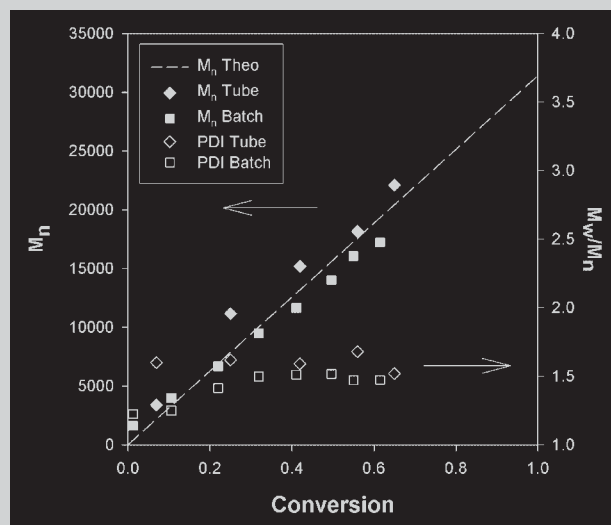


Summary: A unique, multi-tube, continuous reactor has been successfully designed and implemented for the study of reversible addition-fragmentation chain transfer (RAFT) in miniemulsions. Data collection is greatly enhanced by the ability to simultaneously collect samples at five different residence times. The results of a styrene homopolymerization show that kinetically, the reactor exhibits similar behavior to a batch reaction. Number-average molecular weights increased linearly with conversion, typical of living polymerizations.

The number-average molecular weight of the polymers produced in the tubular reactor increased linearly with conversion, indicative of a controlled polymerization.



Continuous Reversible Addition-Fragmentation Chain Transfer Polymerization in Miniemulsion Utilizing a Multi-Tube Reaction System

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Introduction

Living free radical polymerization (LRP) has been demonstrated to be a potentially useful and important new approach to producing polymers with complex architectures in a controlled manner.^[1,2] However, to increase commercial viability, LRP could be combined with a continuous, easily variable process that was environmentally benign in nature. From an industrial standpoint, miniemulsion polymerization is attractive because it is an aqueous system and is generally considered a “green” process. In addition, it has the ability to withstand process and recipe variations, the capacity to produce copolymers of uniform composition and final latexes with excellent shear stability. Combining LRP with continuous miniemulsion would offer many advantages, however, most of the work to date with LRP has

been performed in batch systems. Zhu and co-workers^[3,4] successfully employed continuous LRP of methyl methacrylate in a packed column reactor containing a silica-supported atom-transfer radical polymerization (ATRP) catalyst. More recently, McKenna and co-workers^[5] reported conventional free radical polymerization in a continuous tubular reactor using miniemulsion. However, there is no report in the literature of continuous miniemulsion LRP. In an effort to move towards a commercially attractive process for the production of unique, well-defined polymers using LRP on a large scale, we are investigating its use in conjunction with continuous miniemulsion. We have chosen reversible addition-fragmentation chain transfer (RAFT) as our LRP method of choice because it offers two distinct advantages over other LRP techniques when employed in a miniemulsion. First, the effects of radical

segregation offer the possibility of better control and faster kinetics.^[6] Second, because of the unique nature of the RAFT mechanism in which the control agent is always attached to a growing polymer chain, it is much more likely to remain within the polymer particle and therefore not partition into the aqueous phase. This is in contrast to other currently viable techniques such as atom-transfer radical polymerizations (ATRP)^[7–10] and nitroxide-mediated radical polymerizations (NMP)^[11,12] in which the control agent spends a portion of its lifetime independent from the growing polymer chain. Because these control agents are generally small and mobile they can be more susceptible to aqueous partition.

Here we report a tubular reactor system that facilitates rapid data collection in the study of continuous LRP. Because of the “living”^[13] nature of the RAFT process, the ability to collect data along the entire length of the LRP reaction curve in a practical manner is desirable. The conservation of RAFT agent is also a concern, making small reaction volumes a priority. To overcome these two challenges, a unique tubular reaction system for the study of continuous RAFT polymerization in miniemulsion was designed, built, and implemented. The system employs multiple tubes of different lengths in order to produce residence times at various points along the entire span of the reaction curve. Preliminary styrene homopolymerization using RAFT/miniemulsion in the tubular reactor system is reported.

Experimental Part

Materials

Styrene was purchased from Aldrich and vacuum distilled to remove the inhibitor. Potassium persulfate (KPS), Triton X-405 (TX405), hexadecane, and sodium dodecyl sulfate (SDS) were purchased from Aldrich and used as received. The RAFT agent, 1-phenylethyl phenyldithioacetate (PEPDTA), was prepared according to literature techniques.^[14] Deionized water was generated in-house with a U.S. Filter Systems Deionizer and was used without further purification.

Characterization

Polymer latex samples were dried for 24 h in a vacuum oven (50 °C, ca. 100 kPa vacuum) and monomer conversion was subsequently determined gravimetrically. The number-average molecular weight, \bar{M}_n , and the polydispersity, \bar{M}_w/\bar{M}_n , were calculated using data gathered using size exclusion chromatography in tetrahydrofuran (THF). Three columns (American Polymer Standards styrene-divinylbenzene 100, 1 000, and 10⁵ 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, an LDC Milton Roy Spectromonitor 3 000 UV detector (at 311 nm) and calibrated against

10 narrow polystyrene standards (Polymer Laboratories; $\bar{M}_n = 580\text{--}200\text{ K}$, $\bar{M}_w/\bar{M}_n = 1.02\text{--}1.16$). Latex particle sizes and polydispersities were analyzed using quasi-elastic light scattering (QELS, Protein Solutions DynaPro99 with DynaPro DCS v. 5.26 software).

Setup

A schematic illustration of the reaction system is shown in Figure 1. The reactor was constructed of five separate 1/8" OD and 1/16" ID PFA (perfluoroalkoxy, a copolymer of TFE) tubes with different lengths in order to turn out five different residence times. Table 1 shows the actual working lengths, accounting for where the tubes entered and exited the bath. The miniemulsion was prepared by pumping the components from the main feed tank into a continuous sonication vessel where the miniemulsion was formed and fed to the tubular reactor on a continuous basis. In order to suppress initiation before the feed entered the reactor, the feed tank and sonication vessel were kept at 5 °C. 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 an error margin of $\pm 2\%$. Before starting the tube reactor, a charge of the miniemulsion was bled off in order to perform a concurrent batch experiment.

Results and Discussion

A summary of the reactor parameters used in the homopolymerization of styrene are shown in Table 1. Flow rates and residence times in the tubes were chosen based on previous studies in batch with the same recipe. While the latex in the tubes appeared stable, the concurrent batch reaction showed a minor amount of separation, estimated visually to be $\sim 5\%$ of the total organic phase. The cause is thought to be in the preparation of the miniemulsion for the batch experiment. The target residence time for sonication was 20 min, however, it was noted that the flow from the main emulsion feed pump fluctuated during the preparation of the batch miniemulsion, making the residence time difficult to properly quantify in this case. If the residence time was too short, the miniemulsion may not be formed completely and this could cause minor phase separation as seen in the batch reaction. Latexes prepared and polymerized prior to this work using the same recipe (see Table 2) in conjunction with a more traditional batch approach to sonication were completely stable and showed no visible separation. In any event, the separation was relatively minor, and calculations with the mass fractions to account for the separated organics showed that only a small amount of error in the conversion would be introduced, $\pm 2\%$. In order to insure a steady state, each tube was operated for at least 2 residence times before samples were taken. Figure 2 shows that the number-average molecular weight increased linearly with conversion, indicative of a controlled polymerization.

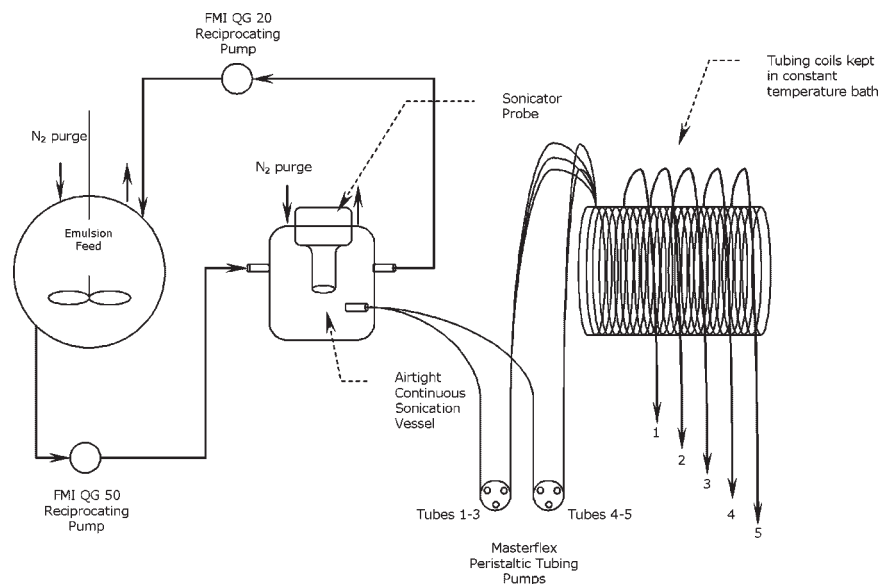


Figure 1. Schematic illustration of the tubular reactor for RAFT polymerizations in continuous miniemulsion.

Table 1. Summary of reactor parameters.

Tube	Length	Flow	Residence time	Reynolds number
	m	$\text{mL} \cdot \text{min}^{-1}$	min	
1	8.2	0.2	79	6
2	15.5	0.2	173	6
3	23.2	0.2	261	6
4	31.1	0.2	322	6
5	39.0	0.2	424	6

In this initial investigation of miniemulsion LRP in tubular reactors, two fundamental questions were of interest. First, how would the tubular reactor behave kinetically? In theory the kinetics should be identical to batch in the limit of plug flow, with the time variable replaced by the length of the tube.^[15] We observed very similar kinetics (see Figure 3) between the tube reactor and the concurrent batch experiment, noting that the tube reactor was operating in the laminar flow regime. However, the reaction was slightly

faster in the tube reactor, making it unlikely that diffusive and/or convective effects were responsible for the variation (dispersion should slow the kinetics). It is postulated that inhomogeneity between the two latexes may be partially responsible based on the observation of the slight separation in the batch. An examination of the number distribution of chains (Figure 4) for both reactions, as determined by monitoring the UV peak absorbance (311 nm) of the C=S group in the RAFT agent, is revealing. While the plot for the polymer produced in the tube reactor shows nothing unusual, a bi-modal distribution of chains is clearly present in the batch polymer. It shows a population of non-growing chains formed early on in the batch reaction, causing the unusual phenomenon of an increasing trend in polydispersity (Figure 2). The particle size evolution in both the batch and tube reactors was basically flat, indicating no significant change in the particle number. This is typical of miniemulsions, where nucleation occurs very early on in the monomer droplets and little or no particles form thereafter.^[16] This mediates against homogeneous nucleation as

Table 2. Miniemulsion recipe.

Component	Quantity	Conditions
	g	
Water	1 600	
Monomer	400	25 wt.-% of water
Surfactants	18.5	$0.005 \text{ mol} \cdot \text{L}^{-1}$ (based on aqueous phase)
	2.3	$0.005 \text{ mol} \cdot \text{L}^{-1}$ (based on aqueous phase)
Costabilizer	8.0	2 wt.-% of monomer
RAFT agent	3.5	$[\text{Sty}]_0/[\text{PEPDTA}]_0 = 300$
Initiator	0.35	$[\text{PEPDTA}]_0/[\text{KPS}]_0 = 10$
Temperature		70°C

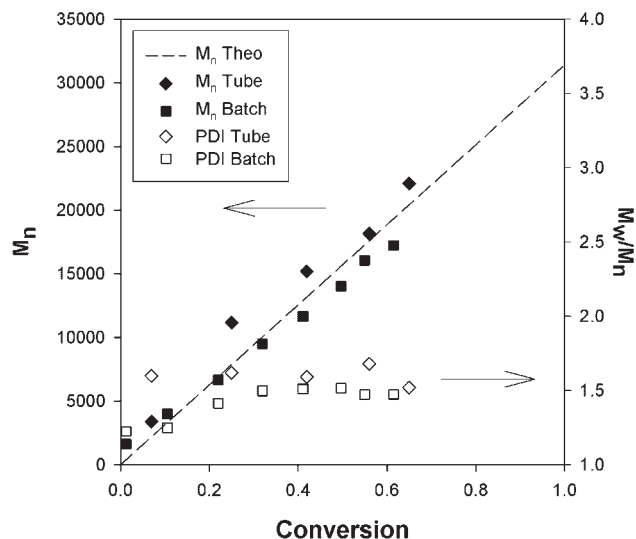


Figure 2. Plot of the number-average molecular weight and polydispersity of polymers produced by the styrene/PEPDTA RAFT miniemulsion as a function of conversion.

the source of the bimodal distribution observed in the batch experiment. Also, since polymer formed by homogeneous nucleation would likely not be controlled because of the negligible concentration of RAFT agent in the aqueous phase,^[17] the fact that the non-growing material has a low molecular weight and possesses the dithio group of the RAFT agent would suggest that some other mechanism was responsible. Work is ongoing in an attempt to identify the source of the bimodality. Despite the variations, the overall kinetic comparison between the batch and tube reactions is favorable.

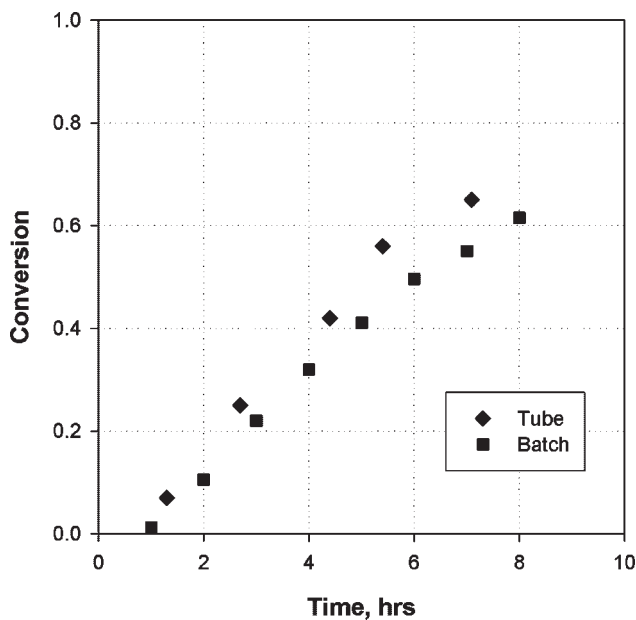


Figure 3. Kinetic plots of tube and concurrent batch styrene/PEPDTA RAFT miniemulsion polymerizations.

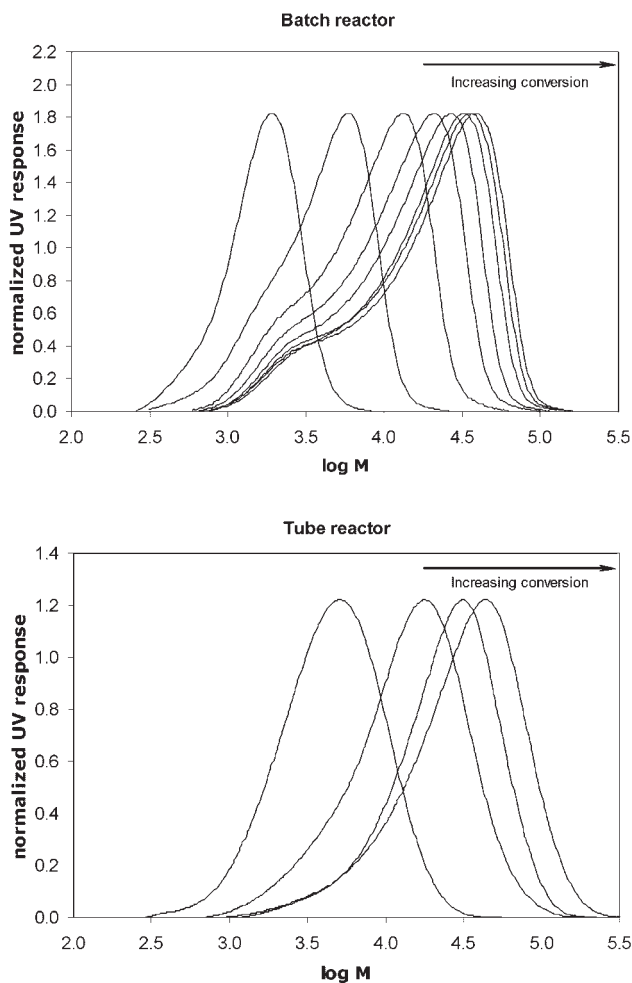


Figure 4. Evolution of the number distribution of chains using the normalized detector response of the UV absorbance at 311 nm, which is indicative of the distribution of the dithioester RAFT agent within the polymer.

The second question of interest concerns axial dispersion and its effects on the final polydispersity index (PDI) of the polymer. Will significant axial dispersion cause an increase in (PDI) since some particles will have longer residence times than others?^[18] At the very low Reynolds numbers employed here ($Re \sim 6$), any influence on the residence time distribution from the laminar flow velocity profile are likely to be negligible. In this case, variations in the residence-time distribution of the polymer latex should be attributable almost entirely to back mixing or axial dispersion. The data in Figure 2 show that while PDI's in the tubular reactor (~ 1.5 – 1.7) were lower than conventional free radical in miniemulsion (~ 1.9 – 2.1), they were higher than typically seen in a well-behaved batch miniemulsion LRP using RAFT (~ 1.1 – 1.3). Even accounting for the bimodality in the batch polymer synthesized here, polydispersities were lower, on the whole, than the polydispersities seen in the tube reactor. While not conclusive, the data support the assertion that axial dispersion will have a

negative effect on PDI. Further study is being conducted to validate the relationship between living polymer polydispersity and axial dispersion.

Conclusion

In this work, a continuous reactor with multiple tubes was successfully designed and implemented for the study of reversible addition-fragmentation chain transfer polymerizations in continuous miniemulsions. Collecting conversion data simultaneously at many different residence times greatly facilitates rapid kinetic characterization of this system. The styrene miniemulsion polymerization in the tube reactor behaved kinetically similar to the concurrent batch miniemulsion polymerization. Number-average molecular weights increased linearly with conversion, indicative of living character.^[13] Polydispersity indices were higher in the tube reactor than the batch reactor, likely owing to back mixing or axial dispersion causing a residence time distribution of the latex particles in the tubes. As typical of miniemulsions, the particle-size evolution was flat. Visual inspection of the clear PFA tubing after the experiment revealed no fouling at the conversion reached in this study (approximately 65%). The feasibility of carrying out miniemulsion RAFT polymerizations in tubular reactors has been demonstrated, illustrating a potential commercially viable polymerization method.

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