

# Continuous Living Polymerization in Miniemulsion Using Reversible Addition Fragmentation Chain Transfer (RAFT) in a Tubular Reactor<sup>†</sup>

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Reversible Addition Fragmentation Chain Transfer (RAFT) polymerizations were conducted in a continuous miniemulsion using a tubular reactor in order to assess the feasibility of employing this combination on an industrial basis. Batch and continuous polymerizations were conducted simultaneously, and the results were compared. In general, the two reaction systems behaved in a similar fashion kinetically. Polydispersities of the final product were higher in the tubular reactor, likely owing to a distribution of residence times of the particles. A population of nongrowing chains was occasionally observed and determined to be independent of the reactor type. A chain extension experiment with the product of the tubular reactor demonstrated the “livingness” of the polymer and the possibility of using the system to make block copolymers.

## Introduction

Living radical polymerization (LRP) is a potential technique of choice for the preparation of polymers with unique and well-defined architectures. Because it is a free radical process, it has relatively mild reaction conditions and is tolerant to the presence of small amounts of impurities such as air, water, and trace chemicals. Until the advent of LRP, little could be done with free radical processes to accurately control molecular weight, to produce polymers with narrow molecular weight distributions or well-defined copolymers. Since by some estimates upward of 50% of polymers are produced industrially via some free radical process,<sup>1</sup> LRP offers a possible solution to synthesizing unique polymers on a large scale economically. While exact mechanisms vary, LRP maintains control by converting the propagating radicals into a dormant species thereby reducing the number of bimolecular termination events. Additionally, because of their “living” nature, in which dormant chains have the potential to add additional monomer units, LRP allows for the relatively facile synthesis of block copolymers (e.g. by simply adding a second, different monomer after the charge of the first monomer has been exhausted).

Most LRP can be classified under two broad categories, either reversible termination or reversible transfer. Atom transfer radical polymerization (ATRP)<sup>2,3</sup> and nitroxide mediated radical polymerization (NMP)<sup>4</sup> are the two most prominent examples of reversible termination. Both techniques use a radical deactivator, a nitroxide (e.g. 2,2,6,6-tetramethylpiperidine-N-oxyl, TEMPO) in the case of NMP and a metal halide complex (e.g.  $\text{RuCl}_2(\text{PPh}_3)_3$ ) in the case of ATRP, to reversibly terminate growing chain ends. The rate of the reversible termination is such that the instantaneous lifetime of

a propagating radical is exceedingly small, making the overall concentration of propagating radicals very small and suppressing bimolecular termination as well as the formation of dead chains. In a well-behaved reaction, each growing chain adds only a few monomer units during its “activated” conformation. The second category, reversible transfer, utilizes a rapid exchange reaction between an active and dormant chain, such that one of the chains will always be active. As such, the transfer mechanism does not affect the radical concentration, rather the number of radicals is determined by the addition of a conventional free-radical initiator. The best results are obtained when the concentration of the initiator is small with respect to the control agent. Reversible addition-fragmentation chain transfer (RAFT) is the most commonly utilized technique for producing living polymers via reversible transfer. RAFT agents are typically dithio compounds of some form because they have been found to be extremely versatile and work with a wide range of monomers.

One of the obstacles to implementing LRP commercially is their ability to work in heterogeneous media, specifically dispersed aqueous systems such as suspensions or emulsions. Aqueous systems are preferred industrially because they are generally considered a “green” way of producing a polymer (by way of eliminating the need for an organic solvent), have an inherently high heat transfer capacity, and result in a low viscosity polymer latex that is relatively easy to manage. Should an LRP system be developed that was compatible with heterogeneous media, the prospect for producing controlled-architecture polymers in a commercially attractive, economically viable manner would be much improved. One of the principle challenges to be overcome has to do with the partitioning of the control agent into the aqueous phase, which can result in a loss of control over the molecular weight and polydispersity. In emulsion polymerizations, highly insoluble control agents (typical of many RAFT compounds) do not effectively transport between droplets and particles in great enough number to maintain

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<sup>†</sup> This paper is dedicated to W. Harmon Ray, teacher, colleague, and friend.

control. On the other hand, if a control agent transports relatively easily, it can interfere with the growth of aqueous phase radicals during particle formation, slowing down and greatly complicating the kinetics. This is often the case when NMP or ATRP is applied to dispersed aqueous systems because they spend a portion of their lifetime unattached to the growing chain, and their small, mobile nature can make them susceptible to aqueous partitioning.

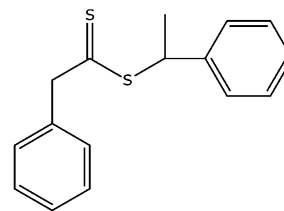
Another difficulty with LRP when applied to dispersed systems is the instability of the latex, exhibited as phase separation or high levels of coagulum. Luo<sup>5</sup> and co-workers have postulated the existence of a super swelling state brought on by the presence of a large population of oligomers early in living polymerizations. Using a theoretical model applied to miniemulsion polymerization, they suggest that the chemical potential of particles containing oligomers is lower than that of the monomer droplets, creating a large driving force for monomer to transport to the particles and causing the colloidal instability that is often observed.

To date, miniemulsions have proven to be the most effective way to conduct LRPs in aqueous systems. Since nucleation is primarily in the droplets, chains can start growing at roughly the same time. Less dependence on transport of monomer and control agent ensures that the reaction remains controlled. We advocate a RAFT/miniemulsion system because it offers two additional advantages over other LRP techniques when combined with miniemulsions. The first advantage accrues from the radical segregation effect that is inherent to miniemulsions. In solution, any radical could terminate with another. However, when the radicals are each segregated into isolated reaction loci, e.g. the particles of a miniemulsion, termination becomes difficult. Because the total concentration of radicals is distributed throughout the particles, the probability that any two radicals will meet and terminate is reduced. The ideal situation is one in which a lone radical in a particle can terminate only with a radical that enters the particle. This is known as the "zero-one" limit,<sup>6</sup> and in this case the rate of bimolecular termination is controlled by radical entry alone. This segregation could be exploited to boost the effectiveness of a living process by decreasing the bimolecular termination events that lead to broader molecular weight distributions and therefore increasing overall rates of reaction. Butte et al.<sup>7</sup> predicted that in the absence of partitioning of the control agent, RAFT would benefit most from segregation.

The second advantage derives from a feature unique to the RAFT mechanism, in which very quickly the control agent becomes bound to a growing polymer chain and remains attached throughout the reaction. The result is that the control agent is much more likely to remain within the polymer particle and not partition into the aqueous phase. This feature also makes RAFT ideally suited for miniemulsion polymerization, where transport of reaction components across the aqueous phase is not a requirement and can often be detrimental.

Given a suitable LRP/dispersed media combination, there remains the issue of how best to employ that combination in an industrial setting. Continuous systems are attractive because of their high throughput and low operating and labor costs. Additionally, when combined with LRP, continuous processes also offer the potential to produce copolymers with more consistent composition as compared to batch or semibatch systems.

### Scheme 1. RAFT Agent Used in This Study



1-phenylethyl phenyldithioacetate (PEPDTA)

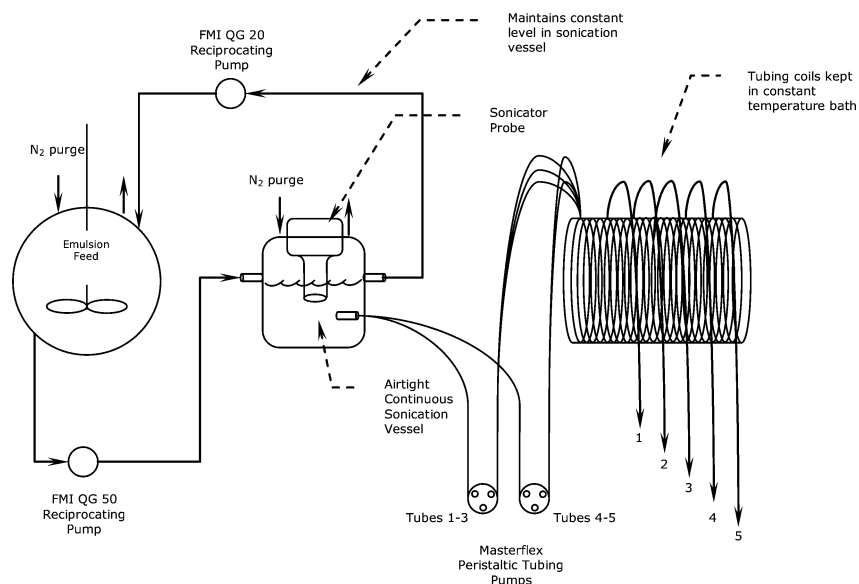
To date, however, most of the reports in the published literature with regard to RAFT, ATRP, and NMP have been conducted in batch or semibatch reaction systems. In one notable exception, Zhu et al.<sup>8,9</sup> successfully employed continuous LRP of methyl methacrylate in a packed column reactor containing silica-supported atom transfer radical polymerization (ATRP) catalyst. More recently, McKenna and co-workers<sup>10</sup> carried out conventional free radical polymerization in a continuous tubular reactor using miniemulsion. In addition, we have reported the polymerization of styrene using RAFT in combination with continuous miniemulsion in a high throughput, multitube reaction system.<sup>11</sup>

In this work, we investigate the feasibility of continuous, miniemulsion RAFT using a tubular reactor system. We have focused on the development of a recipe using mixed surfactants, the results of styrene homopolymerizations in batch and tube, and the results of a chain extension experiment demonstrating the living nature of the chains by forming a copolymer. In conducting these studies, two key questions were the focus. Kinetically, would the tube reactor behave in a similar fashion as a batch reactor, provided identical reaction parameters and plug or near plug flow? In theory, in the limit of plug flow, they should be the same, with the time variable replaced by the length of the tube.<sup>12</sup> Second, what is the effect of significant axial dispersion on the final polydispersity? When axial dispersion is high, there will be a distribution of particle residence times<sup>12</sup> which in principle would contribute to an increase in the final polydispersity of the living polymer.

### Experimental Section

**Materials.** Styrene and butyl acrylate (monomers,  $\geq 99.0\%$ , Aldrich) were cleaned by either vacuum distillation or by running through a column packed with an inhibitor remover. The column packing was purchased from Aldrich and was specific to the type of inhibitor in the monomer. Potassium persulfate (initiator, KPS,  $\geq 99.0\%$ , Aldrich), Triton X-405 (nonionic surfactant, TX405, 70% solution in water, Aldrich), hexadecane (co-stabilizer,  $\geq 99.0\%$ , Aldrich), and sodium dodecyl sulfate (ionic surfactant, SDS,  $\geq 99\%$ , Aldrich) were used as received. The reagents for the RAFT agent synthesis, hydrochloric acid (37% in H<sub>2</sub>O, Aldrich), magnesium sulfate ( $\geq 99\%$ , Aldrich), *p*-toluenesulfonic acid ( $\geq 98\%$ , Aldrich), benzyl chloride ( $\geq 99.9\%$ , J. T. Baker), carbon disulfide ( $\geq 99.9\%$ , J. T. Baker), carbon tetrachloride ( $\geq 99.9\%$ , Aldrich), anhydrous diethyl ether ( $\geq 99.9\%$ , Fisher), and magnesium turnings ( $\geq 98.0\%$ , Aldrich) were used as received. Deionized water was generated in-house with a U.S. Filter Systems Deionizer and was used without further purification.

**Synthesis of RAFT Agent. Synthesis of 1-phenylethyl phenyldithioacetate (PEPDTA, see Scheme 1.)<sup>13,14</sup>** Benzyl chloride (88.0 g, 0.69 mol) was added



**Figure 1.** Schematic illustration of the tubular reactor for RAFT polymerizations in continuous miniemulsion.

dropwise over a period of 4 h under ultrahigh purity nitrogen to magnesium turnings (15.1 g, 0.62 mol) in anhydrous diethyl ether (400 mL). The mixture was stirred and kept on ice. After a thick, gray suspension formed indicating the initial reaction, the mixture was heated to 34 °C and allowed to reflux for 2 h. The mixture was then chilled using an ice bath, and additional diethyl ether (200 mL) was introduced. Carbon disulfide (50.0 g, 0.66 mol) was then added dropwise over a 2 h period. A golden, yellow suspension formed immediately and was stirred for an additional 2 h after complete introduction of the carbon disulfide. The mixture was then poured into ice water (1200 mL), and the aqueous portion was collected following three washes with clean ether. After adding a final layer of ether, the mixture was acidified with 37% aqueous hydrochloric acid. The product, phenyldithioacetic acid (~30.5 g, 0.17 mol, 25%), was collected following rotary evaporation of the ether, filtering with magnesium sulfate to remove any residual moisture, and then placing under high vacuum for 1 h to remove any traces of ether. The phenyldithioacetic acid was then reacted with styrene (19.0 g, 0.18 mol) and a trace amount of *p*-toluenesulfonic acid (~0.05 g) as catalyst in carbon tetrachloride (~50 mL) at 70 °C. The mixture was refluxed under ultrahigh purity argon for 18 h. After removal of the carbon tetrachloride via rotary evaporation, the product was precipitated and recrystallized from cold methanol as bright, yellow crystals and placed under high vacuum overnight (~23.0 g, 0.09 mol, 13% on benzyl chloride).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  (ppm) 1.7 d (3H), 4.2 s (2H), 5.1 q (1H), 7.3 m (10H).

#### Batch Miniemulsion Equipment and Procedure.

All of the batch miniemulsion reactions except those run concurrent to a continuous reaction were prepared and carried out using the following procedure. The surfactants, SDS and TX405, were first added to water and allowed to mix for 15 min. The monomer, hexadecane, and RAFT agent were combined and allowed to mix for 15 min. The organic phase was then added to the aqueous phase and agitated vigorously with a magnetic stirrer for 30 min, forming a light yellow emulsion. The miniemulsion was formed by sonicating for 20 min (Fisher 300 Sonic Dismembrator at 70% output). During the sonication, the miniemulsion was cooled by an ice

bath in order to keep the temperature low so that any thermal initiation of the monomer would be minimized. After sonication, the miniemulsion was transferred to a 100 mL, round-bottomed, 4-neck flask outfitted with a septum, reflux condenser, nitrogen feed, and thermometer to monitor the temperature of the miniemulsion. The miniemulsion was kept agitated by a magnetic stirrer. After allowing the miniemulsion to deoxygenate under ultrahigh purity nitrogen for 30 min, the flask was immersed in an oil bath that had been preheated to the desired reaction temperature. The temperature of the miniemulsion was monitored with the thermometer, and when it had reached the reaction temperature, a solution of initiator and water was injected through the septum. The time of initiator injection was considered time zero, and samples were withdrawn through the septum via syringe at regular intervals for conversion, GPC, and particle size analysis. The reaction was kept under nitrogen for the entire time of the experiment.

**Continuous Miniemulsion Equipment and Procedure.** A schematic illustration of the reaction system is shown in Figure 1. The reactor was constructed of five separate 1/8" o.d. – 1/16" i.d. PFA (perfluoroalkoxy, a copolymer of TFE) tubes with different lengths in order to turn out five different residence times. The transparency of the tubing facilitated inspection for plugging and fouling. The tubes were arranged in 25 cm diameter helical coils and submerged in a constant temperature, 75 L water bath. Lengths varied from 7.6 m to 38.1 m in 7.6 m increments, with the tubes numbered 1 through 5, respectively. The temperature of the bath was controlled with a VWR 1122S immersion circulator. Because of the high heat transfer inherent in tube reactors and the small size of the tubing in relation to the water bath, the temperature was assumed to be constant throughout the length of the submerged tubing.

Two peristaltic tubing pumps were utilized to feed the miniemulsion into the five tubes of the reactor. The drives were Masterflex variable speed (1–100 rpm) console drives outfitted to accommodate multiple pump heads. Tubes 1–3 were supplied via three separate pump heads mounted on the first drive, and tubes 4 and 5 were supplied by two separate pump heads mounted

on the second drive. The pump heads were Masterflex L/S Standard pump heads (polycarbonate housing with SS rollers) and equipped with L/S 13 Viton tubing. The combination of drive, head, and tubing was rated to allow flow rates from 0.06 to 6.0 mL/min. The pumps were calibrated beforehand using deionized water and by measuring the time to fill a 5 mL volumetric flask at four different pump settings. During the actual experiment flows were checked two ways, both by measuring the time for the miniemulsion to traverse a specified length of tubing and volumetrically as before. Measurements were taken throughout the experiment, and it was observed that flowrates remained constant (within  $\pm 0.01$  mL/min), indicating that swelling of the Viton tubing was negligible if existent at all.

The miniemulsion was prepared by separately mixing the organic and aqueous components and then placing all the ingredients except the initiator into the main feed tank, a 3-L round, three neck (center 45/50, sides 24/40) flask, with heavy agitation provided by a Talboys Engineering Model 102 laboratory stirrer outfitted with a glass shaft and Teflon paddle. The formed emulsion was kept under ultrahigh purity nitrogen and allowed to deoxygenate overnight. The miniemulsion was formed by pumping the emulsion into a continuous sonication vessel, where it was stirred with a magnetic stirrer. The miniemulsion then could be fed to the tubular reactor on a continuous basis. The sonication was provided by a Fisher 300 sonic dismembrator set at 80% output. Two reciprocating pumps were used for the continuous sonication loop. An FMI QG 50 laboratory pump supplied the sonication vessel with feed emulsion. The volume (and average residence time of the forming miniemulsion) in the sonication vessel was kept constant via pumping off excess liquid and recycling into the feed tank with an FMI QG 20 laboratory pump. Both pumps were outfitted with Kynar pump heads with  $1/4$ -inch SS pistons and carbon liners. The average residence time in the sonication vessel was  $\sim 30$  min.

To run a concurrent batch experiment, an initial miniemulsion charge without initiator was bled off through the sonication vessel. Initiator was added to the batch after it had been allowed to reach reaction temperature. To begin the tubular experiments, after bleeding off a charge for the batch experiment, sonication was stopped, initiator was added to the feed tank, and the mixture was allowed to mix with the emulsion for 1 h. The tube reactor was then started by again pumping the emulsion into the sonication vessel, sonicating, and sending the formed miniemulsion to the reactor. All of the tubes were initially filled with water. To suppress initiation before the feed entered the reactor, the feed tank and sonication vessel were kept at 5 °C via submersion in a refrigerated water/ethylene glycol bath. Refrigeration and circulation were supplied by a VWR 1186D 28L programmable heating/cooling circulating bath. Samples of the feed were taken throughout the experiment and analyzed gravimetrically for conversion. The analysis indicated no conversion in the feed during the experiment, with a measurement error margin of  $\pm 2\%$  conversion.

**Characterization.** Polymer latex samples were dried for 24 h in a vacuum oven (50 °C,  $\sim 100$  kPa vacuum), and monomer conversion was subsequently determined gravimetrically. Samples were dissolved in THF and run through an alumina pipet column to remove the TX405 polymeric surfactant. The number average molecular

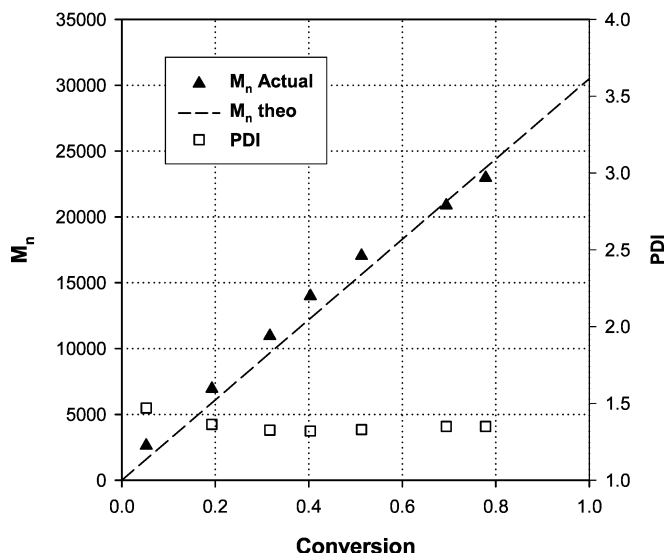
**Table 1. Recipe for the Batch Miniemulsion Polymerization of Styrene**

water		50 g	
monomer	styrene	12.5 g	25 wt-% of water
surfactants	Triton X-405	0.58 g	0.005 mol/L (based on aqueous phase)
	SDS	0.07 g	0.005 mol/L (based on aqueous phase)
costabilizer	hexadecane	0.25 g	2 wt-% of monomer
RAFT agent	PEPDTA	0.11 g	$[\text{Sty}]_0/[\text{PEPDTA}]_0 = 300$
initiator	KPS	0.01 g	$[\text{PEPDTA}]_0/[\text{KPS}]_0 = 10$
temperature		70 °C	

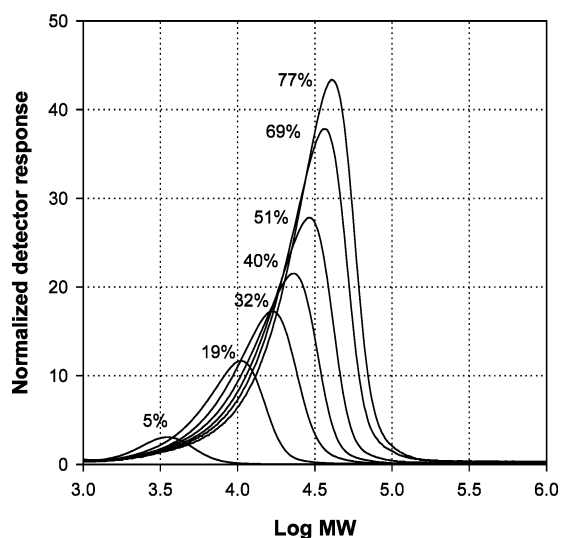
weight,  $M_n$ , and the polydispersity,  $M_w/M_n$ , were calculated using data gathered via size exclusion chromatography in THF. Three columns (American Polymer Standards styrene-divinylbenzene 100 Å, 1000 Å, and 10<sup>5</sup> Å) mounted in a Waters WAT038040 column heater set at 30 °C were utilized. The columns were connected to a Viscotek GPCMax pump/autoinjector, a Waters 410 refractive index detector, and an LDC Milton Roy Spectromonitor 3000 UV detector (at either 254 or 311 nm) and calibrated against 10 narrow polystyrene standards (Polymer Laboratories;  $M_n = 580$ –200 K,  $M_w/M_n = 1.02$ –1.16). Latex particle sizes and polydispersities were analyzed using quasi-elastic light scattering (QELS, Protein Solutions DynaPro99 with DynaPro DCS v 5.26 software).

## Results and Discussion

**Batch Polymerizations.** Before performing homopolymerizations in the tube reactor, it was necessary to develop and test a suitable recipe for the miniemulsion. Our focus was on the choice of an appropriate RAFT agent/surfactant combination. PEPDTA was selected because when used in conjunction with styrene it has a sufficiently high transfer constant (est.  $\sim 130$ )<sup>15</sup> to mediate a well-controlled reaction but likely low enough to avoid problems with latex instability.<sup>16</sup> It has been used in miniemulsions,<sup>15</sup> and the researchers reported no stability issues when combined with SDS as surfactant. However, we observed minor phase separation visible as a yellow layer of monomer ( $\sim 5$ –10% of the total monomer, by visual inspection) in approximately 50% of our preliminary test experiments. Based partially on our prior success combining RAFT with non-ionic surfactants,<sup>17</sup> a dual surfactant system, SDS (ionic) and Triton X-405 (nonionic), was utilized in order to overcome these stability issues. Some versatility was also desired, for example if a different monomer were to be employed with PEPDTA that may result in a higher transfer constant which in turn could affect the stability. El-Aasser and co-workers<sup>18</sup> showed that in certain concentrations, strong adsorption of both surfactants on polystyrene particles leads to larger total coverage than would be obtained with either surfactant acting alone. Greater coverage in principle should provide increased thermodynamic stability to the droplets in the critical first stages of the polymerization. Table 1 shows the recipe used for the batch polymerizations with PEPDTA. As shown in Figure 2, the number average molecular weight increased linearly with conversion, with very little deviation from the theoretical prediction. The fact that the molecular weights at very low conversions were close to theoretical suggests that the transfer constant of PEPDTA with styrene is indeed high enough to ensure that the RAFT agent is incorporated in the growing chains sufficiently early in the

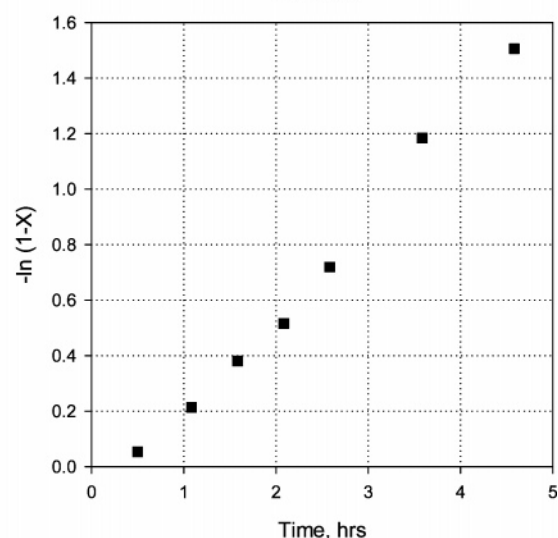
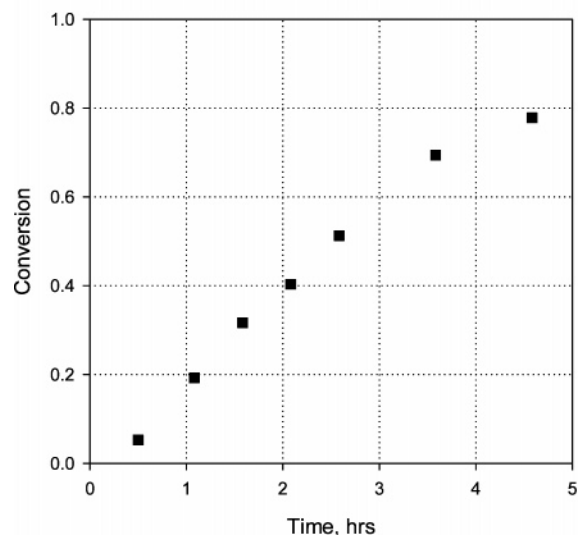


**Figure 2.** Plot of the number average molecular weight and polydispersity of polymers produced via the styrene/PEPDTA RAFT batch miniemulsion as a function of conversion.



**Figure 3.** Experimental MWD curves at increasing conversions for styrene/PEPDTA RAFT batch miniemulsion.

reaction. The final polydispersities were also relatively low,  $\sim 1.35$ , and the progression of the polydispersity from higher values early in the reaction to lower values is consistent with a living polymerization. An analysis of the evolution of the molecular weight distribution (see Figure 3) reveals nothing unusual, and a monomodal distribution was observed. The reaction rate began to decrease at  $\sim 70$ – $80\%$  conversion; however, the first-order plot of monomer conversion shown in Figure 4 reveals that bimolecular termination does not play a significant role in the rate reduction. It should be noted that with respect to RAFT, a first-order plot of monomer conversion cannot be used as an indicator of livingness, since the radical concentration can and does change, albeit very slowly in a well-behaved RAFT polymerization.<sup>19</sup> It can, however, be employed diagnostically as a gauge upon the relative extent of the initiation and termination reactions and that is the manner in which we use it here. Given the fact that the half-life of the initiator, KPS, at  $70^\circ\text{C}$  is approximately 8 h, it is unlikely that the radical flux has changed significantly, meaning any decrease in the overall rate as a result of

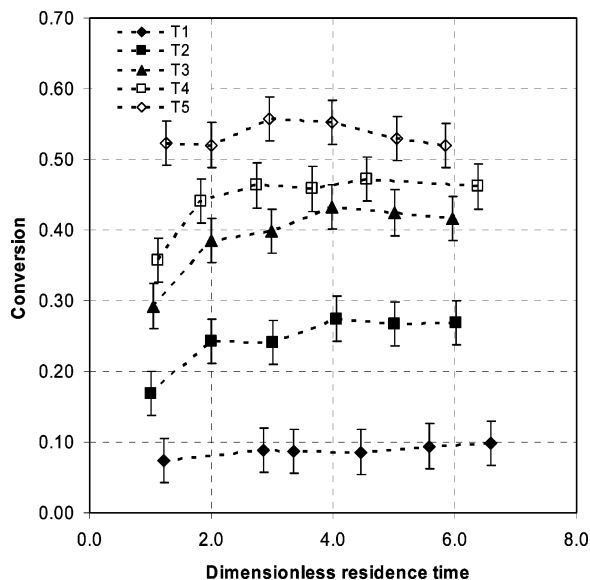


**Figure 4.** Kinetic plots of styrene/PEPDTA RAFT batch miniemulsion

**Table 2. Surfactant Concentrations, Critical Micelle Concentrations, and Concentration Ratios**

surfactant	concn $\text{mol}\cdot\text{L}^{-1}$	CMC $\text{mol}\cdot\text{L}^{-1}$	$[\text{Surf}]_0/\text{CMC}$ ratio
SDS	0.005	0.009	0.6
Triton X-405	0.005	0.00081	6.2

increased termination would likely be reflected in the  $\ln[M]/[M]_0$  plot. An important and encouraging observation from our standpoint was the excellent stability of the miniemulsion. No separation or coagulation was observed at any time during the course of the experiment. Additionally, there was no evidence of secondary nucleation, either in the molecular weight distributions or in the ratio of the final number of particles to the number of particles, which was calculated to be  $\sim 0.96$  (based on the initial and final particle sizes). As Table 2 shows, the initial surfactant concentration/CMC ratio of the TX405 was 6.2, whereas with SDS the ratio was 0.6. This implies that in the extreme situation of no SDS adsorption to the droplets and complete absorption of the TX405 to the droplets, no micelles should be formed. In contrast, the nonionic surfactant TX405 has a very low critical micelle concentration,  $\sim 8.1 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ , and because it was present in a relatively large amount, if only a small percentage ( $\sim 16\%$ ) were not adsorbed



**Figure 5.** Plot of the conversion (Exp T3) as a function of the dimensionless residence time in each of the tubes in the reactor.

**Table 3. Recipe for the Miniemulsion Polymerization of Styrene in a Tubular Reactor**

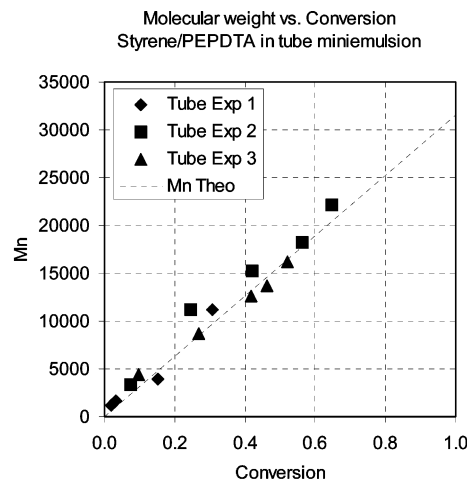
water		1600 g	
monomer	styrene	400 g	25 wt-% of water
surfactants	Triton X-405	18.5 g	0.005 mol/L (based on aqueous phase)
	SDS	2.3 g	0.005 mol/L (based on aqueous phase)
costabilizer	hexadecane	8.0 g	2 wt-% of monomer
RAFT agent	PEPDTA	3.5 g	$[\text{Sty}]_0/[\text{PEPDTA}]_0 = 300$
initiator	KPS	0.35 g	$[\text{PEPDTA}]_0/[\text{KPS}]_0 = 10$
temperature		70 or 80 °C	

**Table 4. Summary of Reactor Parameters**

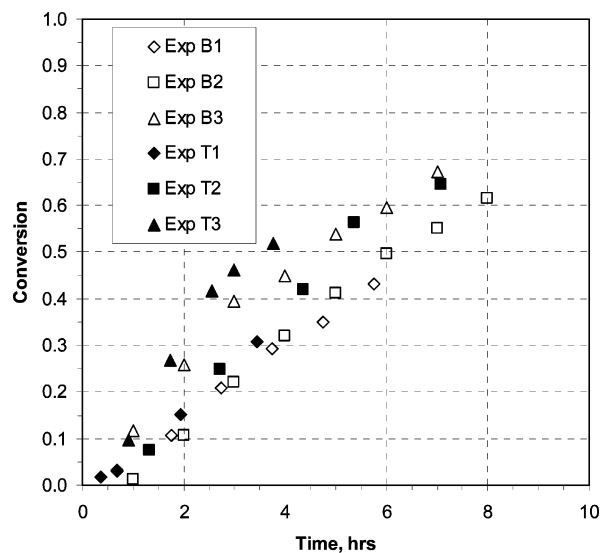
tube	length (m)	flow (mL/min)	residence time (min)	Reynolds number
1	8.1	0.29	55	9.3
2	15.5	0.30	105	9.4
3	23.2	0.30	153	9.5
4	31.0	0.34	180	10.8
5	38.9	0.34	226	10.8

on the surface of the droplets, those remaining molecules could in principle form micelles in the aqueous phase and become a source for secondary nucleation. If significant, this would likely reveal itself as a secondary distribution of high molecular weight, uncontrolled polymer. While the absence of the high polymer does not preclude the existence of micelles, it does suggest that any micellar formation was negligible and that most of the polymeric surfactant resided on the droplets.

**Continuous Polymerizations.** Recipe and reaction parameters for a typical styrene homopolymerization in the tubular reactor are shown in Tables 3 and 4, respectively. Flow rates were set to  $\sim 0.2\text{--}0.35$  mL/min depending on the desired conversion. Conversion profiles of each tube in the reactor for experiment T3 are shown in Figure 5 plotted against the dimensionless residence time. While some transient behavior is noted in tubes 2, 3, and 4, all of the tubes reached steady state after  $\sim 3$  residence times. All of the samples shown here for kinetic and molecular weight analysis for the tubular reactions were taken after at least 3 residence times. The miniemulsion remained stable throughout the reaction, with no visible indication of separation or coagulation. Visual inspection of the clear PTFE tubing



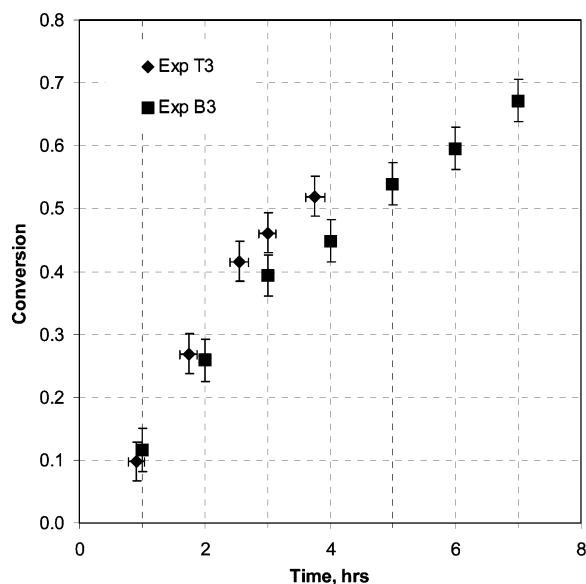
**Figure 6.** Plot of the number average molecular weight of polymers produced via the styrene/PEPDTA RAFT miniemulsion as a function of conversion.



**Figure 7.** Plot of the kinetic profile of the reactions in the tubular reactor along with their corresponding concurrent batch reaction.

afterward revealed no fouling of the tubes. The molecular weight results of three different experiments in the tubular reactor are shown in Figure 6. In each case the number average molecular weight progressed linearly with conversion, with little deviation from the theoretical value.

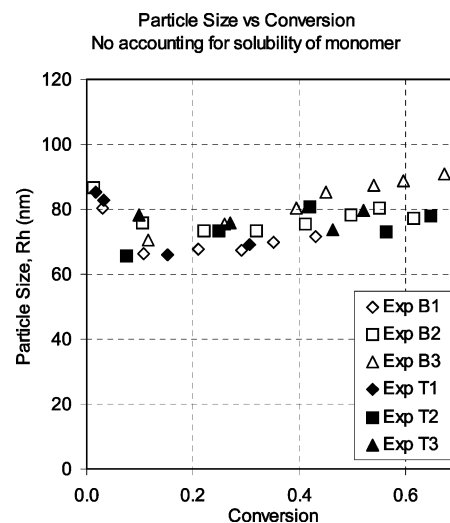
Given the flow regime in the tubular reactor, with  $Re \sim \leq 10$ , axial dispersion might be expected to have an effect on the kinetics, and in the absence of other effects, a lower reaction rate would be observed in the tube as compared to batch. The degree to which this would occur would be dictated by the amount of dispersion and in the high limit should approach mixed flow. The most interesting observation about the kinetics, however, is that while very similar, in each case the tube experiments were slightly faster than those in the batch (see Figure 7). As mentioned earlier, the flow remained consistent after 2 or 3 residence times as indicated by the steady-state profile of the tubular reactor as well as measured flow rates. Propagation of the flow measurement error, shown in Figure 8 for T3, indicates that something else is most likely at play. Initially it was thought that slight temperature differences between the batch and tube experiments might also be at the root of the difference. Temperatures were maintained with



**Figure 8.** Kinetic plot of concurrent tube and batch experiment with error bars. The X-error bars associated with the tube experiment (Exp T3) represent the measurement error in the flow rates.

controllers; however, they were not independently monitored for temperature (i.e., checking the temperature of each system with the same thermometer or temperature probe), allowing for the possibility that a small difference in temperature might exist between the two systems. At 70 °C, a  $\pm 1$  °C temperature difference can result in a  $\pm 5\%$  variation in initiator concentration after 4 h. However at the temperatures and particle sizes seen here, that only translates to  $\pm 3.0$ – $3.5\%$  difference in the value of the average number of radicals per particle. This is not sufficient to explain the kinetic difference seen here. Utilizing kinetic data from the actual experiment with particle size data, the average number of radicals per particle (in this system  $\sim 0.1$ ), and the rate equation for emulsion polymerization,<sup>6</sup> the temperature difference required to account for observed kinetic disparities was estimated. Using data from T3, we estimated that the temperature difference required would be  $\sim 10$  °C to affect the change in the average radical concentration necessary to account for the kinetic variations between the batch and tube.

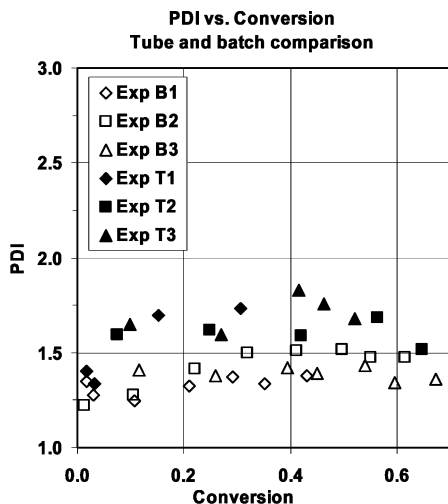
With miniemulsions, differences in particle size can cause large variations in polymerization rates,<sup>6</sup> but since the batch and tube miniemulsions were essentially the same in preparation, significant particle size differences would not be expected. Figure 9 shows the particle radius evolution in each of the experiments, but because the data contain a lot of scatter it is difficult to pinpoint whether a particle size difference between the batch and tube experiments really exists. The slight upward trend in the size evolution is most likely owing to the necessity to seriously dilute the latex ( $\sim 22000:1$ ) in order to perform the light scattering measurements. Monomer left in the particles would tend to partition to the aqueous phase and thus artificially shrink the size of the particle. The solubility of styrene in water at 25 °C is  $\sim 0.03$  g/100 mL or  $\sim 3300:1$  water/styrene. Taken alone, this would indicate that  $\sim 80$ – $85\%$  of the monomer should partition to the aqueous phase, accompanied by a commensurate shrinkage in particle size much greater than indicated here. However, this would be mediated to a certain degree thermodynamically by



**Figure 9.** Particle size evolution in tube and batch latex of polymers produced via the styrene/PEPDTA RAFT miniemulsion as a function of conversion. Monomer solubility is not accounted for in the values of the radii.

the need for the polymer particles to remain somewhat saturated with monomer. The monomer would only partition to the extent that the chemical potential of the monomer in the aqueous phase equaled that in the particles. While the data clearly indicate that some monomer remains, the degree of the partition is unclear, further complicating the particle size assessment. What can be said is that at the reaction conditions here, changes in the average particle radius of as little  $\pm 5$  nm can change the average number of radicals per particle by  $\sim 15$ – $20\%$ , which would be reflected in higher rates of polymerization. As such, kinetic variations owing to differences in particle size between batch and tube cannot be entirely ruled out as a possibility. One way to test for this in the future would be to carry both reactions to higher conversions,  $\sim 80\%$  or higher, where effects from sample dilution in the size analysis would be less troublesome and the final particle size as determined from light scattering would likely reflect more accurately the actual particle size. We also would like to make clear that we are not suggesting that there were no effects on the kinetics in the tube reactor from dispersion. However, since dispersion would tend to depress the reaction rate, some other phenomenon is occurring simultaneously to cause the discrepancy to appear as elevated, not depressed, rates in the tube. It may also be that the “true” rate at the set temperature is reflected in the tubular data and that the anomaly occurred in the batch.

Given some measure of axial dispersion and a corresponding broadening of the residence time distribution, it is expected that the polydispersity of a living polymerization conducted in a tubular reactor will be affected adversely. As Figure 10 clearly indicates, in each case the polydispersities in the tube reactor were higher than those in the batch. In general, faster kinetics in RAFT polymerizations will not necessarily lead to broader molecular weight distributions unless they are brought about by high initiator concentrations. In that case, given termination primarily by combination (as is the case with styrene), the build-up of initiator derived chains would show up in the molecular weight distribution as the population of high molecular weight material. Since the concentration of initiator, KPS, was low ( $[\text{PEPDTA}]_0/[\text{KPS}]_0 \sim 10:1$ ), and no high polymer was



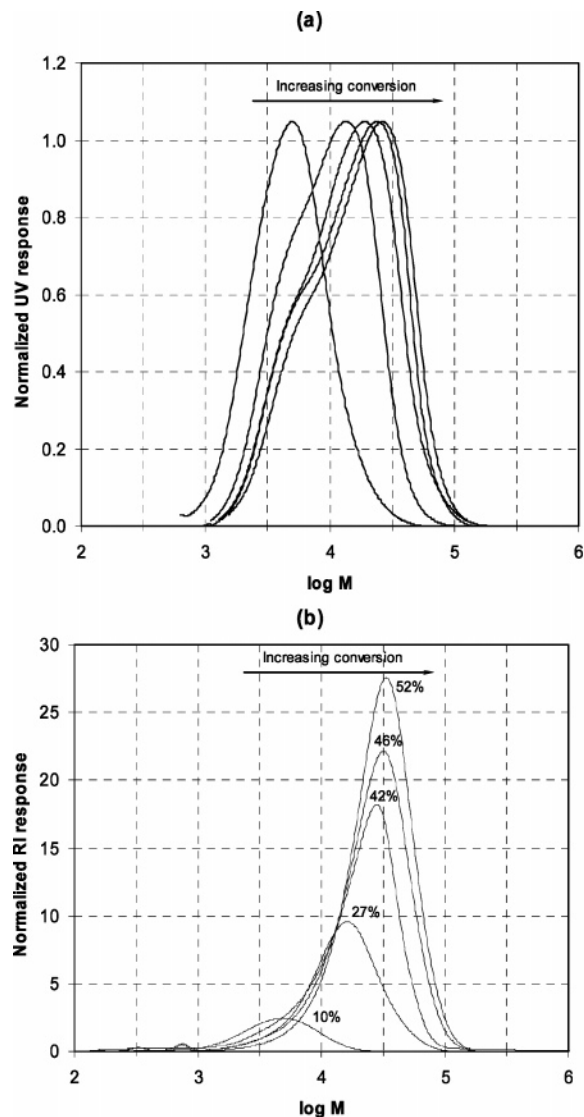
**Figure 10.** Plot of the polydispersities of styrene/PEPDTA RAFT miniemulsion in both the tubular and batch reactors.

observed (see Figure 11b), the most likely source of the broader distributions was dispersion in the tube reactor. We are currently working toward establishing and quantifying this relationship.

Another curious aspect of this system is shown (Figure 11a) in the GPC traces of the UV signal at 311 nm, reflecting the C=S of the dithioester, of experiment T3. It reveals an underlying population of nongrowing chains, evidenced by an emerging low molecular weight peak that does not progress with the reaction. Because the UV signal at this wavelength is proportional to only the incorporated RAFT agent, the traces reflect the number distribution, not the molecular weight distribution. The bimodality does not appear in the GPC traces generated by the RI signal since the weight distribution is recovered from the number distribution by multiplying the number distribution by the square of the molecular weight.<sup>6</sup> As such, the weight distribution will show some commensurate degree of low molecular weight tailing that may or may not reveal the bimodality.

Since the chains still possess the dithioester moiety, it is very unlikely that they are dead chains. Rather, they appear to be chains that for whatever reason no longer had access to monomer and therefore could no longer propagate. A similar phenomenon has been observed in our group and has been tested by soaking the dried latex in additional monomer, adding initiator and attempting to “grow” the chains.<sup>20</sup> It was observed that by doing so the bimodality disappeared very quickly, and the formerly nongrowing chains incorporated into the overall growing chain population. This would indicate that the chains were in fact nongrowing, not dead, and that some anomaly in the miniemulsion might be responsible for the observed bimodality. Further evidence for the livingness of these chains is revealed in the UV (311 nm) traces of a miniemulsion that was used in a batch chain extension experiment using butyl acrylate. Figure 12 shows that the initial polystyrene contained a population of these nongrowing chains. The final copolymer peak indicates that the chains all shifted toward higher molecular weights.

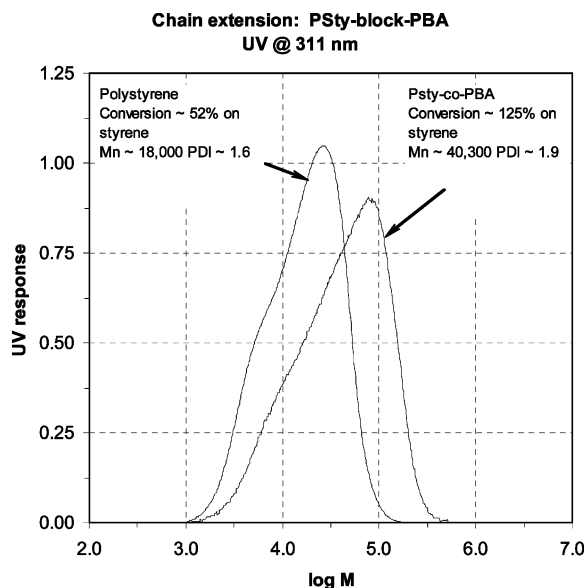
Uneven droplet nucleation has been hypothesized as the cause for the observed bimodality, in which case the earliest nucleated droplets would grow at the expense of monomer in droplets nucleated later. If the effect were large enough, the early nucleated droplets could deplete



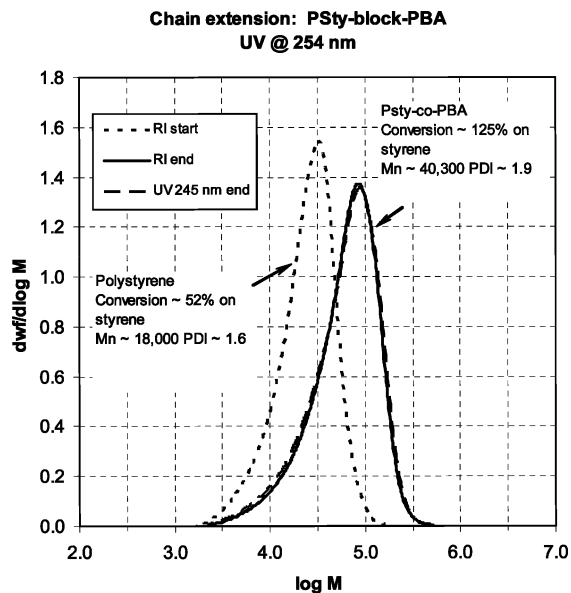
**Figure 11.** (a) GPC UV traces of Exp T3 at 311 nm representing the number distribution of chains. The data have been normalized for concentration. (b) GPC RI traces of Exp T3 representing the molecular weight distribution. The data have been normalized for conversion.

the monomer in the late nucleated droplets to the extent that they would begin to propagate either very slowly or not at all. Another possible scenario is a population of very small droplets that in the presence of relatively even nucleation quickly deplete their supply of monomer. Because this phenomenon has been observed at times in either of the two reaction systems, it does not appear to be reactor-related. The nongrowing chains can cause the polydispersity to increase, not decrease as expected, as the reaction progresses. The  $M_w/M_n$  evolution of Exp B2 is emblematic, clearly showing an increasing trend. What is significant is that even with the increased polydispersity of B2, the trend was still below that of T2, its tube analogue experiment. In fact, in each case, regardless of whether nongrowing chains were observed, tube polydispersities were consistently higher than batch, suggesting the effects from dispersion were likely significant.

As mentioned earlier, a chain extension experiment was conducted with latex from the tubular reactor as a test of the “livingness” of the chains. Latex was taken from the longest residence time tube in Exp T3 (~52%



**Figure 12.** GPC UV traces at 311 nm reflecting the number distribution of the starting polystyrene and the final polystyrene-*block*-poly(*n*-butyl acrylate) produced by chain extension of the polymer latex from Exp T3.



**Figure 13.** GPC traces of starting polystyrene, RI only, and final copolymer, polystyrene-*block*-poly(*n*-butyl acrylate), RI and UV at 254 nm, produced by chain extension of the polymer latex from Exp T3.

conversion) and placed in a three-neck reaction flask outfitted with septum, N<sub>2</sub> purge, and condenser. A second monomer, *n*-butyl acrylate, was added to the flask, and the miniemulsion was allowed to purge for ~30 min and then placed in a heated bath. No additional initiator was added to the system. Since poly(*n*-butyl acrylate) is invisible to UV at 254 nm, the GPC UV trace can be used with this system to verify incorporation of the *n*-butyl acrylate. This is shown in Figure 13, where a shift in the signal toward high molecular weights combined with >100% conversion on styrene indicates growth of the chains and confirms integration of the second monomer and formation of copolymer. Additionally, since the UV signal and RI signal essentially overlap, the copolymer formed was very pure, i.e., with little or no formation of homopolymer.

## Conclusions

In this work the RAFT polymerization technique has been combined with miniemulsion in a tubular reaction system. Recipes were developed in batch using a dual surfactant system to promote stable latexes. It was demonstrated that a 1/1 molar SDS/Triton X-405 surfactant system provided excellent stability of the miniemulsions, in both tube and batch, with no visible latex separation or coagulum. The efficacy of the RAFT agent PEPDTA was explored in batch miniemulsions and was found to work reasonably well in miniemulsion with styrene. Experiments in a continuous tubular reaction system revealed similar kinetics to batch; however, in each case the reaction progressed at a slightly faster rate in the tube reactor. The error in flow rate was quantified and, taken in conjunction with the steady-state reactor profile, was eliminated as a possible source of the advanced rates. Slight temperature differences between the batch and tube were offered as a possible cause of the variation; however, calculations of initiator decomposition at the particle sizes and reaction parameters used here effectively ruled out this suggestion. Small differences in the particle size could cause the discrepancy, and the data presented here, while inconclusive, cannot positively rule out the possibility. The polydispersity of the polymer produced in the tube reactor was consistently higher than that produced in concurrent batch experiments, which suggests that axial dispersion played a contributing role. The extent of axial dispersion and its effect on the polydispersity remains under investigation.

An underlying population of nongrowing chains which served to broaden the molecular weight distribution was identified at times in both the batch and tube polymer. It was demonstrated experimentally that the chains were indeed nongrowing, possibly monomer deprived chains and not simply dead chains. Uneven droplet nucleation was postulated as the cause, leaving some particles without sufficient monomer to propagate. However, further work will need to be done in order to positively identify this as the culprit. Finally, it was shown through chain extension that the polymer produced in the tube retained its living character to produce block copolymer of polystyrene-*block*-poly(*n*-butyl acrylate), opening the possibility of employing the system in the production of block copolymers.

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