,11] under agitation. If the alcohol is

instead first dissolved in the oil phase, unstable emulsions are formed. Microemulsions, however, can be prepared by first dissolving the short-chain alcohol in the oil phase before the addition to the aqueous phase containing the ionic surfactant. The most stable miniemulsions are formed when the ionic surfactant/short-chain alcohol molar ratio is between 1:1 and 1:3, with the stability increasing as the short-chain alcohol chain length increases from C₁₂ to C₁₈; better stability is attained when the hydrocarbon chain length of the emulsifier and the short-chain alcohol are similar [10,12]. When the cosurfactant is a long chain alkane such as hexadecane, however, it is recommended that the alkane be added to the oil phase while the surfactant is dissolved in the aqueous phase [13,14]. These two phases are then mixed together in a high shear device such as a sonifier to create stable emulsions. An emulsification method similar to that used with a fatty alcohol as the cosurfactant was presented using hexadecane [15]. In this case hexadecane, at a level of 1 to 2% based on the oil phase, was homogenized into the aqueous solution of ionic surfactant with the monomer later being dispersed in this medium. Studies on the miniemulsion stability using hexadecane as cosurfactant showed the existence of a plateau for cosurfactant/surfactant molar ratios greater than 3. Using hexadecane with the appropriate surfactant concentration and the emulsification method similar to that used with a fatty alcohol led to higher adsorption of surfactant, smaller droplet size, higher stability of the emulsions, lower polymerization rates, and larger latex particle size in the miniemulsion copolymerization of vinyl acetate and butyl acrylate [7].

Several hypotheses have been proposed to explain the formation and stabilization of oil-in-water emulsions using mixed emulsifier systems. One such hypothesis attributes the enhanced stability to the formation of a complex at the oil-water interface which lowers the interfacial tension [17,18]. Another suggested that it was due to the formation of liquid crystals which reduce the van der Waals attractive forces [19]. These may also explain mechanisms that prevent emulsion degradation due to coalescence by decreasing the efficiency of the collisions

between droplets, hence making the collisions more elastic. An alternate explanation is the slower destabilization of the emulsion because of hindered diffusion of the oil phase through the continuous water phase. Higuchi and Misra [20] reported that this degradation resulted from the increased water solubility of oils and monomers with decreasing droplet size so that diffusion would occur from smaller to larger droplets. They suggested that the addition of a small amount of a low water soluble component to the oil phase could stabilize the emulsion because this also would have to diffuse out of the small oil droplets before they could totally disappear. Ugelstad *et al.* [4,21] have shown that the stability of emulsions is improved by dissolving fatty alcohols or alkanes, which have low water solubility, in the oil phase.

Once the miniemulsion is formed, initiation of the monomer droplets must be induced so as to create polymer particles. Several mechanisms of nucleation have been postulated in emulsion polymerization: (1) initiation in monomer-swollen micelles, (2) initiation in the aqueous phase with subsequent precipitation of the formed oligomeric radical, and (3) initiation in the monomer droplets. The first two mechanisms have been widely accepted as the primary means of initiation in conventional emulsion polymerizations and have been intensively studied. It was believed that the monomer droplets were not a feasible location for the initiation of polymerization because their overall surface area was small compared to that of the monomer-swollen micelles, and therefore could not capture many free radicals. By dispersing the monomer into smaller stable droplets through the use of hexadecane (forming miniemulsions), the area available for radical capture was greatly increased and much more of the anionic surfactant was taken away from the micelles and adsorbed on the monomer droplet surface to cover the new formed area. It was found that by increasing the initial concentration of surfactant with a certain amount of hexadecane, the droplet size could be decreased to a minimum value with an increased amount of surfactant adsorbed [7]. In this manner, the monomer droplets could be the principal locus for particle formation in miniemulsion systems

because of the smaller droplet size and the enhanced stability.

Work has been done to apply the theories of emulsion homopolymerization kinetics to that of emulsion copolymerization [22,23]. Once initiation of the monomer droplets occurs, emulsion polymerizations proceed according to a rate governed by

$$R_p = \frac{k_p [M]_p \bar{n} N_p}{N_a} \quad (2.1)$$

where k_p is the rate coefficient for radical propagation, $[M]_p$ is the monomer concentration in the polymer particles, N_p is the number of particles per unit volume of aqueous phase, \bar{n} is the average number of radicals per particle, and N_a is Avagadro's number. For an emulsion copolymerization, the rate will be given by the addition of the individual rates of polymerization of the monomers

$$R_p = R_{pa} + R_{pb} \quad (2.2)$$

where a and b refer to the different monomers, in this case vinyl acetate and butyl acrylate.

Because of the two monomers present, there will be two different radicals formed and four different possibilities for addition. This can be seen by the equations



and are applied in the equations for the individual rates of polymerization of monomers a and b

$$R_{pa} = k_{aa} [R_a]_p [A]_p + k_{ba} [R_b]_p [A]_p \quad (2.7)$$

$$R_{pb} = k_{bb} [R_b]_p [B]_p + k_{ab} [R_a]_p [B]_p \quad (2.8)$$

where $[R_i]_p$ is the concentration of radicals of type i in the polymer particles which can be expressed by

$$[R_i] = \frac{\bar{n}_i N_p}{N_a} \quad (2.9)$$

The crosspropagation rate constants can be obtained in terms of the homopropagation rate constants and the reactivity ratios (r_i) [6]

$$k_{ij} = \frac{k_{ii}}{r_i} \quad (2.10)$$

The average number of radicals per particle, \bar{n} , is important in the determination of the rate of polymerization. Several different approaches have been developed in an effort to attain this value [22,23,24]. Smith and Ewart [24] proposed three limiting cases for the value of \bar{n} in order to better understand the kinetics of an emulsion polymerization. The three cases are

$$\text{case I } \bar{n} \ll 1 \quad (2.11)$$

$$\text{case II } \bar{n} = .5 \quad (2.12)$$

$$\text{case III } \bar{n} \gg 1 \quad (2.13)$$

and are the basis that many theories are founded upon and tested against. Two rate constants that greatly affect \bar{n} are the mean rate coefficient for radical desorption from the polymer particle (\bar{k}_f) and the mean termination rate coefficient in polymer particles (\bar{k}_t) which is dependent upon the termination rates of the monomers.

For the system of vinyl acetate and butyl acrylate, the low termination rate coefficient for BuA ($10^3 - 10^4$ 1/mole/sec) as compared to that of VAc (10^8 1/mole/sec) will mean that the value of \bar{n} will be greater than .5 up until all of the BuA is consumed. Experiments done by Delgado [6] with a 50:50 molar ratio of the two monomers showed a high value of \bar{n} that decreased to less than .5 for both conventional and miniemulsions. This means that the major part of the miniemulsion copolymerization of this system can be described by Smith-Ewart case III kinetics. A kinetic model of this system was proposed by Delgado [6] that extended

existing theories for homopolymerization and copolymerizations to the miniemulsion system. Predictions from this model were found to agree well with experimental results.

Differences in the kinetics of polymerization were found between the conventional and the miniemulsion processes [6,16,18]. The rate of polymerization in the conventional system was found to always be faster than that of the miniemulsion system. This may be attributed to the lower number of particles produced in a miniemulsion, which is dependent upon the initiator concentration, as compared to a conventional emulsion polymerization, which is independent of the initiator concentration [6]. The generation and nucleation of particles was also lower for miniemulsions due to a reduced rate of radical absorption by the monomer droplets. This low radical capture efficiency could be the result of the high adsorption of emulsifier on the droplets. Intermolecular complexes formed at the oil-water interface act as a barrier to prevent free radicals from entering into the monomer droplets and initiating nucleation. Styrene miniemulsion polymerizations were also found to differ from conventional emulsion polymerizations because they did not exhibit the interval-II characteristic of a constant rate of polymerization [16]. When all the droplets disappear, the rate begins to decrease as a result of the decrease in monomer concentration in the particles. This supports particle nucleation occurring in the monomer droplets with the fraction becoming particles determined by the initiator level.

Dependence of the polymerization kinetics on temperature and reactor type can not be neglected. For most polymerizations, an increase in the polymerization temperature will cause an increase in the polymerization rate. Also, particle size will decrease due to the increasing number of droplets that become particles. This is due to an increase in the rate of radical generation with increasing temperature. As with temperature, varying the reactor design can have a large effect on the kinetics of the polymerization. The differences between batch and continuous reactors can lead to quite different kinetic models even if the same recipe is used. An

example of this is the Smith-Ewart case II emulsion polymerization of styrene. The polymerization rate of this system is compared for a batch reactor and a single continuous stirred tank reactor (CSTR) [2]

$$R_{p,BATCH} \approx R_i^{0.4} [S]^{0.6} \quad (2.14)$$

$$R_{p,CSTR} \approx R_i^0 [S]^{1.0} \Theta^{-0.67} \quad (2.15)$$

where [S] is the emulsifier concentration, R_i is the rate of initiation, and Θ is the reactor mean residence time. The effect of varying reactor type can be seen through these rates and difficulties could arise if batch data was used to design a continuous system.

One continuous type of reactor that behaves kinetically like a batch reactor is a tubular reactor operating in a plug flow regime. For this reactor, the residence time distribution will be narrow and result in a narrow particle size distribution. By contrast, a CSTR will exhibit a broad residence time distribution as expressed by

$$f(t) = \frac{1}{\Theta} e^{-t/\Theta} \quad (2.16)$$

where t is the particle residence time. This will lead to a broad particle size distribution and hence a broad molecular weight distribution [2]. Industrially, most continuous emulsion polymerization systems are comprised of a number of CSTR's connected in series; this is usually between two and five. For these systems, reactants normally enter the first reactor and the product is withdrawn from the last. Monomer addition, however, can easily be introduced into any reactor along the train to achieve a specific product quality.

Tubular reactors have not been used commercially because of the difficulty in understanding the kinetics of the system [8]. High soap concentrations needed to maintain stability and prevent plugging also degrade the polymer product, making tubular reactors not feasible. Gonzales [3] demonstrated that a tubular prereactor, used as a seed generator, could be used upstream from a CSTR to eliminate commonly observed conversion oscillations caused by

competing functions of the surfactant. Work has been done using tubular reactors to polymerize acrylamide, styrene, and vinyl acetate [8,25,26]. Models have been postulated for the emulsion polymerization of styrene [25,27] and the inverse emulsion polymerization of acrylamide [8] in a tubular reactor. Ghosh and Forsyth [25] assumed Smith-Ewart case II kinetics for their model which agreed fairly well with experimental data at high conversions. They found, however, that the theories developed for batch and CSTR reactors do not accurately predict the rate data obtained from a continuous tubular reactor. Lee and Forsyth [26] found that the conversion of vinyl acetate in this type of reactor was always lower than for a batch reactor and that it oscillated with constant frequency and amplitude after maximum conversion was attained after two residence times. Discrepancies between the conversion results for batch and continuous systems may partly be attributed to varying flow characteristics. By inserting slugs of nitrogen into the tubular reactor, the emulsion is broken into plugs that act as individual batch reactors. In this way, backmixing of the emulsion is eliminated and the residence time distribution is narrowed [28]. The conversion from a tubular reactor operating under this condition should ideally equal that of a batch reactor if the residence time in each is the same. To date, no work has been published using a tubular reactor operating in plug flow for the copolymerization of a miniemulsion.

This research program is focused on the study of the performance of miniemulsions in a tubular reactor. The emphasis is on the effect of the reactor dynamics on the kinetics of the polymerization and on the quality of the product — overall conversion, copolymer composition and particle size. The variables studied are the mean residence time of the miniemulsion in the reactor, the flow regime inside the reactor and the initiator concentration in the miniemulsion.

Chapter 3 Experimental

3.1 MATERIALS

The vinyl acetate (VAc) (Polysciences) monomer was distilled at atmospheric pressure using a rectifying column and refrigerated. The *n*-butyl acrylate (BuA) (Badische Co.) monomer was washed several times with a 5 weight percent aqueous solution of sodium hydroxide and then with distilled-and-deionized (DDI) water until the wash water was neutral pH. The monomer was dried with anhydrous sodium sulfate and distilled with a reduced pressure of 60 mm Hg under a dry nitrogen atmosphere and then refrigerated until needed.

Sodium hexadecyl sulfate (SHS) was prepared by reacting hexadecanol with chlorosulfonic acid with subsequent neutralization of the alkyl sulfuric acid with sodium hydroxide in isobutanol. The salt formed (SHS) was crystallized from an isobutanol/water mixture and then from pure isobutanol. The product was extracted with diethyl ether for 3 days [7]. This was then placed in a vacuum oven until the ether was removed.

Hexadecane (HD) (certified grade from Fisher), sodium bicarbonate (certified grade from Fisher) and ammonium persulfate (reagent grade from Baker) were used as received. The water used was DDI.

3.2 APPARATUS

The tubular reactor system used in this study was originally assembled for the inverse emulsion polymerization of acrylamide [8] and is shown in Figure 3-1. It consists of 100 feet of 1/8 inch inside diameter teflon tubing that is coiled in a plexiglass frame and submerged vertically in a constant temperature water bath. A Milton-Roy duplex minipump is used to pump the emulsion through the system with a maximum output of 540 cc/hour (only one

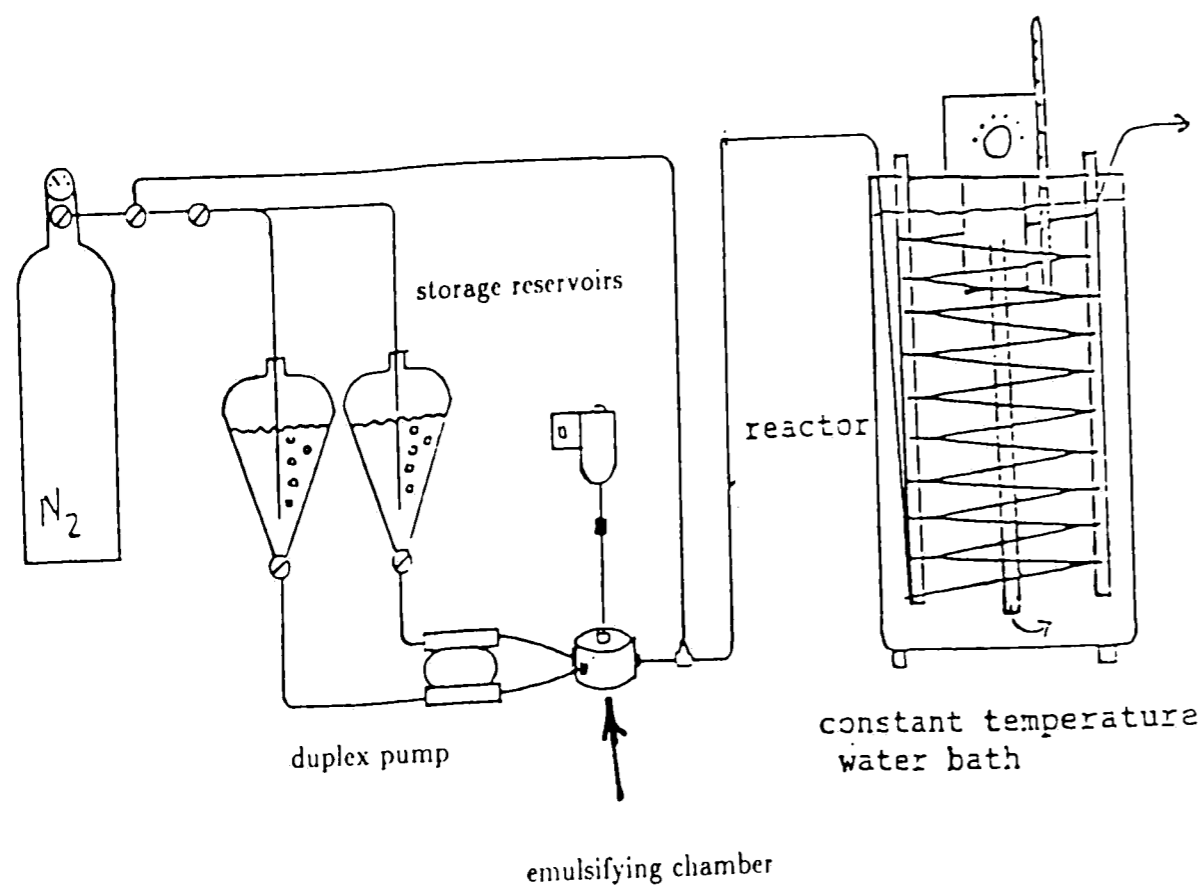


Figure 3-1: Schematic representation of the tubular reactor set-up with the emulsifying chamber in line.

side of the pump is utilized). A 1 liter separatory funnel is used as a storage reservoir for the emulsion after it has been prepared. Agitation in the reservoir ensures that no creaming of the miniemulsion droplets occurs. All connecting tubing in the system is teflon and all joints are stainless steel.

Zero grade nitrogen is used to purge the system prior to use, blanket the reservoir and separate the emulsion flow into slugs before it reaches the reactor. A tee joint in the emulsion outlet from the pump is used to introduce the nitrogen slugs. The nitrogen flow is regulated with a Nupro fine metering needle valve to attain the required flow rates.

A three-way valve is attached in-line directly after the pump output for sampling the emulsion prior to the reactor. A tee joint can also be installed at the reactor midpoint to allow sampling of the partially reacted monomers. An 80 cc mixing chamber is also available for in-line use when necessary.

3.3 PROCEDURE

Before operating the reactor, the emulsion must be prepared. The miniemulsion recipe used in this work was used by Delgado in his studies and was found to be stable and capable of attaining high conversion [6]. The recipe is based on a 50 : 50 mole ratio of VAc and BuA monomers and is as follows:

DDI Water	225g
VAc	30.14g
BuA	44.86g
Sodium Hexadecyl Sulfate (SHS)	0.775g
Hexadecane	2.038g
$NaHCO_3$	0.225g
$(NH_4)_2S_2O_8$	0.225g

The DDI water must be boiled prior to use to drive off any dissolved oxygen which will inhibit the polymerization by reacting with the free radicals. Nitrogen was bubbled through the water during cool down to ensure that the water remains oxygen free.

The SHS was dissolved in about 150 cc of warm water in a covered flask. About 40 cc of this solution was transferred to a small beaker and a pre-emulsion was made with the hexadecane by using a Sonifier Disruptor W-350 for 60 seconds at power level 7 and 50 % duty cycle. This emulsion, along with the rest of the water-SHS mixture and the monomers, was transferred to an Omni mixer (Figure 3-2) and stirred at 70 % duty cycle for 10 minutes. This was then transferred to a storage bottle.

The initiator, ammonium persulfate, and buffer, sodium bicarbonate, were added to the remaining 75 cc of boiled DDI water and dissolved. This mixture was then added to the emulsion in the storage bottle and shaken thoroughly. Previous tests have shown that no appreciable conversion will occur by having the initiator in the emulsion at room temperature; the polymerization is very temperature dependent. This mixture was then transferred to the storage reservoir where agitation was performed by a single blade impeller. Nitrogen was used to initially blanket the vessel.

Prior to starting any run in the tubular reactor, the water bath was heated to 60 °C and the system purged with nitrogen for several minutes. Once accomplished, the valve from the storage reservoir was opened and emulsion was allowed into the system. The stroke adjustment on the pump was then set to deliver the desired flow rate and residence time. The nitrogen flow was regulated using the needle valve to attain uniform emulsion slugs of approximately 1 inch. The nitrogen slugs were of similar size. Residence time measurements were made by introducing a large slug of emulsion and timing its motion through the reactor. This was done several times during a run and an average value was used.

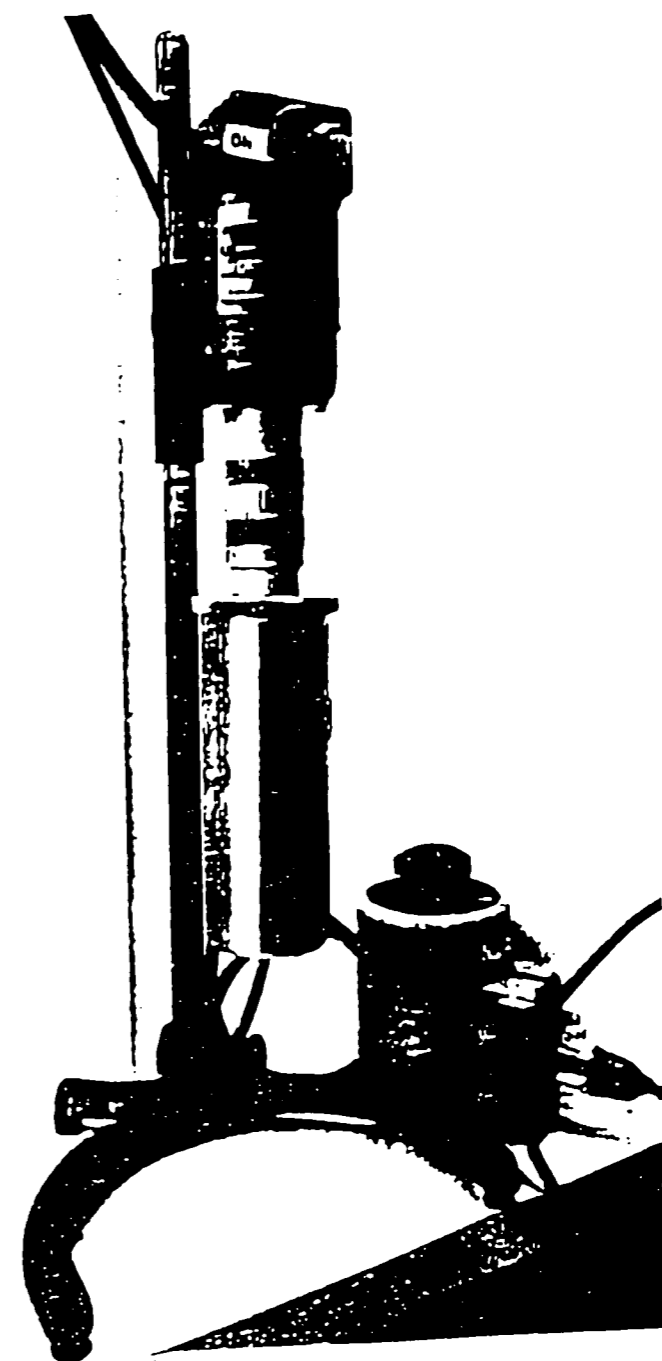


Figure 3-2: Photograph of the Omni mixer used to prepare the miniemulsions.

After a run was made, the system was cleaned by pumping two solutions through— DDI water until it exits clear and then methanol, which was the recommended solvent for the pump. Nitrogen was then passed through the system to blow out any remaining rinsing solution.

3.4 SAMPLING

During each run, samples were collected by connecting a pre-weighed sample bottle to the end of the tubular reactor via its cap with a hole drilled in it to allow the tube to pass through. The sample bottle contained 0.5 cc of a 1% Hydroquinone solution to stop the reaction. This was then weighed using a Mettler balance to attain the amount of sample taken, which was between 2 to 3 grams. The sample was transferred to a weighed tin, along with DDI water that was used to rinse out the sample bottle to assure full removal of polymer, and placed in an oven at 60 °C until completely dry. Gravimetric analysis was then performed to find the percent conversion of monomers.

Several samples were also taken to determine the copolymer composition through Gas Chromatographic (GC) analysis (see Appendix A). These samples were taken at the same time as the gravimetric samples so as to have a reference point. They were taken by collecting 6 - 10 drops of emulsion from the end of the reactor in a small sample bottle containing DDI water, some 1% Hydroquinone solution and a predetermined amount of dioxane. The dioxane was used as a reference point to determine the amount of monomers left unreacted by comparing the peak areas from the GC. Similar samples were also taken prior to the reactor to determine the actual amount of monomers being sent to the reactor.

Conversion of the monomers was found as overall conversion through the use of gravimetrics. It was determined in the following way:

$$\begin{aligned} \text{conversion} &= \frac{\text{monomer reacted}}{\text{initial amount of monomers}} & (3.1) \\ &= \frac{\text{weight of polymer formed}}{\text{initial amount of monomers}} \\ &= \frac{\text{weight of polymer in sample}}{\text{initial weight of monomers in sample}} \end{aligned}$$

The mass of the polymer formed in the sample can be found by finding the mass of the contents of the weighing tin once completely dry and subtracting the mass of solids— SHS, sodium bicarbonate, and ammonium persulfate— initially in the sample and the amount of hydroquinone added to halt polymerization. The unreacted monomers and the wash water are evaporated. The initial mass of monomers in the sample is found by GC analysis of the emulsion prior to entering the reactor. A GC calibration was performed so that the monomer/dioxane retention area could be translated to weight fraction of monomer in the sample (theoretically $X_{M} = 0.247$). In this way we arrive at the equation used to calculate monomer conversion:

$$\chi_p = \frac{W_p - X_s W_s - W_h}{X_m W_s} \quad (3.2)$$

where χ_p = overall conversion to polymer
 W_p = mass of polymer and solids (g)
 X_s = weight fraction of solids in recipe
 W_s = weight of sample (g)
 W_h = weight of hydroquinone (g)
 X_m = weight fraction of monomers in sample

Particle size was determined using a Coulter N4MD particle size analyzer. A unimodal and an SDP analysis were performed over a particle size range of 10 – 1000 nm. A viscosity of 0.942 cp and a refractive index of 1.333 were used for DDI water, which was the solvent used to dilute the sample to the required scanning concentration. Also, a Phillips 300 Transmission Electron Microscope was used to take micrographs of the latex.

Chapter 4

Results and Discussion

4.1 EMULSION PREPARATION AND REACTOR SET-UP

The scope of this research was to investigate the usage of a continuous tubular reactor for the miniemulsion copolymerization of vinyl acetate and butyl acrylate and to characterize the resulting latex. In an effort to make the process continuous from starting materials to finished latex, in line emulsification was attempted before reaching the tubular reactor. The emulsification chamber was placed downstream from the pump and equipped with a five blade, high shear impeller (see Figure 3-1). The monomers and aqueous solution of emulsifier and initiator were pumped separately into the chamber at rates to achieve recipe proportions. The residence time within the chamber was approximately 10 minutes. The resulting emulsion was found to have low stability; phase separation occurred after only 30 minutes. Several levels of emulsifier were tried with the same result. The level of shear available could not achieve the stability required for use with the tubular reactor. If this emulsion was used, phase separation would have occurred within the reactor. Bash [8], however, was able to attain high stability for his inverse emulsion system with the emulsifying chamber and could create his emulsions in line with the tubular reactor.

Because of the low emulsion stability when made in line, the emulsion was made separately using the pre-emulsification technique described in the experimental procedure section. The emulsions prepared in this way exhibited very high stability – in the range of several weeks and longer. This ensured that there would be no phase separation of the emulsion while it was pumped through the reactor.

4.2 CONTINUOUS POLYMERIZATION

Continuous polymerization runs were carried out with the tubular reactor operated in batch mode. Monomer conversion was determined through gravimetric and GC analysis for reactor runs varying the residence time and the initiator concentration while holding the reaction temperature constant at 60 °C. These results are shown in Figures 4-1 and 4-2 respectively. The maximum monomer conversion increased from 40 % to 60 % as the reactor residence time was increased for a constant initiator level of 4.4 mM as seen in Figure 4-1. Oscillations in the conversion occurred after a maximum conversion had been reached at the two highest residence times. These oscillations were unexpected since nucleation was assumed to occur in the monomer droplets. This would disallow decreasing conversion since monomer is readily available for polymerization. More work is needed to determine the site of particle nucleation.

The oscillations seem to have constant frequency and amplitude, just as Lee and Forsyth [26] found in their polymerization of vinyl acetate in a tubular reactor. They attributed the oscillations to the competing functions of the surfactant. That is, as the conversion increases, the particle size increases and more surfactant is needed to cover the surface. As the surfactant is adsorbed onto the surface, there are fewer total particles that can be nucleated and the reaction rate decreases. With the decreasing rate, the particle size becomes smaller, thereby freeing some of the surfactant and creating more particles. Once these particles are initiated, the conversion goes back up and the cycle starts over.

Oscillations in the conversion were dampened by an increased concentration of initiator as seen in Figure 4-2 for a residence time of 115 minutes. A plateau was reached around 70% conversion and an initiator concentration of 8.8 mM. Raising the initiator concentration above this level had no effect on the conversion but seemed to dampen the oscillation. This may be attributed to reaching an upper boundary in the final number of particles formed. Delgado [6]

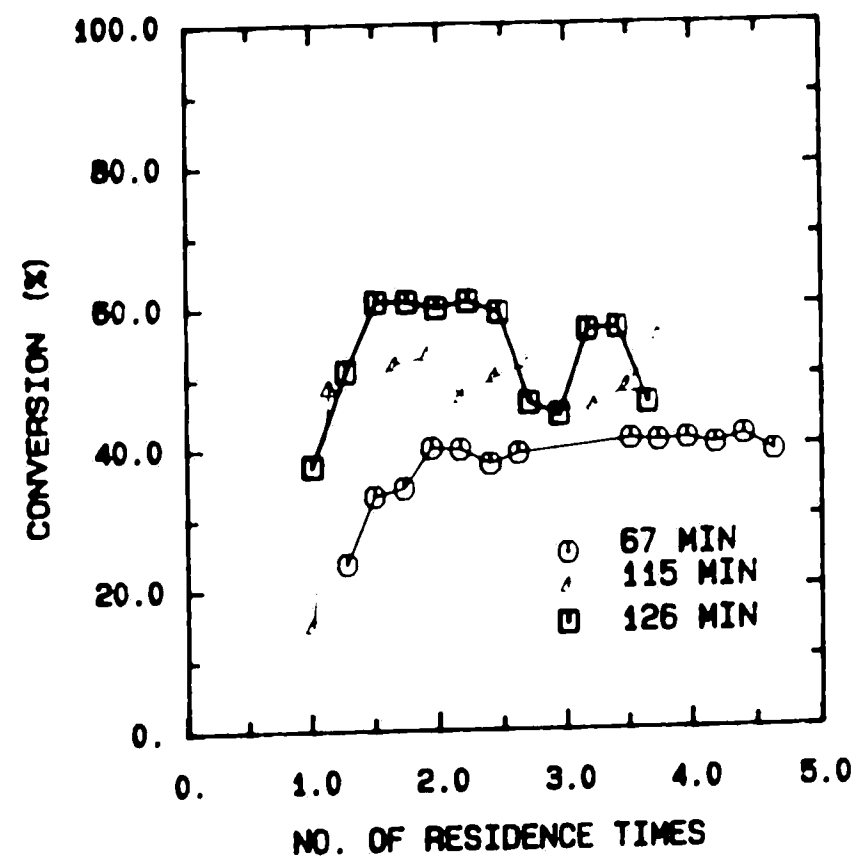


Figure 4-1: Conversion of continuous miniemulsion copolymerization runs of 50:50 mole ratio of VAc-BuA for varying residence times with a constant initiator concentration of 4.4 mM at 60 °C.

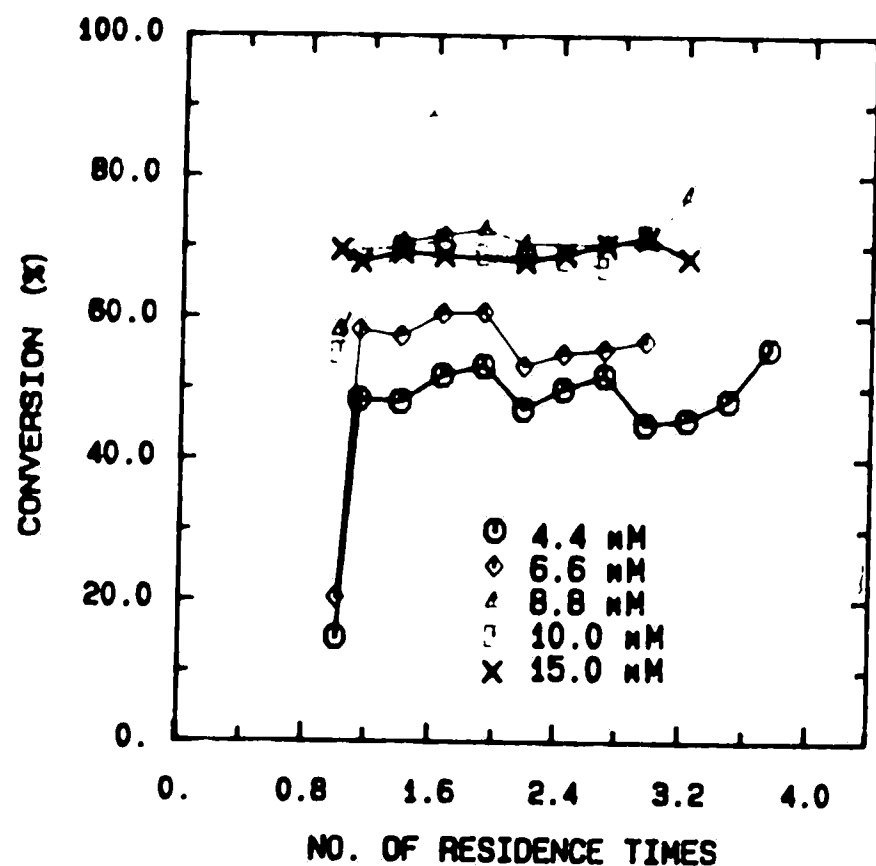


Figure 4-2: Conversion of continuous miniemulsion copolymerization runs of 50:50 mole ratio of VAc-BuA for varying initiator concentrations with a constant residence time of 115 min at 60 °C.

Table 4.1: Monomer conversion and copolymer composition determined through GC analysis for continuous miniemulsion copolymerizations with varying initiator concentrations and a residence time of 115 minutes.

	Run 13	Run 21	Run 20	Run 22
[I]	4.4 mM	6.6 mM	10 mM	15 mM
χ_{VAc}	.115	.223	.271	.296
χ_{BuA}	.724	.812	.981	.970
wt% BuA	87.5	78.4	78.5	76.6 (in copolymer)
wt% VAc	12.5	21.6	21.5	23.4 (in copolymer)
conversion	48	55	69	70

found a strong dependence of the number of particles on the initiator concentration, but did not try levels above 4.4 mM so did not find the upper bound. Increases in the initiator concentration and hence the number of particles led to the increased conversion since the rate of polymerization is dependent upon the number of particles.

4.3 COPOLYMER COMPOSITION

Table 4.1 shows the monomer conversion and the copolymer composition as calculated through GC analysis for the runs shown in Figure 4-2 (see Appendix A for sample calculations). It is evident that the butyl acrylate is preferentially consumed instead of the vinyl acetate, which is expected due to the large difference in their respective reactivity ratios ($r_{BuA} = 5.5$ and $r_{VAc} = .04$). This leads to a polymer product with a BuA rich core and a VAc rich shell. The particle size was an average of 220 ± 30 nm for all runs, regardless of the initiator concentration in the range of 4.4 to 15 mM, as compared to 195 nm found by Delgado for the batch run [6].

4.4 COMPARISONS BETWEEN CONTINUOUS AND BATCH

The maximum conversion found from all of the runs varying initiator concentration and residence time did not exceed 70%, which was unexpected. By running the tubular reactor in simulated plug flow (also referred to as continuous in this paper), the kinetics are expected to be the same as that of a batch reactor because each separate slug of emulsion passing through the tubular reactor acts as an individual batch reactor that is isolated by plugs of nitrogen. Delgado [6] achieved conversions close to 100% after 120 minutes in a batch reactor using an identical recipe and preparation method. Figure 4-3 shows the results of a batch and simulated plug flow run done simultaneously using freshly prepared emulsion at an initiator level of 4.4 mM. The simulated plug flow run achieved a maximum conversion of about 50%, which is consistent with the results from Figure 4-2. The batch run, however, achieved 95% conversion in the same amount of time as one residence time for the simulated plug flow run. Figure 4-4 compares these batch results with those found by Delgado. Very good agreement between these results verifies the accuracy of the methodology used and the discrepancy between the batch and simulated plug flow results.

This discrepancy between batch and simulated plug flow results poses the possibility of a different kinetic model for reaction in the tubular reactor or indicates the presence of an inhibiting agent to the polymerization in the tubular reactor system, possibly due to the tube itself. Another explanation for lower conversion is the vaporization of monomers within the tubular reactor. The nitrogen slugs used to separate the emulsion into plugs were observed to increase about one and a half times their original size. This would leave less monomer in solution that is available for polymerization.

A miniemulsion batch run was made with pieces of the teflon tubing added to the batch reactor to ascertain if the tubing had any effect upon the kinetics of polymerization. The conversion of this run, seen in Figure 4-5, was consistently at least 25% less than that of a

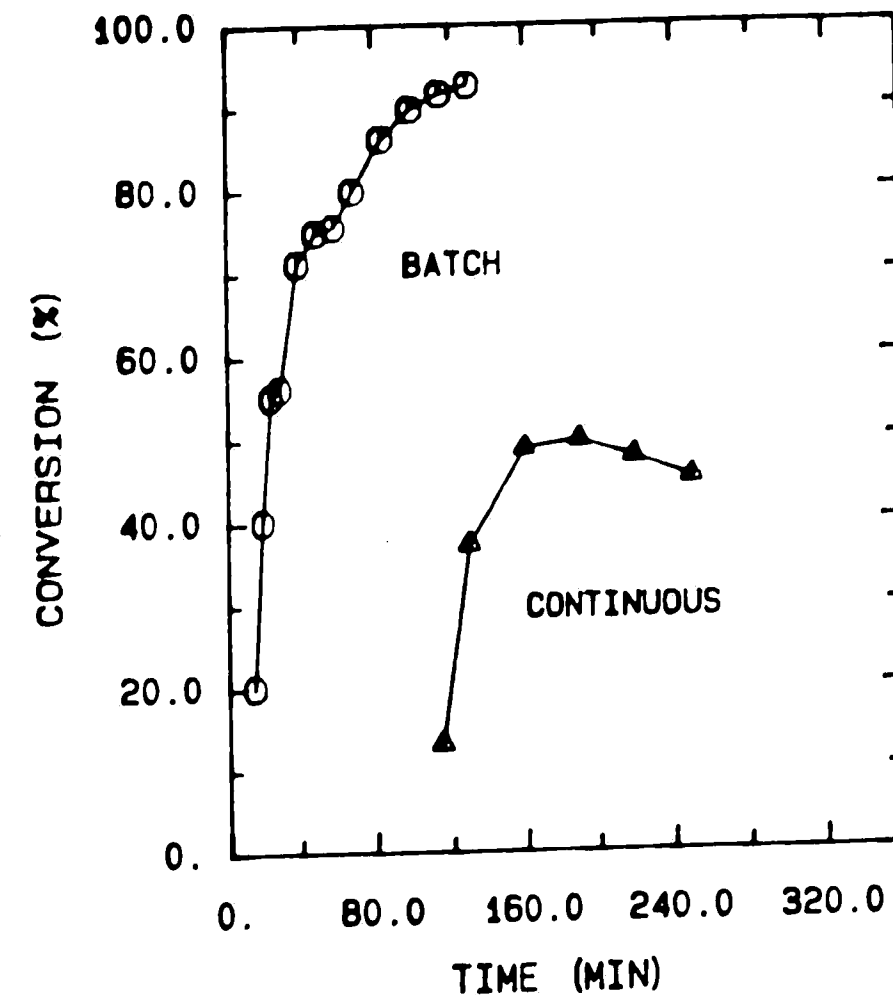


Figure 4-3: Comparison of batch and continuous miniemulsion copolymerization runs of 50:50 mole ratio VAc-BuA for an initiator concentration of 4.4 mM and a tubular reactor residence time of 115 min at 60 °C.

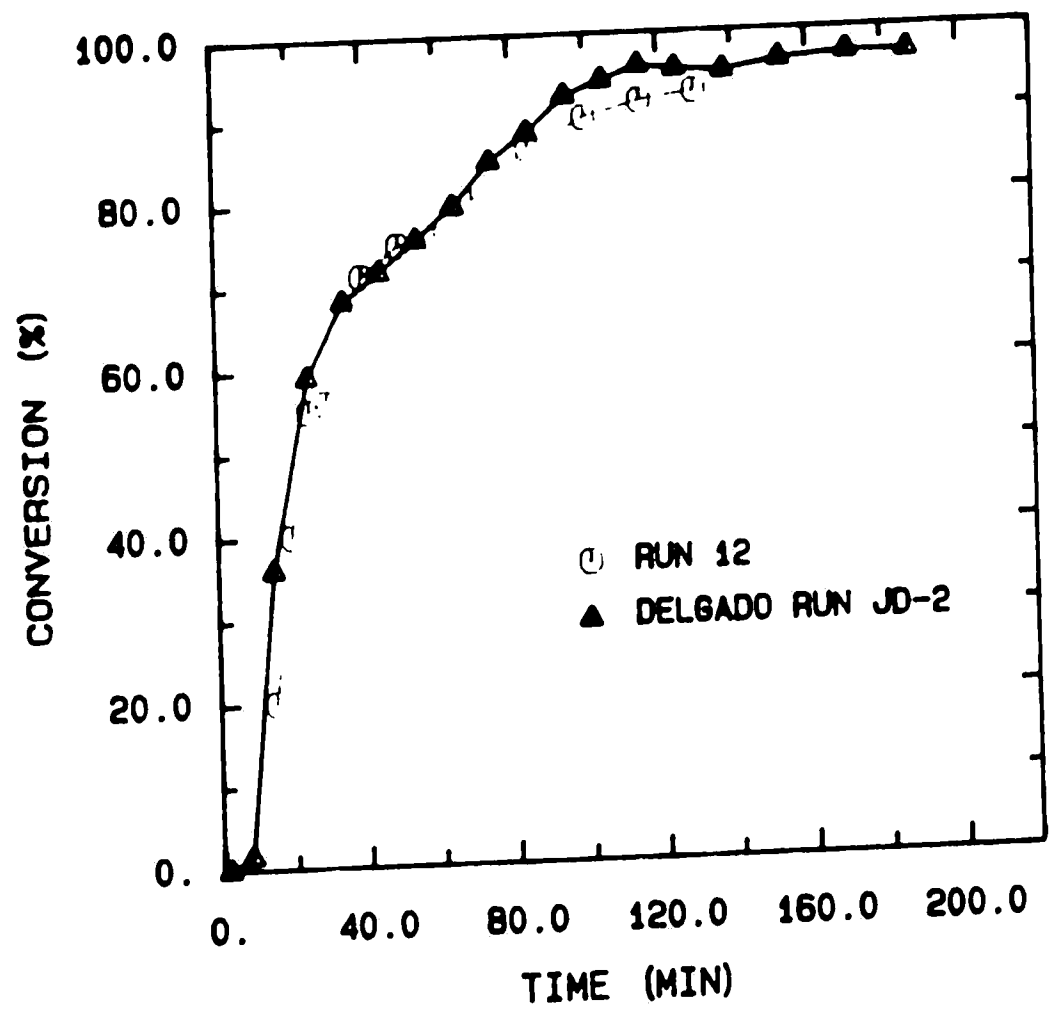


Figure 4-4: Comparison of batch miniemulsion copolymerization runs of 50:50 mole ratio VAc-BuA with an initiator concentration of 4.4 mM at 60 °C for this work and Delgado's work.

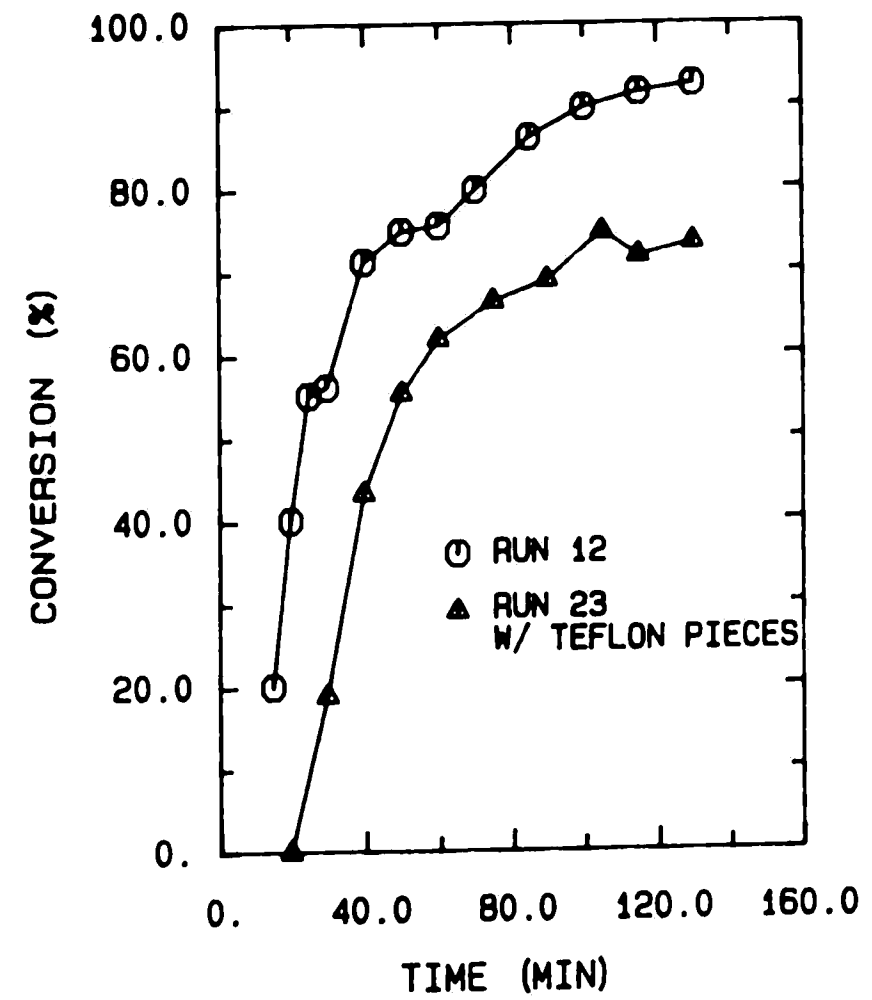


Figure 4-5: Comparison of batch miniemulsion copolymerization runs of 50:50 mole ratio VAc-BuA with (run 23) and without (run 12) teflon tubing pieces for an initiator concentration of 4.4 mM at 60 °C.

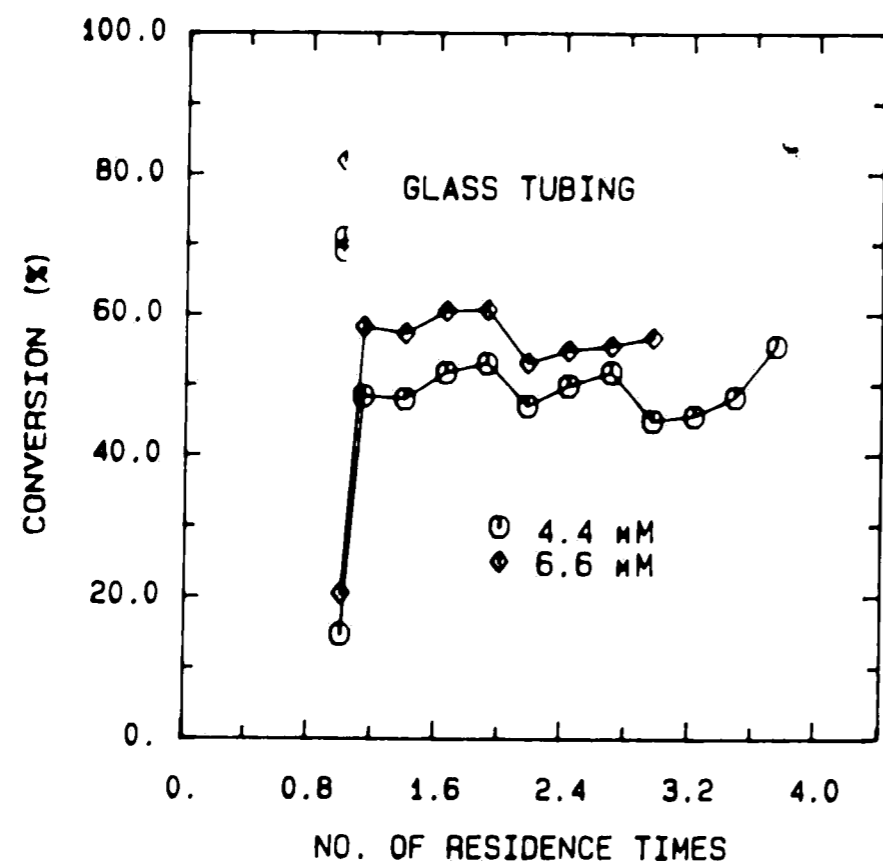


Figure 4-6: Comparison between miniemulsion copolymerization runs of 50:50 mole ratio VAc-BuA made with teflon tubing and trials made using glass tubing for a residence time of 115 min. and with the indicated initiator level at 60°C.

normal batch run without the added tubing pieces. The teflon tubing definitely affects the polymerization kinetics, most likely by scavenging some of the free radicals and thereby slowing down the rate of polymerization and limiting the overall conversion to a value appreciably less than total conversion. Several trial polymerizations were made in a length of glass tubing that had the same inside diameter as the teflon tube. Several slugs of emulsion were introduced into the pieces of tubing, after which the ends were capped. These trials attained 20% more overall conversion than those from the teflon tubing for similar residence times and initiator concentrations. Figure 4-6 graphically shows these results. By using a tubular reactor constructed totally from glass, monomer conversions would approach those of batch runs, but not equal them. Other nonreactive materials besides glass could be used to construct a tubular reactor that would not interfere with the polymerization kinetics. High conversion of monomer was attained with high emulsifier and initiator concentrations in a stainless steel tubular reactor for vinyl acetate [26] and styrene [25].

Chapter 5 Conclusions and Recommendations

From the discussion presented, it is possible to make the following conclusion:

1. Miniemulsion copolymerizations can successfully be carried out in a continuous tubular reactor as long as the emulsion is stable long enough to go through the reactor. The conversion attained, though, is less than that achieved for a batch reactor.
2. There is an optimum level of initiator concentration in this system of 8.8 mM. Anything above this level will have no effect on the copolymer % conversion, overall polymerization rate, or particle size. Also, conversion oscillations are decreased when operating at this level.
3. Teflon tubing retards the miniemulsion copolymerization of VAc and BuA, possibly by scavenging free radicals.

From the above conclusions and previously presented results, the following recommendations can be made for future work with the tubular reactor:

1. Try a tubular reactor constructed of some other material, such as glass or stainless steel, to see if conversions comparable to batch results can be attained. This could prove that the teflon tubing of the present reactor indeed inhibited the polymerization.
2. Perform a monomer balance around the reactor to determine if an appreciable amount of monomer is being lost to vaporization in the tubular reactor.
3. Perform experiments to determine the site of particle nucleation.

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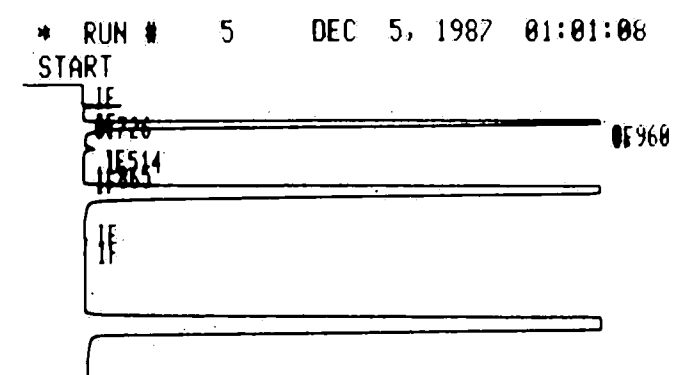
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APPENDIX A

GC Analysis of Latex

A Gas Chromatograph (GC) was used to analyze the amount of residual monomer in the formed latex through flame ionization (FID detector). A 0.1 μ L sample was injected into the GC and tested. The temperature was incremented from 40 °C to 70 °C by 10 °C step every minute. A signal was then recorded for anything that burned. A sample output is shown below.



STOP

Closing signal file M:SIGNAL .RAW

RUN# 5 DEC 5, 1987 01:01:08

METHOD NAME: A:NEAL.MET

SIGNAL FILE: M:SIGNAL.RAW

CALIBRATION

AREA%	RT	AREA	TYPE	WIDTH	AREA%
	.529	45193	PB	.021	.04678
	.960	20968496	PB	.058	21.70696
	1.514	52980	BB	.093	.05485
	2.531	20146480	PB	.131	20.85600
	3.643	18836	BP	.154	.01950
	4.376	17881	PV	.165	.01851
	5.724	55348160	PB	.180	57.29739

TOTAL AREA=9.6598E+07
MUL FACTOR=1.0000E+00

The detector was first calibrated for varying levels of monomers and dioxane to be able to get the relative weight ratio of monomer to dioxane from the area ratio of the output. The calibration curves are shown by Figures A-1 and A-2. Table A-1 gives the linear regression results for each and the equation that describes the line.

The monomer conversion is found by determining the weight of each monomer in the sample and then comparing it with the original amount used in the emulsion. First, a weight ratio of monomer/dioxane is found from Figures A-1 and A-2 using the area ratio from the GC output. Now the weight of the monomer in the sample can be determined since the weight of the dioxane added to the sample was known. Once the weights of both monomers are known in the sample, a ratio is formed:

$$Z = \frac{\text{grams VAc}}{\text{grams BuA}} \quad (\text{A-1})$$

Now the weight fractions of monomers in the sample are found:

$$W_{\text{BuA}} = \frac{1}{1 + Z} \quad (\text{A-2})$$

$$W_{\text{VAc}} = \frac{1}{1 + \frac{1}{Z}} \quad (\text{A-3})$$

The monomer conversions are then found by:

$$X_{\text{VAc}} = \frac{[30.14 - (1 - \chi) \cdot W_{\text{VAc}} \cdot 75]}{30.14} \quad (\text{A-4})$$

$$X_{\text{BuA}} = \frac{[44.86 - (1 - \chi) \cdot W_{\text{BuA}} \cdot 75]}{44.86} \quad (\text{A-5})$$

where 30.14 = initial weight of VAc in emulsion (grams)

44.86 = initial weight of BuA in emulsion (grams)

75.0 = total initial weight of monomers in emulsion (grams)

χ = fractional conversion found through gravimetrics

The weight fractions of monomers in the copolymer were found by:

$$W_{\text{VAc CO}} = \frac{X_{\text{VAc}}}{X_{\text{VAc}} + X_{\text{BuA}}} \quad (\text{A-6})$$

$$W_{\text{BuA CO}} = \frac{X_{\text{BuA}}}{X_{\text{VAc}} + X_{\text{BuA}}} \quad (\text{A-7})$$

Figures A-1 and A-2 were also used to attain the percent monomer in the emulsion prior to entering the tubular reactor by analyzing a sample taken through the valve prior to the reactor.

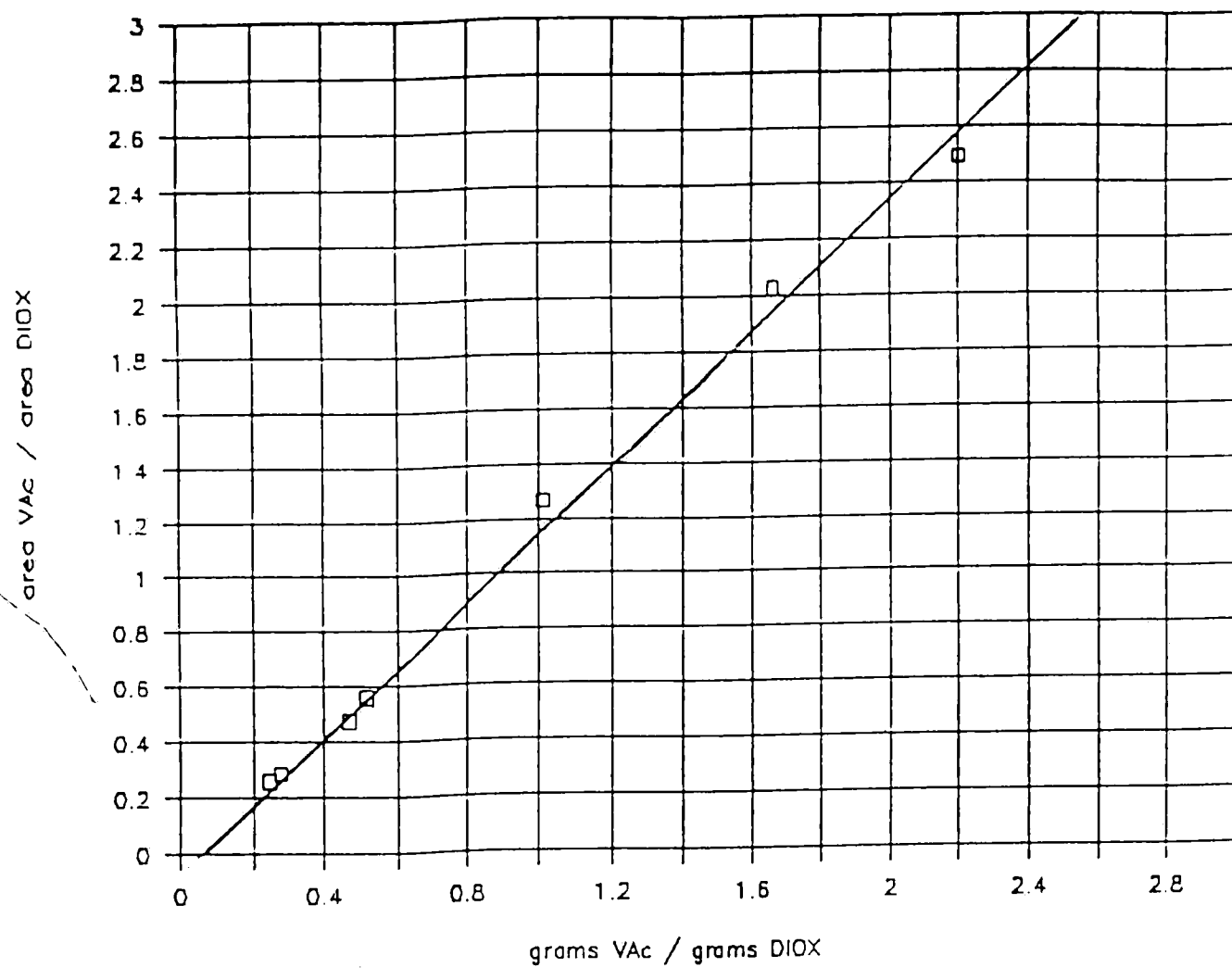


Figure A-1: Calibration curve for vinyl acetate/dioxane in emulsion for use with FID detector on GC.

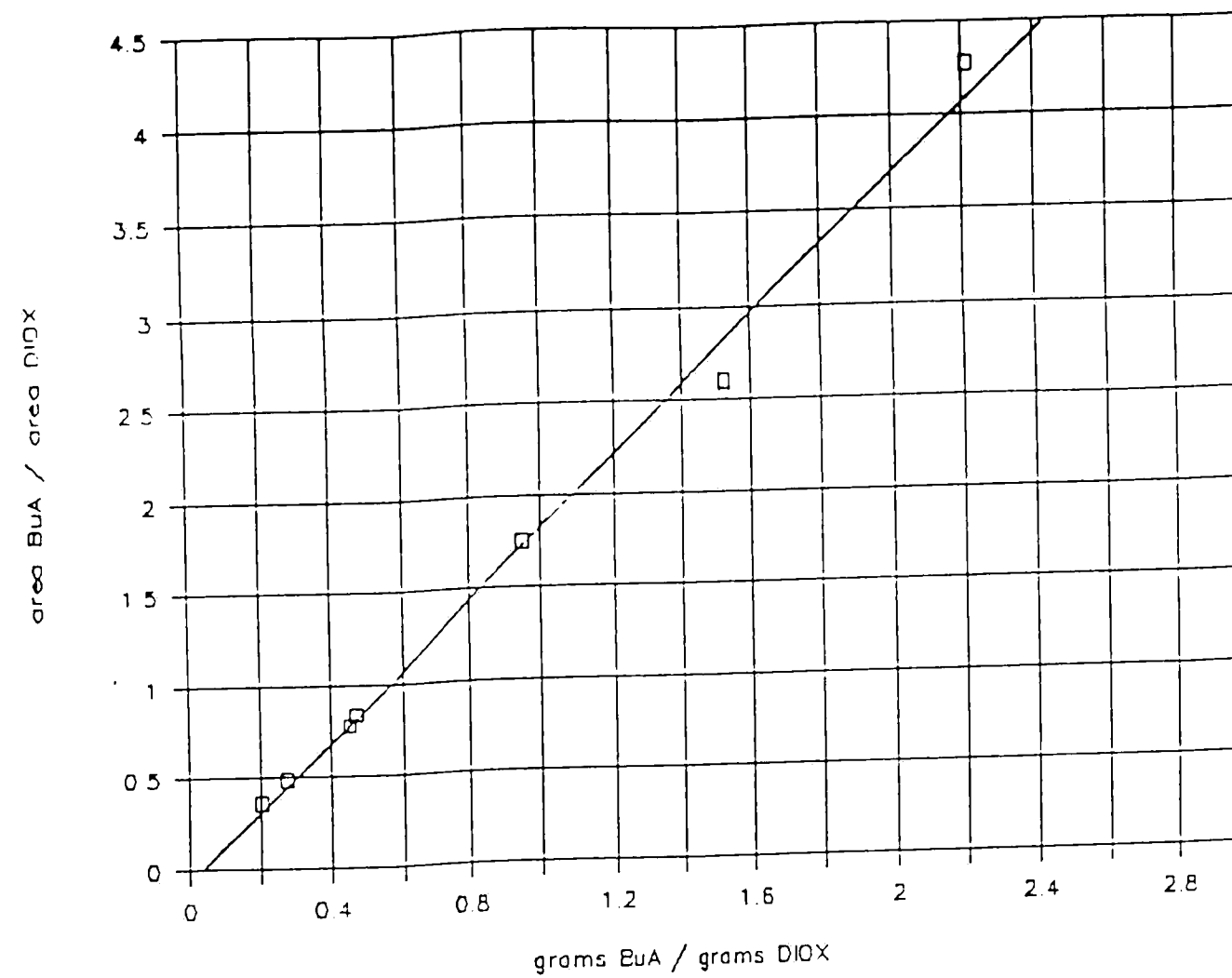


Figure A-2: Calibration curve for butyl acrylate/dioxane in emulsion for use with FID detector in GC.

BUA/DIOX

AREAS GRAMS

4.2765 2.2113
 2.5962 1.5232
 1.754 0.9524
 0.7761 0.4499
 0.4866 0.2773
 0.3584 0.2048
 0.8341 0.4669

VAC/DIOX

AREAS GRAMS

2.491 2.1989
 2.0266 1.6642
 1.26519 1.0116
 0.47878 0.4669
 0.28743 0.2756
 0.2593 0.247
 0.5617 0.5168

Regression Output:

Constant -0.06871
 Std Err of Y Est 0.123248
 R Squared 0.993786
 No. of Observations 7
 Degrees of Freedom 5

 X Coefficient(s) 1.899980
 Std Err of Coef. 0.067184

Regression Output:

Constant -0.02742
 Std Err of Y Est 0.072213
 R Squared 0.994621
 No. of Observations 7
 Degrees of Freedom 5

 X Coefficient(s) 1.185078
 Std Err of Coef. 0.038972

$y = 1.9x - .0687$

$y = 1.185x - .0274$

Table A-1: Linear regression results for Figures A-1 and A-2. The equation of the line of each is given below the respective results.

Appendix B

Gravimetric Data

For 50 : 50 mole ratio VAc - BuA comonomer system at 60 °C

RUN 4

[I] = 4.4 mM Tau = 48 min Continuous

No. of Residence Times	Conversion
1.0	70.2
1.25	50.8
1.56	68.9
1.88	69.6
2.19	67.2
2.5	69.5
2.81	68.6

RUN 7

[I] = 4.4 mM Tau = 67 min Continuous

No. of Residence Times	Conversion
1.0	—
1.27	23.7
1.49	33.3
1.72	34.4
1.94	40.1
2.16	39.9
2.39	37.8
2.61	39.3
3.51	41.2
3.73	40.9
3.96	41.2
4.18	40.4
4.4	41.6
4.63	39.3

RUN 9

[I] = 4.4 mM Tau = 115 min Continuous

No. of Residence Times	Conversion
1.0	14.8
1.13	48.5
1.39	48.1
1.65	51.8
1.91	53.2
2.17	47.1
2.43	50.0
2.7	51.9
2.96	45.0
3.22	45.7
3.48	48.4
3.74	55.7

RUN 10

[I] = 4.4 mM Tau = 126 min Continuous

No. of Residence Times	Conversion
1.0	37.6
1.27	51.1
1.51	60.9
1.75	60.9
1.98	60.0
2.22	60.9
2.46	59.3
2.7	46.4
2.94	44.7
3.17	56.7
3.41	57.0
3.65	46.3

RUN 12

[I] = 4.4 mM Tau = 116 min Continuous

No. of Residence Times	Conversion
1.0	13.1
1.12	37.2
1.34	48.7
1.64	49.7
1.89	47.7
2.16	45.1

Run 12

[I] = 4.4 mM Tau = - Batch

Time (min)	Conversion
10	-
15	20.1
20	40.1
25	55.1
30	56.1
40	71.2
50	74.8
60	75.5
70	79.8
85	86.1
100	89.7
115	91.5
130	92.5

RUN 15

[I] = 4.4 mM Tau = 126 min Continuous

No. of Residence Times	Conversion
1.0	—
1.27	64.1
1.51	65.6
1.75	65.7
1.98	66.1
2.22	65.2
2.38	65.8

RUN 16

[I] = 4.4 mM Tau = — Batch

Time (min)	Conversion
10	—
45	32.6
60	60.6
75	70.8
90	72.5
120	83.4
180	97.1
210	97.4

RUN 19

[I] = 8.8 mM Tau = 115 min Continuous

No. of Residence Times	Conversion
1.0	58.2
1.39	70.7
1.65	71.7
1.91	72.6
2.17	70.5
2.70	70.5
2.96	70.8
3.22	77.6

RUN 20

[I] = 10.0 mM Tau = 115 min Continuous

No. of Residence Times	Conversion
1.0	54.9
1.13	69.5
1.39	69.9
1.65	70.9
1.91	68.9
2.17	68.7
2.43	68.3
2.70	67.1
2.96	71.7

RUN 21

[I] = 6.6 mM Tau = 115 min Continuous

No. of Residence Times	Conversion
1.0	20.5
1.13	58.3
1.39	57.4
1.65	60.6
1.91	60.8
2.17	53.2
2.43	55.0
2.70	55.6
2.96	56.8

RUN 22

[I] = 15.0 mM Tau = 115 min Continuous

No. of Residence Times	Conversion
1.0	69.6
1.13	67.9
1.39	69.2
1.65	68.8
2.17	68.0
2.43	69.1
2.7	70.4
2.96	71.4
3.22	68.5

RUN 23

(with Teflon tubing pieces)

[I] = 4.4 mM Tau = - Batch

Time (min)	Conversion
20	-
30	18.9
40	43.3
50	55.3
60	61.8
75	66.3
90	68.8
105	74.6
115	71.7
130	73.3

Glass Tubing Runs

[I] = 4.4 mM Tau = 115 min

No. of Residence Times	Conversion
1.0	69.2
1.0	71.2

[I] = 6.6 mM Tau = 115 min

No. of Residence Times	Conversion
1.0	82.1

RUN JD-2

[I] = 4.4 mM Tau = - Batch

Time (min)	Conversion
2	-
8	1.5
15	36.0
25	59.2
35	68.2
45	71.6
55	75.4
65	79.3
75	84.6
85	88.0
95	92.3
105	94.1
115	95.8
125	95.3
138	94.9
153	96.1
171	96.8
187	96.7